Stainless Steels and Specialty Alloys
for Modern Pulp and Paper Mills
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Prepared by a Task Force of the Metals Subcommittee of the Corrosion and Materials Engineering Committee of the Technical Association of the Pulp and Paper Industry and the Nickel Development Institute

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1. INTRODUCTION

by Arthur H. Tuthill, Nickel Development Institute

1.1 THE PRESENT

by Arthur H. Tuthill, Nickel Development Institute

This bulletin is a major expansion and a complete rewrite and update of the American Iron and Steel Institute (AISI) 1982 bulletin, “Stainless Steels for Pulp and Paper”. It has been prepared to provide mill engineers with a good overview of the wrought and cast alloys currently used in sulphate and sulphite mills. The bulletin is application oriented. Alloys useful in the principal equipment found in 12 different sections of paper mills are supplemented by sections on alloy characteristics, fasteners, abrasion, welding and corrosion. Since the AISI Committee of Stainless Steel Producers, which sponsored the 1982 bulletin, no longer exists, this updated edition has been prepared by a Task Force of the Metals Subcommittee of the Corrosion and Materials Engineering Committee of the Technical Association of the Pulp and Paper Industry (TAPPI). The 1982 edition covered only wrought stainless steels. This edition includes both wrought and cast stainless steels and other alloys commonly used in this industry. New sections on tall oil, air quality control, mechanical pulping, waste paper, suction rolls, fasteners and abrasion have been added. The bulletin is designed to be a useful reference for mill engineers concerned with materials of construction for the equipment in everyday use. Figure 1-1 is a generalized flow diagram of the principal processes in pulp and paper making.

Pulp and paper mills use stainless steel to avoid iron contamination of the product paper and to resist process corrosion. Although most mills use nominally the same sulphate kraft or sulphite process, there are sufficient mill-to-mill differences that can affect corrosion behaviour. This bulletin identifies alloys that are known to perform well in the individual applications cited, but mill engineers should be aware that conditions in their mill may differ sufficiently for performance to be somewhat different. Experience in each mill is the best guideline.

Each section of the original bulletin and the new sections have been prepared by a knowledgeable industry materials specialist, incorporating the many changes in the environment, mill processes and alloy usage that have occurred since 1982. Principal factors that have affected alloy usage and performance include the recycling of wash water streams, discontinuation of chlorine bleaching, expanded use of oxygen and hydrogen peroxide bleaching, increased corrosivity in chemical recovery and brown stock washing, as well as the increased sand and grit loading in pumps.

Discontinuation of chlorine stage bleaching has come to be known as elemental chlorine-free bleaching (ECF). Totally chlorine-free bleaching
1. INTRODUCTION

Figure 1-1 Generalized Pulp and Paper Making Flow Diagram

Figure 1-2 Elemental Chlorine-Free (ECF) Bleaching has Virtually Replaced Chlorine-Free Bleaching. Totally Chlorine-Free Bleaching (TCF) is Growing but Quite Slowly
1. Introduction

(TCF), using oxygen and hydrogen peroxide, was introduced in 1990 and is growing more slowly than ECF. Refer to Figure 1-2.

The reduction of the historic twice per year two week maintenance shutdowns has also increased the need for more resistant alloys. The first “all stainless steel” mill, Metsa-Rauma, with a capacity of 500,000 tonnes per year, has been built on the west coast of Finland. Metsa-Rauma has a chlorine-free, oxygen-based bleaching system and makes extensive use of duplex stainless steel for its large vessels. In many respects Metsa-Rauma is the prototype for new mills of the 21st Century.

1.2 Life Cycle Costs

Consideration of the full life cycle costs of equipment is an increasingly important and necessary consideration in the highly competitive worldwide marketplace for the products pulp and paper mills produce. The alloy suggestions for applications cited in this bulletin are generally alloys that normally will serve 20 years with minimal maintenance. In many but not all cases, the alloys suggested are also the lowest cost material that will serve well in each particular application. In some cases, particularly in the alkaline environment of kraft mills, there is a choice between lower cost carbon steel and higher cost, longer lived and lower maintenance cost stainless steel.

Mills incur several downstream costs when the lowest first cost material selection philosophy prevails: 1) increased maintenance costs; 2) increased cost of inspection and 3) loss of production while the unit is out of service for inspection and repairs. Table 1-1 gives a comparison of the initial investment and principal downstream costs for a carbon steel and a duplex batch digester over a 20-year life cycle. The costs and service lives used in the example are believed to be reasonably representative, however; they are intended as an example only.

The higher maintenance costs of the carbon steel digester are written off in the year in which they are incurred. The higher initial cost of the duplex digester is written off as depreciation over the 25-year life of the duplex digester. In mills with excess batch digester capacity, there is no lost production. In mills which are utilizing their full batch digester capacity, the cost of lost production is additive to the cost of maintenance.
1. Introduction

Other Cost Factors and Considerations

This analysis assumes that the Type 309L and the Type 312 overlays are properly done and achieve the 8-year life expected from a high quality Type 309L weld overlay and the 10-year life expected from the Type 312 weld overlay. Unfortunately in actual practice, a quality overlay is not always achieved. In those cases even higher maintenance costs are incurred.

The service life and costs for Type 309 overlay and duplex are based on long term experience. The initial cost for Type 312 overlay is based on experience but the downstream costs are based on good engineering judgment for a properly applied overlay as the long term experience with Type 312 overlays is not yet available. Developing reasonable life cycle costs often involves projections beyond immediate experience.

In some cases, only half the carbon steel digester requires overlay at the end of the first 10 years. The other half usually requires overlay in several more years. This will reduce the costs for the Type 309L or the Type 312 overlays somewhat but will not significantly alter the comparative position of the three alternatives.

Table 1-1 Life Cycle Cost Comparison

<table>
<thead>
<tr>
<th>6500 Cu Ft Batch Digester – Replacement Cost (13.25 ft. diam. x 57 ft. high - 2000 sq. ft. ID)</th>
<th>Carbon Steel</th>
<th>Duplex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion Allowance - inches (mm)</td>
<td>Type 309L</td>
<td>Type 312</td>
</tr>
<tr>
<td>Overlay</td>
<td>0.50* (12.7)</td>
<td>0.50* (12.7)</td>
</tr>
<tr>
<td>Maintenance Costs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Years 1–9</td>
<td>minimal</td>
<td>minimal</td>
</tr>
<tr>
<td>Year 10 Overlay full surface of C.S. digester</td>
<td>300,000</td>
<td>350,000</td>
</tr>
<tr>
<td>Years 11–14</td>
<td>minimal</td>
<td>minimal</td>
</tr>
<tr>
<td>Year 15 Repair 100 sq. ft. of overlaid surface</td>
<td>20,000</td>
<td>minimal</td>
</tr>
<tr>
<td>Year 16</td>
<td>20,000</td>
<td>minimal</td>
</tr>
<tr>
<td>Year 17</td>
<td>20,000</td>
<td>minimal</td>
</tr>
<tr>
<td>Year 18 Arc gouge off and apply new overlay</td>
<td>350,000</td>
<td>minimal</td>
</tr>
<tr>
<td>Year 20</td>
<td>minimal</td>
<td>minimal</td>
</tr>
<tr>
<td>20 year totals</td>
<td>1,010,000</td>
<td>650,000</td>
</tr>
</tbody>
</table>

* The 0.50* corrosion allowance provides 10 years’ service for the steel digester before weld buildup is required to restore the corrosion allowance. The 0.25* corrosion allowance for the duplex digester provides 25 years’ service before weld buildup to restore the corrosion allowance is needed.

Summary

Life cycle cost analyses are useful in providing general guidance but are only as good as the assumptions on which they are based. The foregoing example is based on the best available information but is not intended to be used as such. Mills should use cost and durability estimates from their own, or directly related, experience for life cycle cost analyses. Mills with good maintenance records will find life cycle cost analyses very useful in minimizing the total costs of producing their product, paper.

1.3 The Future

by Andrew Garner, Paprican

Future Materials Needs of the Pulp and Paper Industry

Alloys and their uses in pulp and paper described in this bulletin represent the latest technology as of the year 2000. These alloys and their applications represent several decades of development. In the relentless drive to do things better, further developments are to be expected. What changes will most influence these further developments? Here are some personal thoughts on industry changes and the implications for maintenance and materials in the pulp and paper industry.
1. Introduction

Process Improvements

After many years of process technology development, the industry is ready to make things more cheaply and simply with faster and larger scale equipment. Most new plants will embody these trends. Higher yield, more selective pulping, including polysulphide pulping, will lower costs. Brighter, stronger mechanical pulps should appear. Compact fibre processing equipment will be perfected to screen, clean, wash and bleach pulps. Paper machines will become faster and shorter. Higher pressure boilers and more cogeneration plants should be installed in response to electrical industry deregulation. Gasification technology may eventually be perfected. Larger digesters, larger vessels, larger evaporators, larger recausticizers and larger tanks are here to stay.

Add the demand for minimal maintenance shutdowns, (e.g., every 18 months) and it is likely that carbon steel will be phased out of the alkaline section of kraft mills. The all stainless steel paper machine is already with us. For old equipment these changes are made by upgrading. For example, granite and bronze are being replaced by ceramics and stainless steel. New mills will specify stainless steel from the start with liberal use of duplex as Metsa-Rauma has done.

Outsourcing

Pulp and paper producers are following other industries by outsourcing maintenance and technical support. Perhaps outsourced operations may be next. More efficient manpower management and tax efficiency are two drivers of these trends.

What are the implications for equipment, materials of construction, and maintenance? We may finally see widespread standardization of equipment, pumps, bearings and other frequently replaced equipment, i.e., standardization of wrought and cast materials and welding consumables, and standardization of construction, inspection and repair procedures, all in the name of lower cost operation. Standards development should continue to be helped through collective work in TAPPI/NACE/PAPTAC and other committees.

The companies that perform outsourced maintenance and inspection already own and manage large-scale computerized databases on equipment performance. The learning afforded by these computerized databases will shrink the high costs of surprise failures that have occurred in the past. Mills will continue to demand more disciplined, informed maintenance practices and more predictability. The smart ones will get it.
 Consolidation

Consolidation and a new market focus should give the industry the opportunity to regain respectable profitability. This in turn should allow companies to increase their investment in operational reliability and predictability. Rationalization into single product line mills and a drive toward greater product uniformity are other expected trends. All told, expect the group that updates this document 20 years hence to look back in wonder at the referenced knowledge base and its advisory nature. In the future much less will be left to chance.

REFERENCES

2. Tables of Composition and Properties of Common Alloys

Table 2-1  Typical Composition of Wrought Corrosion Resistant Alloys for the Pulp and Paper Industry, in Weight Percent

<table>
<thead>
<tr>
<th>Common</th>
<th>UNS</th>
<th>EN[1]</th>
<th>Typical Composition - %</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Cmax</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Austenitic

| 303    | S30300 | 1.4305 | 0.15 | 18  | 9   | —   | —   | 0.20 max P | 0.15 min S |
| 304    | S30400 | 1.4301 | 0.08 | 18  | 9   | —   | —   | —           | —           |
| 304L   | S30403 | 1.4306 | 0.03 | 18  | 10  | —   | —   | —           | —           |
| 321    | S32100 | 1.4541 | 0.08 | 18  | 10.5| —   | —   | 5x (C + N) min, 0.70 max |
| 347    | S34700 | 1.4550 | 0.08 | 18  | 11  | —   | —   | (Nb+Ta) 10xC min, 1.0 max |
| N60    | S21800 | —      | 0.10 | 17  | 8.5 | 0.15| —   | 8 Mn, 4 Si |
| 316    | S31600 | 1.4401 | 0.08 | 17  | 11  | 2.1 | —   | —           |
| 316L   | S31603 | 1.4404 | 0.03 | 17  | 11  | 2.1 | —   | —           |
| 316L-2.5% MinMo | S31603 | 1.4435 | 0.03 | 17  | 12  | 2.6 | —   | —           |
| 317    | S31703 | —      | 0.08 | 19  | 12  | 3.1 | —   | —           |
| 317L   | S31703 | 1.4438 | 0.03 | 19  | 12  | 3.1 | —   | —           |
| 317LMN | S31726 | 1.4439 | 0.025| 18.5| 14.5| 4.1 | 0.15| —           |
| Alloy 20 | N08020 | (2.4660)| 0.07 | 20  | 34  | 2.1 | —   | 3.5 Nb x C min, 1.00 min |
| Alloy 825 | N08825 | (2.4858)| 0.05 | 21.5| 42  | 3.1 | —   | 2 0.9 Ti |
| Alloy 904L | N08904 | 1.4539 | 0.02 | 20  | 25  | 4.1 | —   | 1.5 —       |
| 6% Mo | N08367 | —      | 0.03 | 20.5| 24.5| 6.1 | 0.20| 0.1  —      |
|        | S31254 | 1.4547 | 0.02 | 20  | 17  | 6.1 | 0.20| 0.8 —      |
|        | N08926 | 1.4529 | 0.02 | 20  | 25  | 6.1 | 0.20| 1.0 —      |
|        | N08026 | —      | 0.03 | 24  | 42  | 6.1 | 0.13| 3 —        |
| 7% Mo | S32654 | 1.4652 | 0.02 | 24.5| 22  | 7.2 | 0.50| 0.5 3.5 Mn |
|        | S31266 | —      | 0.03 | 24  | 22.5| 6   | 0.45| 1.5 2.0 W* 3.0 Mn |

Ferritic

| 430    | S43000 | 1.4016 | 0.12 | 17.0| —   | —   | —   | —           |
| 3CR12  | S41003 | 1.4003 | 0.03 | 11.5| 0.65| —   | —   | —           |

Martensitic

| 410    | S41000 | 1.4006 | 0.15 | 12.5| —   | —   | —   | —           |
| 416    | S41600 | 1.4005 | 0.15 | 13  | —   | —   | —   | —           |
| 420    | S42000 | 1.4021 | >0.15| 13  | —   | —   | —   | 0.15 min S |
| 440C   | S44004 | 1.4125 | 1.20 | 17  | —   | 0.75| —   | —           |
| 16Cr/5Ni/1Mo | —      | 1.4418 | 0.05 | 16  | 5   | 1.00| —   | —           |

Precipitation Hardening

| 15-5   | S15500 | 1.4545 | 0.07 | 14.7| 4.5 | —   | —   | 3.5 0.30 (Nb+Ta) |
| 17-4   | S17400 | 1.4542 | 0.12 | 16.5| 4.0 | —   | —   | 4.0 0.30 (Nb+Ta) |

Duplex

| 2304   | S32304 | 1.4382 | 0.03 | 23.0| 4.5 | 0.5 | 0.10| 0.5 —       |
| 2205   | S31803 | 1.4462 | 0.03 | 22.0| 5.5 | 3.0 | 0.12| —           |
|        | S32205[1] | —      | 0.03 | 22.5| 5.5 | 3.25| 0.17| —           |
| 329    | S32900 | 1.4460 | 0.08 | 25.0| 4.0 | 1.5 | —   | —           |
| 2507   | S32750 | 1.4410 | 0.03 | 25.0| 7.0 | 4.0 | 0.28| —           |
| 3RE60  | S31500 | 1.4417 | 0.03 | 18.5| 4.75| 2.75| 0.07| —           |

Ni Base

| 625    | N06625 | (2.4856)| 0.02 | 22.0| 62  | 9.0 | —   | —           |
| 2276   | N10276 | (2.4819)| 0.02 | 15.5| 60  | 16.0| —   | 3.8 W* 5.5 Fe 0.35 V |
| 222    | N06022 | (2.4602)| 0.015| 21.0| 60  | 13.5| —   | 3 W* 2.5 Co 0.35 V |
| G30    | N06030 | (2.4603)| 0.03 | 30.0| 46  | 5.0 | —   | 1.5 2.5 W* 15 Fe |
| K500   | N05500 | (2.4375)| 0.25 | 65  | —   | —   | 30 2.0 Fe, 1.5 Mn, 3 Al, 0.5 Si, Ti 0.5 |

Ti and Zr

<table>
<thead>
<tr>
<th>UNS</th>
<th>EN</th>
<th>C</th>
<th>Fe</th>
<th>Nmax</th>
<th>Hmax</th>
<th>Omax</th>
<th>Other</th>
</tr>
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<tbody>
<tr>
<td>TiGr2 (B265)</td>
<td>R50400</td>
<td>—</td>
<td>0.1</td>
<td>0.2</td>
<td>0.03</td>
<td>0.015</td>
<td>0.25</td>
</tr>
<tr>
<td>Zr (B551)</td>
<td>R60702</td>
<td>—</td>
<td>0.5</td>
<td>0.2[2]</td>
<td>0.025</td>
<td>0.005</td>
<td>0.16</td>
</tr>
</tbody>
</table>

[1] The EN number is the closest to the UNS, but not identical in all respects. ( ) Tentative EN designations.
[2] The original S31803 UNS designation has been supplemented by S32205 which has higher minimum N, Cr, and Mo. S32205 is often preferred for procurement.
[3] Fe + Cr *W is about half as effective as Mo in increasing corrosion resistance in acid-chloride environments.
<table>
<thead>
<tr>
<th>Common</th>
<th>UNS</th>
<th>EN</th>
<th>Yield Strength* (ksi (MPa))</th>
<th>Tensile Strength* (ksi (MPa))</th>
<th>Elongation* in 2%</th>
<th>PREN(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>S30300</td>
<td>1.4305</td>
<td>Not Specified in ASTM A582</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>304</td>
<td>S30400</td>
<td>1.4301</td>
<td>30 (205)</td>
<td>75 (515)</td>
<td>40</td>
<td>18</td>
</tr>
<tr>
<td>304L</td>
<td>S30403</td>
<td>1.4306</td>
<td>25 (170)</td>
<td>70 (485)</td>
<td>40</td>
<td>18</td>
</tr>
<tr>
<td>321</td>
<td>S32100</td>
<td>1.4541</td>
<td>30 (205)</td>
<td>75 (515)</td>
<td>40</td>
<td>17</td>
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* Minimum values for hot rolled plate per ASTM A240 unless otherwise indicated.
(1) Pitting Resistance Equivalent Number % Cr + 3.3% Mo + 16% N based on minimum composition. The PREN rankings, while useful in bleach plant acidic chloride environments, may not be applicable to other pulp and paper environments.
(2) The original S31803 UNS designation has been supplemented by S32205 which has higher minimum N, Cr, and Mo. S32205 is often preferred for procurement.

(3) ASTM A479
(4) ASTM B643 hardened and tempered condition
(5) ASTM A424
(6) ASTM A790
(7) Typical for H1150 condition
(8) ASTM A564
(9) ASTM B582
(10) ASTM B575
(11) ASTM B551
## 2. ALLOY COMPOSITION & PROPERTIES

### NOTES

<table>
<thead>
<tr>
<th>Table 2-3</th>
<th>6% and 7% Mo Austenitic Stainless Steels for Use in the Pulp and Paper Industry</th>
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<tbody>
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<td>Type</td>
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<tr>
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<td>N08367</td>
<td>A312, A358</td>
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<td>A312, A358</td>
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<td>A312, A358</td>
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ASTM Specifications for 6% and 7% Mo Stainless Steel Plate, Sheet and Strip

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<th>Type</th>
<th>ASTM Stainless Steel Specifications</th>
<th>ASTM Ni-Base Alloy Specifications*</th>
<th>Minimum Annealing Temperature</th>
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Producers of the 6% and 7% Mo Austenitic Stainless Steels

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<th>Producer</th>
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<td>S31254</td>
<td>AvestaPolarit</td>
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<td>AL-6XN®</td>
<td>N08367</td>
<td>Allegheny Ludlum</td>
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<td>1925hMO™</td>
<td>N08926</td>
<td>Krupp VDM, Creusot Industeel</td>
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<td>25 - 6MO™</td>
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™ & ® Trademark or Registered Trademark, as indicated, of producer shown.

* Prior to the year 2000, B specifications were used for procurement of plate, sheet, strip and pipe of several of the 6% Mo alloys. As of 2000, these product forms are found in A312, A358 and A240. See footnote below.

Footnote: In about 1990, the ASTM sought to harmonize its definitions with those of the rest of the world. One result was that alloys in which iron is the largest element by weight percent (with low carbon content) were defined as steels, and steels with more than 10.5% chromium were defined as stainless steels. Previously the ASTM had required that an alloy have at least 50% iron to be treated as stainless steel. Therefore, most but not quite all of the existing grades with UNS designations of N08xxx became eligible for inclusion in the ASTM A specifications covering steels. It was agreed that these grades would be individually qualified for inclusion in the A specifications. Those grades already having a UNS designation in the form N08xxx would retain that designation as an indication of their history. New grades that would previously have been "nickel-base alloys" designated N08xxx are now designated as stainless steels with an appropriate S3xxxx designation. It was agreed that the B specifications for the existing N08xxx stainless steels would eventually be terminated, but that there would be no great hurry to do so because users have drawings and qualified procedures for these grades as nickel-base alloys. Examples of grades that are now in the A specifications are 904L (N08904), Alloy 20 (N08020), and two of the 6% Mo grades (N08367 and N08926).
## Alloy Composition & Properties

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<th>C&lt;sub&gt;max&lt;/sub&gt;</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
<th>Yield Strength (ksi (MPa))</th>
<th>Tensile Strength (ksi (MPa))</th>
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</tr>
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<td>CN-7M</td>
<td>N08007</td>
<td>Alloy 20</td>
<td>0.07</td>
<td>20.5</td>
<td>29</td>
<td>2.5</td>
<td>—</td>
<td>25 (170)</td>
<td>62 (425)</td>
<td>27</td>
</tr>
<tr>
<td>CU-5MCu&lt;sup&gt;(3)&lt;/sup&gt;</td>
<td>N08826</td>
<td>825</td>
<td>0.05</td>
<td>21</td>
<td>41</td>
<td>3</td>
<td>—</td>
<td>35 (240)</td>
<td>75 (520)</td>
<td>30</td>
</tr>
<tr>
<td><strong>SUPERAUSTENITIC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CK-3MCuN</td>
<td>J93254</td>
<td>S31254</td>
<td>0.025</td>
<td>20</td>
<td>18.5</td>
<td>6.5</td>
<td>0.2</td>
<td>38 (260)</td>
<td>80 (550)</td>
<td>41</td>
</tr>
<tr>
<td>CN-3MN</td>
<td>J94651</td>
<td>N08367</td>
<td>0.03</td>
<td>21</td>
<td>24.5</td>
<td>6.5</td>
<td>0.2</td>
<td>38 (260)</td>
<td>80 (550)</td>
<td>43</td>
</tr>
<tr>
<td>7% Mo&lt;sup&gt;(5)&lt;/sup&gt;</td>
<td>—</td>
<td>S32654</td>
<td>0.01</td>
<td>24.5</td>
<td>7.5</td>
<td>0.5</td>
<td>64 (440)</td>
<td>106 (725)</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td><strong>NICKEL BASE</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CW-2M</td>
<td>N26455</td>
<td>C276</td>
<td>0.02</td>
<td>16.25</td>
<td>62</td>
<td>16.25</td>
<td>—</td>
<td>52 (356)</td>
<td>85 (585)</td>
<td>65</td>
</tr>
</tbody>
</table>

### Table 2-4: Typical Composition, Mechanical Properties and Pitting Resistance Equivalent Number (PREN) of Cast Corrosion Resistant Alloys Used in Pumps and Valves in the Pulp and Paper Industry

**Notes:**
- The PREN rankings, while useful in bleach plant acidic chloride environments, may not be directly applicable to all pulp and paper environments.
- ASTM A532; No UNS designation.
- German alloy designation.
- Minimum; can be increased by variations in heat treatment.
- Contains 1.0 Nb.
- UNS designation not yet assigned.
NOTES

3.1 DESIGNATIONS, PROPERTIES AND SPECIFICATIONS

This section is designed to acquaint mill engineers with the principal characteristics of the different families of stainless steels and other corrosion resistant alloys widely used in the pulp and paper industry. The alloy tables in the front of this bulletin give the common, the Unified Numbering System (UNS), and the European Number (EN), which is similar to the German (DIN) designation, for the principal alloys used. These tables are designed to assist mill engineers in identifying the alloys in their mills regardless of the country in which the equipment was made and regardless of which alloy designation is used. The composition and properties of the wrought alloys are shown in Tables 2-1 and 2-2, and of the cast alloys in Table 2-4. The wrought equivalent of the less familiar cast alloys is also shown in Table 2-4.

Table 2-3 shows the ASTM Specifications for piping, plate, sheet and strip, and the alloy producers of the 6% Mo and 7% Mo stainless steels. Neither the 6% Mo nor the 7% Mo stainless steels have a single UNS or EN designation. While the molybdenum content is similar, other elements vary significantly. This family of highly resistant stainless steels is divided into the older 6% Mo grades and the newer, even more resistant, high nitrogen grades designated “7% Mo” grades.

The pitting resistance equivalent number, PREN, for the wrought alloys is shown in Table 2-2 and for the cast alloys in Table 2-4. The significance of PREN is discussed in the section on “Corrosion.”

The composition of special purpose alloys used in rolls, fasteners, welding filler metals, and special applications are given in the individual sections of this bulletin. The common designation of the wrought alloys and the cast grade of the cast alloys is used throughout the text, followed by the UNS designation in parentheses ( ) on first mention in each section of the bulletin.

The mechanical properties, weldability, corrosion resistance, and wear and abrasion resistance of stainless steels depend to a large extent upon the microstructure. The microstructure and its constituents in turn depend upon the alloy composition, the steel making or casting practice, the thermal history, and the finishing treatment. Stainless steels are normally subdivided into four different groups: austenitic, ferritic, martensitic, and duplex. Each group has distinctive characteristics which are discussed below to assist mill engineers in gaining a better
3. CHARACTERISTICS OF COMMON ALLOYS

by Arthur H. Tuthill, Nickel Development Institute

understanding of these terms and general properties as they are encountered in the literature and discussions on corrosion.

3.2 AUSTENITIC STAINLESS STEELS

Most of the stainless steels used in pulp and paper are austenitic. Austenitic alloys are distinguished by a face centred cubic (FCC) crystal lattice. This face centred cubic structure, while not as strong as the body centred cubic (BCC) structure of carbon steel and of ferritic stainless steels, is tough, ductile and easily welded. The heat affected zone alongside the weld is tough and ductile, quite the opposite of the hard, brittle heat affected zone of martensitic stainless steels and low alloy steels. The austenitic alloys are either non-magnetic or only slightly magnetic, and are hardenable by cold work, not by heat treatment. Their excellent corrosion resistance is due primarily to their chromium content, which enables stainless steels to form a very thin, durable and tenacious Cr/Fe oxide film. Mo and N, when present, enhance the corrosion resistance of this film. Stainless steels are normally produced and used in the “annealed” condition. The term anneal, when used for stainless steels, means heat treated at temperatures of 1900°F (1040°C) or higher and water quenched, not slow cooled as the term “annealed” means for carbon and low alloy steels.

The basic austenitic grade, Type 304 (S30400) has 18% Cr, 8% Ni and up to 0.08% C. This grade is still often referred to as 18-8. Type 304 has a similar composition to Type 304. Interestingly, if Mo and N are added, it becomes similar to Type 316. Type 316 has 2 to 3% Mo, which greatly improves resistance to localized corrosion in most, but not all, aggressive environments.

The 0.08% max C allowed in Types 304 and 316 leaves stainless steel vulnerable to intergranular corrosion when welded. The heat of welding is sufficient for chromium to combine with carbon and precipitate at grain boundaries in the zone alongside the weld, referred to as the heat affected zone (HAZ). The chromium that precipitates as chromium carbide leaves a zone adjacent to the weld depleted in chromium and susceptible to intergranular corrosion, or intergranular attack (IGA).

Prior to the present argon oxygen decarburization (AOD) process for stainless steel production, either Nb or Ti was added to the base composition to combine with carbon, leaving no carbon to combine with chromium and thereby preventing IGA. Type 347 (S34700) is the designation for the grade with Nb; Type 321 (S32100) is the grade with Ti. Type 316Ti (UNS S31635) is the stabilized grade of Type 316 more widely used in Europe than in North America. These “stabilized” grades are suitable for welded fabrication and resistant to IGA under most circumstances.

The advent of the AOD process for stainless steel making in the 1960s made it possible to produce stainless steels with a carbon content so low there was no significant chromium carbide formation during normal welding. The low carbon grades became known as the “L” grades, with a maximum of 0.03 or 0.035% carbon. They are now standard worldwide for fabricated products. The “L” following the common designation, as in 304L (S30403), 316L (S31603), 317L (S31703) and 904L (N08904), designates the low carbon grade of the alloy suitable for welded fabrication. In the UNS numbering system, which is replacing the older American Iron and Steel Institute (AISI) designations, the “03” in S30403 and S31603 designates the 0.03% max C or low carbon “L” grade. In the UNS designation system “00” in S30400 and S31600 indicates the 0.08% max C high carbon grade not suitable for welded fabrication. It is important when purchasing stainless steels that the low carbon grade be specified; otherwise there is a risk that the high carbon grade will be received.

In Scandinavia the national standards include a 0.05% max C grade. This slightly higher level of carbon is not recognized elsewhere as an L grade. The carbon is still low enough for the 0.05% max C grade stainless steel to be resistant to IGA after welded fabrication in the lighter gauges commonly used in pulp and paper vessels and piping. In heavier gauges, the 0.05% max C grades may be susceptible to IGA after welding. The Swedish designation for the 0.05% max C grade of Type 304 is 2333, and the more widely used EN/DIN is 1.4301. For Type 316, the
3. CHARACTERISTICS OF COMMON ALLOYS

Swedish designation for the 0.05% max C grade is 2347, and the EN/DIN is 1.4401. There are no UNS designations for the 0.05% max C grades. In mixed stainless steel and carbon steel assemblies where the carbon steel must be stress relieved, it is always better to specify the 0.03% C grade rather than the 0.05% carbon grade to guard against IGA during service.

Austenitic stainless steels are susceptible to localized corrosion in acidic chloride and other aggressive environments. Corrosion, when it occurs, tends to be localized, at existing defect sites in the Cr/Fe oxide film, at sites created during fabrication or erection, or at sites created by abuse in service. Embedded iron and other fabrication related defects often destroy the protective film locally, creating a defect site where unnecessary localized corrosion frequently occurs. Restoration of fabrication damaged film defects is a prime consideration during post fabrication cleanup. Refer to 18.6 and 20.4.

The basic grades are also susceptible to chloride stress corrosion cracking (chloride SCC) in certain chloride environments at moderately elevated temperatures. They are also susceptible to caustic stress corrosion cracking in highly caustic environments at temperatures above about 240°F (120°C).

Since the 2-3% Mo addition improved the resistance to localized corrosion so greatly, higher Mo grades were developed that provide even better resistance to localized corrosion. Type 317L with 3-4% Mo, and Type 317LMN (S31726) with 4% min. Mo in North America, and Type 904L with 4% min. Mo in Europe, became standard upgrades in pulp and paper for applications where Type 316L suffered excessive corrosion, most notably in bleach plant applications. The 6% Mo alloys introduced in the 1980s are even more resistant to localized corrosion and have become standard in many of the most aggressive bleach plant environments. The family of alloys derived from the original 18-8, 18Cr-8Ni composition are shown in Figure 3-1.

Nitrogen, which is easily added in AOD produced stainless steels, was found to be quite beneficial in enhancing resistance to localized corrosion and has become a standard addition in the 6% Mo, duplex, and other alloys. Nitrogen additions made to the lower Mo and Mo-free grades carry an “N” at the end of the common designation (e.g., Types 304LN (S30453), 317LN (S31753) etc.). Nitrogen also strengthens austenitic alloys. The strengthening effect of N has allowed warehouses to offer “dual certified grades.” Dual certified grades have the slightly higher strength of the 0.08% C grades and the low carbon of the “L” grades, which makes the dual certified grades suitable for welded fabrication.

The 6% Mo stainless steels, which have become so important for the
most corrosive chlorine and chlorine dioxide bleach plant environments, have no single designation. They have been divided into two groups, the older 6% Mo alloys and the newer “7% Mo” alloys. The 7% Mo alloys have much higher nitrogen, in the 0.4 to 0.5% range. Their composition and properties are shown in Tables 2-1, 2-2 and 2-4. The very high nitrogen provides substantially greater corrosion resistance than the five with about 0.15–0.20% N. The five with 0.15–0.20% N have comparable corrosion resistance, which is considerably greater than the corrosion resistance of the 3–4.5% Mo stainless steels. Table 2-3 gives the ASTM specifications for pipe, plate, sheet and strip, and the producers of this family of 6% Mo and 7% Mo highly corrosion resistant austenitic stainless steels, to assist mill engineers in identifying and procuring these important alloys.

Figure 3-1 Family of Alloys Derived from Type 304 (S30400 or “18-8”) Stainless Steels

<table>
<thead>
<tr>
<th>Welding Grades</th>
<th>Add Ti</th>
<th>Add Cu, Ti, Al, Reduce Ni</th>
<th>Add Nb</th>
<th>Add Cu, Ti, Al, Reduce Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>321</td>
<td></td>
<td>17-4</td>
<td></td>
<td>15-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High Strength</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add 2-3% Mo</td>
<td>316L</td>
<td></td>
<td>347</td>
<td></td>
</tr>
<tr>
<td>Add 3-4% Mo</td>
<td>347</td>
<td></td>
<td>304L</td>
<td></td>
</tr>
<tr>
<td>Add 4-5% Mo</td>
<td>304L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add 6% Mo</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add 7% Mo</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add More Mo</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add Ni</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Add More Mo + Ni</th>
<th>Ni Cr Mo Alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add Mo to Increase Corrosion Resistance</td>
<td>316L</td>
</tr>
<tr>
<td></td>
<td>316L</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Machining Grades</th>
<th>Add S or Se</th>
<th>Increase Cr</th>
<th>Reduce Ni</th>
<th>Add N</th>
<th>Add Mo</th>
<th>Increase Strength and Corrosion Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>303Se</td>
<td>Increase Cr</td>
<td>Reduce Ni</td>
<td>Add N</td>
<td>Add Mo</td>
<td>Increase Strength and Corrosion Resistance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Increase Cr</td>
<td>Reduce Ni</td>
<td>Add N</td>
<td>Add Mo</td>
<td>Increase Strength and Corrosion Resistance</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Duplex Grades</th>
<th>Increase Cr</th>
<th>Reduce Ni</th>
<th>Add N</th>
<th>Add Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>2304</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2205</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>2507</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

| Figure 3-1 Family of Alloys Derived from Type 304 (S30400 or “18-8”) Stainless Steels |
3. CHARACTERISTICS OF COMMON ALLOYS

3.3 FERRITIC STAINLESS STEELS

Ferritic stainless steels are distinguished by a body centred cubic (BCC) lattice structure, are magnetic, and can be hardened by cold work. Type 430 (S43000), with 16–18% Cr, is the principal ferritic grade of interest. Type 430 is less expensive, and less corrosion resistant, than Type 304. Type 430 is used principally in consumer products, but is occasionally offered by some equipment suppliers as an alternative to Type 304. Type 444 (S44400), an 18Cr 2Mo ferritic stainless steel, is used for Yankee drier hoods.

A newer low carbon 12% chromium ferritic stainless steel, S41003, has found applications as tanks and vessels in the alkaline section of mills. The 0.03% maximum carbon of this ferritic greatly improves weldability, increasing its usefulness as an alternative to Type 304L in the alkaline section of the mills.

3.4 MARTENSITIC STAINLESS STEELS

Martensitic alloys are distinguished by a modified body centred tetragonal lattice structure, elongated along one axis of the cube. The distorted lattice gives martensitic stainless steels the ability to develop high strength after heat treatment, but at the same time limits their ability to be cold worked or welded, except under very carefully controlled conditions. Five martensitic compositions that have applications in pulp and paper machinery are shown in Tables 2-1 and 2-2. While not as corrosion resistant as Type 304, their higher strength and hardness make them useful in many machinery components, especially where wear and abrasion are factors. Ferritic and martensitic stainless steels are resistant to chloride stress corrosion cracking but are susceptible to hydrogen cracking. This limits their usefulness in certain mixed metal assemblies, in equipment where hydrogen may be generated in corrosion reactions, and where cathodic protection is being used or considered. Martensitic stainless steels are also subject to an 850°F (450°C) embrittlement when exposed to temperatures in the 600-1200°F (315-650°C) range during heat treatment.

The lower carbon martensitic stainless steels, CB6 (J91804) and CA-6NM (J91540) like the low carbon ferritic, S41003, were developed for increased weldability. They have found applications where higher strength and abrasion resistance are needed.
3. CHARACTERISTICS OF COMMON ALLOYS

3.5 AGE HARDENING STAINLESS STEELS

It is possible to harden and strengthen the body centred cubic (BCC) structure by including a small amount of other elements that form small, granular, solid state precipitates when heated in the 930-1650°F (500-900°C) range. The corrosion resistance of these high strength grades, approximating that of Type 304, and their high strength make these age hardening alloys quite useful for many machinery components and for bolting. Two of the more common age hardening, or precipitation hardening, alloys used in pulp and paper are listed in Tables 2-1 and 2-2. It is important to recognize that welding may reduce the high strength of these age hardening alloys.

3.6 DUPLEX STAINLESS STEELS

Duplex stainless steels are distinguished by a half austenite and half ferrite, banded type of microstructure in the rolled condition. This duplex structure provides increased strength, resistance to chloride stress corrosion cracking, and better impingement and abrasion resistance (due to its higher hardness) as compared to Type 316L and its cast counterparts, CF-3M (J92800) and CF-8M (J92900). The higher chromium content of the duplex grades provides improved corrosion resistance in many environments. The cast duplex stainless steels were found very useful in pumps and rolls in pulp and paper mills even before the AOD process of stainless steel made possible the addition of nitrogen. Today the duplex stainless steels are the principal and preferred alloys for suction rolls. Cast duplex stainless steels, due to their better resistance to sand and grit abrasion and better corrosion resistance, have replaced and continue to replace CF-3M, CF-8M, CG-3M (J92999), and CG-8M (J93000) pumps in many pulp mill applications.

In the wrought form, the nitrogen alloyed wrought duplex alloys have become a very successful alternative to carbon steel, clad and weld overlaid digesters for new construction. Over a hundred duplex digesters are now in service, some approaching 18 years of service. Duplex has become the preferred material of construction for new batch digesters as its advantages are now widely recognized. Section 4 of this bulletin on digesters provides a great deal of useful information on the performance of duplex and alternative materials for digesters.

The higher strength and better corrosion of duplex vessels are allowing duplex to replace Type 316L digester blow tanks, steaming vessels and other large vessels. Fabrication of duplex vessels is similar to that of austenitic stainless steel but requires more precise control of welding variables, as discussed in section 18 of this bulletin. As additional fabricators become skilled in welding duplex, it will continue to be used in an increasing number of applications where Type 316L, 317L and 904L are now used.

There are two UNS designations for the most common wrought duplex grade, Alloy 2205. The older one, S31803, allows N to be as low as 0.08%. The newer designation, S32205, requires N to be at least 0.14%. S32205 should be used for procurement even though the older designation, S31803, may be the only designation in many individual ASTM specifications.

3.7 NICKEL BASE ALLOYS

Nickel base alloys have the same FCC austenitic structure as stainless steel. Alloy 625 (N06625) is used principally as a filler metal for welding 6% Mo alloys, weld and spray weld overlays. Alloy C276 (N10276) is also used as a filler metal for welding 6% Mo alloys. There are several cast counterparts for C276 that have been used in high shear mixers. The preferred cast material is CW-2M which has a more closely controlled chemistry required for best performance. It is essential that castings be annealed at 2150°F (1180°C) minimum and water quenched, in order to keep the deleterious second phases in solution, not at lower temperatures for longer times as some foundries with inadequate furnace facilities request. The cast
3. Characteristics of Common Alloys

Versions of Alloy C276 used in high shear mixers have been superseded by titanium due to variations in performance. Out-of-specification compositions, improper heat treatment and difficulty in forming a good protective film in the high shear mixer environment all contributed to variations in performance of the several compositions of C276 that were used. There has been some use of Alloy C276 in C and D stage washers. Usage in D stage has been limited by substantial transpassive corrosion in near neutral D stage environments.

Alloy G30 (N06030) has been used for piping in red liquor in sulphite mills. Alloy K500 (N05500) has been used for doctor blades on paper machines where its mechanical properties make it useful.

3.8 Other Alloys

Titanium and zirconium have useful applications in pulp and paper. When welding titanium it is essential to prevent air from reaching the weld and heat affected zone. Welding is best done in a separate area or clean room where air can be excluded. Zirconium has been found useful in the high shear mixers in hydrogen peroxide bleaching.

Alloys specific for the lime kiln, tall oil, suction rolls, fasteners and welding are covered in the appropriate individual sections.
4. DIGESTERS

4.1 BATCH DIGESTERS

A typical batch digester consists of a vertical cylindrical vessel with a hemispherical or ellipsoidal top head and a conical bottom, as shown in cross-sectional view in Figure 4-1. Batch digesters are typically 8 to 13 ft (2.4 to 4.0 m) in diameter and up to 60 ft (18.3 m) high. Soft or hard wood chips are fed into the top of the vessel, along with hot cooking liquor, which helps pack the chips in the vessel. The liquor consists of a mixture of white and black liquors in various volume ratios depending on the pulp product being manufactured.

After filling with wood chips and liquor, the vessel is closed and cooking begins, with heat supplied by direct injection of steam (Figure 4-1(A)) or by indirect steam heating (Figure 4-1(B)) in an external heat exchanger. A typical batch cook lasts about 2 hours. The cooking temperature of approximately 338°F (170°C) is reached after about one hour. At this time direct steaming is usually stopped. Some facilities remove the liquors and pulp by displacement instead of blowing, but this is not a common practice.

At the end of the cook the pulp is blown from the bottom of the vessel into a blow tank. From there the pulp goes to brown stock washers where the spent cooking liquor is separated from the pulp. Steam from the blow tank is removed for heat recovery and condensed in brown stock wash water.

Over the years there has been a trend to increase production by decreasing batch cook times. This requires the use of higher ratios of white-to-black liquor and higher temperatures. Both these practices cause increased corrosion rates in both carbon steel and stainless steel digesters.

Materials of Construction

Although there is a trend to construct batch digesters from solid duplex stainless steels, most batch digesters have been constructed from carbon steel with generous corrosion allowances (0.75 in., 19 mm, or more), such that they can remain in service for perhaps 10 years before some means of protection must be used. In the 1950s and 1960s digesters in North America were constructed using a modified low-silicon (0.02% Si max) grade of ASTM A285 carbon steel, with low-silicon welds on the process side. Today most new carbon steel batch digesters are made from ASTM A516-Grade 70, a higher-strength pressure vessel steel in which the silicon content is controlled in the range 0.15–0.30% Si, and without low-silicon weld caps. Higher silicon steels corrode more rapidly in alkaline pulping liquors.

Numerous batch digesters have been constructed from clad plate (either roll- or explosion-bonded) with stainless steel on the inside and carbon steel on the outside. Types 304L (S30403) and 316L (S31603) stainless steels have been most commonly selected for clad plate (although these experience corrosion). Some batch digesters have been constructed with a stainless steel weld overlay lining, although this practice is not common. Stainless steel weld overlays are discussed in some depth in this section under “Protection of Batch Digesters.” Some have been constructed of cold stretched Type 304 (S30400) stainless steel in accordance with the Swedish cold stretching code.

Duplex stainless steels in either solid or clad form have been used for several years for construction of new batch digesters worldwide. North America has been slow to adopt these materials, but the number of new duplex stainless steel batch digesters is expected to increase. The most common duplex alloy used for duplex digester construction is UNS S32205 (formerly known as S31803 and commonly known as “Alloy 2205”). Due to their higher strength, duplex stainless steel digesters may be significantly thinner than carbon steel digesters designed to hold the same pressure. Figure 4-2 shows three Alloy 2205 digesters at a mill in Thailand.

Corrosion

Corrosion of carbon steel kraft batch digesters has been a known problem for over 50 years. Pioneering work1–6 revealed that the silicon content of the steel controlled
Figure 4-1 (A) Direct-Heating Digester, (B) Indirect-Heating Digester

(A) Batch Digester Direct Heating
(B) Batch Digester Indirect Heating
the corrosion rate of digester steels, with higher silicon contents being increasingly susceptible. Carbon steel batch digesters do not corrode uniformly, and often experience the most corrosion in an inverted horseshoe-shaped pattern where the liquor contacts the wall during filling. The zone of most severe corrosion varies from mill to mill, and perhaps from digester to digester. In most digesters the corrosion is most pronounced in the cylindrical section. In other digesters it is worst in the bottom cone; in yet others, in the top dome.

Figure 4-2  Three 200 Cubic Metre Alloy 2205 Duplex Digesters - Thailand

Corrosion of stainless steels (both in wrought form and
4. Digesters

Weld overlays) is primarily a function of the chromium content of the overlay. Austenitic stainless steel grades such as Type 316L (16–18% Cr) and Type 304L (18–20% Cr) can experience rapid corrosion, up to 40 mpy (1 mm/y). With its higher chromium content, Type 304L performs better in digesters than Type 316L. Work by Audouard to investigate corrosion during “hot plate boiling” has revealed that duplex stainless steel with even higher chromium content (22–27% Cr) resists corrosion better than conventional austenitic grades.8–12 Corrosion testing has also shown that molybdenum is not a beneficial alloying addition for corrosion resistance of stainless steels in digester liquors.

Stainless steel weld overlays with low chromium content can also experience rapid corrosion. Conventional Type 309L (S30980) stainless steel weld overlays may have an as-deposited chromium content of 20%, which is higher than for Type 304L but is still insufficient for corrosion resistance in aggressive batch digester environments. Corrosion testing in several batch digester liquors has revealed that at least 25% Cr is required for stainless steel weld overlays to have best corrosion resistance in aggressive digester environments.13 Duplex stainless steel weld overlays such as Type 312 (S31200) can give 22% to 28% Cr when applied over a carbon steel substrate, depending on the welding process and mode employed.

Early work suggested that lower-than-intended chromium content resulted in poor weld microstructures, which in turn corroded.14 (See Figure 4-3.) More recent work has focused on the role of chromium content on overlay corrosion. TAPPI guidelines give minimum as-deposited chemistry requirements for austenitic stainless steel weld overlays, along with criteria for soundness and structural uniformity. However even weld overlays that meet the minimum of 18% Cr in the TAPPI guideline can experience rapid corrosion in many batch digesters.15 Another problem with stainless steel weld overlays is that once the overlay is penetrated (e.g., at a pinhole), the underlying carbon steel can corrode at a great rate, producing a large cavity that can grow completely through the digester wall.

Although duplex stainless steels resist corrosion in digesters better than conventional austenitic stainless steels,8–11 duplex stainless steels can experience selective corrosion of the austenite phase in the microstructure because this phase is lower in chromium content than the ferrite phase.16 Olsson reports very low corrosion rate - approximately 5 mils (0.1 mm) after 3 years in service - where selective phase corrosion has occurred.17 For particularly aggressive batch digester environments, superduplex stainless steels (such as UNS S32750) have superior corrosion resistance because the ferrite phase has a higher chromium content than that in conventional grades (such as UNS...
The modern trend is to construct new batch digesters from duplex stainless steels. The higher strength and low corrosion allowance for duplex allow thinner walls to offset much of the higher cost of duplex digesters, as compared to carbon steel.

Thinned carbon steel batch digesters are most commonly protected by application of a layer of stainless steel weld overlay. Weld overlay has also been applied to extend the service life of digesters with corroded stainless steel.
4. **Digesters**

NOTES

Steel cladding or with corroded overlay. Other protective measures include application of thermal spray coatings and anodic protection. Buildup with carbon steel weld metal is not considered to be a protective option, as such buildup (e.g., E7018) characteristically has high silicon content and typically corrodes much faster than the original digester wall. However, build-up of very thin sections with carbon steel before applying stainless steel overlay or thermal spray coating is good practice and normally done.

**Stainless Steel Weld Overlays**

Stainless steel weld overlays are best applied before the corrosion allowance has been completely consumed. TAPPI TIP 0402-03 “Guidelines for Corrosion Resistant Weld Overlays in Sulphate and Soda Digester Vessels” provides much useful information. These overlays are applied automatically using either the submerged arc welding (SAW) process or the gas metal arc welding (GMAW) process. Other welding processes may be used for pickup repairs or for smaller areas of overlay, such as around projecting nozzles where automatic equipment does not work.

SAW overlay is typically applied horizontally, with twin electrodes travelling around the circumference of the digester; the second electrode follows behind the first, completely remelting the deposit. GMAW overlay can be applied both horizontally (“conventional” overlay with a single electrode) or vertically over lengths up to 13 ft (4 m), with single or dual torches.

Horizontal weld overlay has been the “conventional” overlay mode for over 40 years, and typically gives an overlay thickness of 0.25 in. (6 mm), for either the SAW or GMAW processes, with a minimum of 0.188 in. (4.8 mm) overlay thickness. The vertical down mode typically gives an overlay with a nominal thickness of 0.188 in. (4.8 mm) and a minimum thickness of 0.100 in. (2.5 mm). Vertical overlay may be suitable in certain batch digesters if it can be established (either by corrosion testing or by service experience) that the overlay alloy does not corrode rapidly in the particular liquor environment.

The as-deposited composition of a weld overlay is a result of the dilution of the filler metal with the substrate. For overlay on carbon steel, dilution with the carbon steel results in a lower alloy content than that of the wire or electrode. For overlay on stainless steel (or for two-layer overlay) the as-deposited composition may be close to that of the wire or electrode.

In the past, most stainless steel weld overlays in digesters were Type 309 with 20 to 23% Cr and 10 to 12% Ni in the weld deposit. For SAW
4. DIGESTERS

Overlay the wire and flux are specially manufactured to provide the desired as-deposited chemistry. For GMAW overlay, Type ER309LSi (S30988) wire has been widely used.

In recent years there has been an increasing interest in application of Type 312 duplex stainless steel weld overlays. SAW wire and flux chemistries that give as-deposited compositions resembling Type 312 stainless steel are available. GMAW overlay can be done with ER312 wire. Internal microcracking has occurred in some Type 312 overlays. Provided the internal microcracks are not exposed to the surface, there is little driving force for their growth and no way for them to act as paths for liquor to gain access to the carbon steel substrate.

Overlays made with either Type 309 or 312 stainless steels have microstructures consisting of a mixture of austenite and ferrite. Conventionally, however, the Type 309 overlays have been called “austenitic” because they have lower ferrite than their Type 312 counterparts, which are termed “duplex.” SAW overlays tend to have higher ferrite contents than their GMAW counterparts. The presence of ferrite in the microstructure of stainless steel weld overlays is highly desirable. Stainless steel overlays with less than 3% ferrite are prone to hot cracking, particularly if sulphur is present as a contaminant.

Thermal Spray Coatings

Many batch digesters have been protected from corrosion by the application of thermal spray coatings. Most coating alloys are either Alloy 625 (N06625) or similar alloy but with somewhat lower molybdenum content. The predominant process for applying these coatings has been twin-wire arc spray (TWAS). In recent years coatings have also been applied by the high velocity oxygen fuel (HVOF) process.

TWAS coatings are typically applied 80 mils (2 mm) thick to overcome the porosity inherent in that process, and to prevent liquor access to the carbon steel substrate. HVOF coatings are characteristically much less porous and are applied thinner (e.g., 25 mils or 0.6 mm).

Thermal spray coatings are maintenance coatings inasmuch as they typically have a service life of up to 8 years before re-coating is required. The main advantage of thermal spray coatings is that they introduce no significant heating, and thus there are no heat affected zones as with welds, and no distortion or delamination of the vessel (as sometimes happens with weld overlays).

In-service problems with thermal spray coatings include disbonding and blistering. The bond to the carbon steel substrate is mechanical and poor surface preparation can lead to poor bonding. The blistering is believed to be caused by osmotic pressure buildup when liquor permeates the coating.

Anodic Protection

Monitoring corrosion potential in carbon steel batch digesters has revealed that the potential cycles change from active to passive over the course of a cook. With anodic protection an external rectifier and internal cathodes are used to supply current to the digester wall, thus raising the corrosion potential more rapidly to the passive zone. Although the concept of anodic protection of batch digesters has been understood for many years, there are as yet no anodically protected batch digesters in North America. However, there are numerous anodically protected continuous digesters in Finland.

Anodic protection is only able to protect the digester wall below the liquor level. For those digesters where corrosion of the top dome is the problem, anodic protection would be of no benefit.

4.2 CONTINUOUS DIGESTERS

Continuous digesters first appeared commercially in the late 1950s. Figure 4-4 shows a cross-sectional view and flow diagram for a typical continuous digester, the majority of which are of a “Kamyr” design. A prominent feature of most Kamyr systems is a cylindrical digester shell, having a vertical axis and a length-to-diameter ratio ranging from...
about 5 to 1 to 15 to 1. The shell diameter typically decreases from bottom to top with a series of conical transitions. The top and bottom heads are ellipsoidal.

As the chips descend through the digester they are impregnated with liquor, cooked, washed, and discharged into a blow tank. The spent liquor is extracted through extraction screens. Heat is supplied by indirect heating of the cooking liquor in external heat exchangers. Continuous digesters can be either of “hydraulic” (filled to the top

**Figure 4-4** Kamyr Continuous Digester
with cooking liquor) or “vapour phase” (with steam injection in the top) design. The hydraulic digester is by far the predominant type.

Digesters can also be single-vessel or two-vessel systems. In two-vessel systems there is a separate impregnation vessel, with cooking, extraction, and washing done in the digester. For this section, the term “digester vessel” refers to either the single-vessel or two-vessel systems, including the impregnation vessel.

In conventional operation the cooking liquor (a mixture of white and black liquors) is added in the top of either the digester (for single-vessel systems) or impregnation vessel (for two-vessel systems). In extended delignification processes such as modified continuous cooking (MCC), extended modified continuous cooking (EMCC), isothermal cooking (ITC), or low-solids cooking, white liquor is added lower in the digester. The extended delignification processes are also characterized by higher temperatures in the bottom of the digester (e.g., below the extraction screens).

Materials of Construction

The pressure shell of the earliest continuous digesters were built of low-Si A285-Grade C carbon steel “modified for digester service,” together with low-silicon caps for the process-side welds. In the late 1960s, medium-silicon steels such as A516-Grade 70 became the predominant material of construction for continuous digesters and the use of low-silicon weld metal was discontinued.

Some of the non-pressurized internal equipment in continuous digesters have traditionally been constructed from Type 304L stainless steel. This includes the central pipes, screens, and internal cone. Many of the nozzles in carbon steel digesters are also Type 304L stainless steel. There is a recent trend to replace corroded carbon steel blank plates with Type 304L stainless steel blank plates and Type 304L stand-off rods on the back.

Several continuous digesters have been constructed from roll-clad plate with Type 304L stainless steel on the process side and A516-Grade 70 carbon steel on the outside. Indeed, most digesters have also been constructed with Type 304L stainless-clad top and bottom heads, either as a loose liner or with roll-clad plate.

Some new continuous digesters have been built from duplex stainless steel (UNS S31803). This alloy is quite resistant to corrosion in continuous digester environments. Duplex stainless steel has also been used for the replacement of one digester top.

Corrosion

The most serious corrosion problem with carbon steel continuous digesters has been caustic stress corrosion cracking (SCC) of un-stress-relieved seam welds in the impregnation zone or in the impregnation vessel for two-vessel systems. The ASME Boiler and Pressure Vessel Code does not require post weld stress relief treatment for wall thicknesses less than 1.25 in. (32 mm), which often is the case at the top of continuous digesters. In 1980 there was catastrophic caustic SCC failure of an un-stress-relieved top section of a continuous digester. The combination of high tensile stress (from residual welding stresses) and corrosion potential in a critical range is a prerequisite for caustic SCC. Since the early 1980s most if not all continuous digesters have been fully post weld heat treated, even though stress relief was not mandated by the ASME Code for wall thicknesses less than 1.25 in. (32 mm).

Carbon steel welds and weld buildup made in the impregnation zone of digester vessels and not subsequently stress relieved are susceptible to caustic SCC. Below the cooking screens caustic SCC has not been reported.

Until the late 1980s corrosion thinning was not a serious problem with continuous digesters, except in unusual cases where corrosive wood species such as western red cedar were being pulped. Earlier research had identified wood extractives such as catechols as very corrosive to steel under conditions of alkaline pulping. In more recent years there have been many cases of rapid thinning at rates approaching 250 mils per year (6 mm/y) of carbon steel continuous digesters, around and below the
4. Digesters

Many digesters have experienced extensive metal loss from cleaning with hydrochloric acid. Even when properly inhibited, corrosion damage (usually in the form of pitting) can occur if the temperature is above 160°F (70°C), which is often the case. Acid cleaning done at ≤120°F (50°C) is not considered to be corrosive. Pitting of the carbon steel wall in the impregnation zone is usually a sign of acid cleaning damage, as continuous digesters do not usually experience corrosion thinning or pitting in this area. Alternative acids for cleaning, such as sulphamic acid and formic acid, are less corrosive to digesters.

Preferential weld corrosion is often observed in continuous digesters, and is the result of the poorer corrosion resistance of weld metal (which has a coarse grained structure similar to a casting), compared with the parent metal plate (which is typically lower in silicon content). The common practice of restoring corroded weld seams without subsequent stress relief results in welds with high residual stresses that may make the digester more susceptible to caustic SCC.

Stainless steel in digester vessels can experience corrosion as a result of hydrochloric acid cleaning, which preferentially attacks the ferrite phase in welds, but can also cause widespread pitting if the temperature is high enough. Attack of circumferential welds in Type 304L central pipes has resulted in central pipe failures. The welds often have incomplete penetration, which contributes to failure. Stainless steel top and bottom dome liners may experience SCC or intergranular attack (IGA) if they are heat treated with the digester. This practice can result in sensitization through chromium carbide precipitation at the grain boundaries. Continuous digester vessels constructed from roll-clad austenitic stainless steel can also undergo intergranular attack (IGA) if they become sensitized during post weld heat treatment, which is mandatory for the carbon steel digester shell.

Protection of Continuous Digesters

As corrosion rates have been observed to increase, protective measures such as corrosion-resistant weld overlay, thermal spray coating, and anodic protection have been increasingly employed. Measures such as anodic protection, taken to prevent corrosion by the pulping liquor, will not
4. Digester

Protect the digester from acid damage because the anodic protection system must be turned off during acid cleaning.

As with batch digesters, carbon steel weld buildup is not considered a permanent protective measure because it is susceptible to high corrosion rates, which can expose welding defects such as porosity. It is also susceptible to caustic SCC if in the impregnation zone.

**Stainless Steel Weld Overlay**

Stainless steel weld overlays are being increasingly used in continuous digesters for protection of the carbon steel shell from corrosion thinning. The overlay properties in continuous digesters are essentially the same as those discussed in the section above on stainless steel weld overlay of batch digesters. Service experience and corrosion testing have shown that Type 309 stainless steel weld overlays (applied by either the SAW or GMAW processes) have good corrosion resistance, even under non-conventional cooking operation. Indeed, the 18% minimum Cr level recommended in the TAPPI guidelines is likely adequate for good corrosion resistance. A minimum of 20% Cr is recommended for aggressive continuous digester environments.

Since continuous digesters are so large, it is often not practical to overlay large areas in one shutdown; so overlay is typically done over a period of years. For digesters thinned to near minimum, stainless steel weld overlay of digester walls is sometimes done in combination with anodic protection.

Preferential corrosion or “fingernailing” is often seen in the carbon steel adjacent to stainless steel weld overlay, most often in the impregnation and cooking zones. While fingernailing resembles galvanic corrosion, it is simply the preferential corrosion of the heat affected zone in the carbon steel, which has poorer corrosion resistance than the parent metal. Caustic SCC often begins at the bottom of a fingernailing crevice.

Protection of carbon steel weld seams susceptible to caustic SCC (in the impregnation zone) with stainless weld overlay bands has not been successful. The residual tensile stresses in the carbon steel at the termination of the overlay are high enough to promote caustic SCC. However, anodic protection can prevent caustic SCC in these heat affected zones adjacent to the overlay.

Alloy 625 (ERNiCrMo3) and Alloy 82 (ERNiCr3) nickel-base weld overlays have good corrosion resistance in continuous digester liquors and were widely used in the 1980s. However, most overlay being applied in continuous digesters today is Type 309 stainless steel.

**Thermal Spray Coating**

Thermal spray coatings, both TWAS and HVOF, have been applied in continuous digesters to protect large areas just above or below the extraction screens from corrosion thinning. Because thermal sprays do not produce a heat affected zone, they can also protect weld seams in the impregnation zone from caustic SCC. The thermal spray coatings applied in continuous digesters are the same as those applied in batch digesters, i.e., predominantly Alloy 625 and similar nickel-base alloys.

Although laboratory testing has indicated thermal spray coatings can protect against both caustic SCC and thinning, service experience has been mixed. With good surface preparation, coatings adhere well and provide several years of corrosion protection. However, there have been problems with blistering and disbonding.

**Anodic Protection**

Since the early 1980s anodic protection has been successfully used to protect partially stress-relieved continuous digesters from both caustic SCC and corrosion thinning. Anodic protection of continuous digesters requires multiple external rectifiers and internal cathodes. There are two main cathode designs: centrally mounted (on standoffs from the central pipe) and wall-mounted. Anodic protection for thinning can reduce corrosion rates, but may not necessarily reduce them to zero. Anodic protection can, however, extend the life of the corrosion allowance so that more permanent protective measures (such as stainless steel weld overlay) can be carried out later.
4. D IGESTERS

4.3 A NCILLARY E Q UIPMENT

Stainless steels have been used as materials of construction for much of the equipment ancillary to digesters. This includes piping, valves, and pumps. Some of the major ancillary equipment are discussed below.

Liquor Heaters

External heat exchangers are used for indirect heating of the digester, most of which today are a two-pass shell and tube construction, Figure 4-5. Batch digesters usually have one heat exchanger, while Kamyr units usually have three, Figure 4-4. While the continuous cook, two exchangers are in service while the third is being cleaned or in a standby mode. Tubing is 1 to 1.5 in. (25 to 37 mm) in outer diameter (OD), and from 10 to 15 ft (3 to 4.6 m) in length. Cooking liquor circulates through the tubes, with saturated steam on the shell side. Shell side temperature is approximately 390°F (200°C), while the liquor is 300 to 340°F (150 to 170°C).

For many years welded Type 304L stainless steel tubes have been the “standard” material of construction in liquor heaters. Unfortunately, austenitic stainless steels Types 304L and 316L are susceptible to both chloride and caustic SCC, which has caused many tube failures. SCC of liquor heater tubes can occur from either the steam side or the liquor side. Inadvertent introduction of superheated steam has caused rapid SCC of Type 304 tubing. Type 304L stainless steel tubes are also susceptible to rapid liquor-side thinning, which eventually leads to tube rupture. Thinning in batch digester liquor heaters is believed to be due to high temperature operation. In continuous digester liquor heaters, thinning may be due to HCl cleaning. HCl cleaning is detrimental to the welds in Type 304L stainless steel welded tubing, unless the manufacturer of the welded tubing has processed the tubing to reduce the normal ferritic content of the welds.

Type 304L tubes are normally used for new construction – where cost often controls material selection – and they are replaced when SCC or thinning causes unacceptable amounts of downtime. Duplex stainless steels such as 3RE60 (S31500), Alloy 2205 (S32205), and Alloy 2507 (S32750) are resistant to SCC in liquor heater service but are also susceptible to thinning, especially at higher temperatures. High nickel alloys such as Alloy 600 (N06600) and Alloy 800 (N08800) are resistant to SCC and have improved resistance to acid cleaning damage.
4. DIGESTERS

Figure 4-5  Digester Liquor Heater
4. **Digesters**

**Chip Conveyors**

Chip conveyors, which bring chips from the wood yard to the chip feeders, use Type 304 for bends and other components subject to chip abrasion. Chip feeders for continuous digesters are typically made from centrifugally cast, precipitation hardened stainless steel Alloy CB-7C u-1 (J92180), in the solution annealed and aged (H925) condition, for best abrasion resistance. Rotors are manufactured from cast martensitic Alloy CA-6MN (J91540) or from Alloy CB-6 (J91804). Rotors are quenched and tempered to BHN (Brinell hardness number) 240-302. Modified versions of Alloy CA-6NM have been used to enhance weldability. Rotor cracking problems have been experienced, and have been largely due to casting shrinkage. Manufacturers and users have begun to specify radiographic testing of rotors to ensure quality of the casting. Worn rotors are typically rebuilt by welding with modified Type 410 (S41000) stainless steel applied by the sub-arc welding method. Corrosion of carbon steel feeder housings beneath the liner is a common problem and can result in cracking of the liner. Significant corrosion must be repaired by removal of the liner and welding a stainless steel overlay onto the housing. This is then precision machined to accept the liner.

**Steaming Vessels**

Chips are usually presteamed in a steaming vessel prior to introduction into the cooking vessel through a rotary type high-pressure feeder. The steaming vessel is a horizontal cylindrical vessel which has conventionally been constructed from carbon steel with a partial cladding of Type 304L stainless steel on the inside. A wear plate of Type 304L or Type 316L stainless steel is usually installed along the bottom of the vessel to protect the carbon steel wall from wear by the chips as they pass through the vessel. The wear plate usually corrodes rapidly and needs to be replaced every few years. The steaming nozzles, if constructed from Type 304L or Type 316L, may also experience SCC from the inside.

In the 1980s several steaming vessels were constructed from solid Type 304L stainless steel. Most of these vessels experienced external SCC beneath the insulation when the insulation became wet from liquor spills. These vessels also had internal SCC in the steaming nozzles.

Duplex stainless steels such as Alloy 2304 (S32304) and Alloy 2205 have superior resistance to SCC and wear and are preferred for the internal lining, particularly the wear plate. Some steaming vessels have been constructed from clad duplex stainless steel (roll-clad or explosion clad) and are relatively maintenance-free.
4. Digesters

Flash Tanks, Blow Tanks, Valves, and Pumps

In a continuous digester there are typically two flash tanks for the liquor extracted from the digester. The flash tanks were typically made from carbon steel, but there have been many reports of severe corrosion or erosion corrosion of these vessels. High rates of flash tank corrosion usually occur when the digester is also experiencing rapid corrosion thinning. Types 304L and 316L were rated as marginal and duplex Alloy 2205 is preferred. Corrosion was attributed to the presence of organic acids in the flash tank environment.

Thermal spray coating or lining with Type 304L stainless steel has extended the life of corroding flash tanks. Replacement of flash tanks with solid duplex Alloy 2205 is a solution to the corrosion problem.

The blow tank for batch digesters may be of carbon steel, Type 304L, or for larger tanks, Alloy 2205 construction. Blow valves are usually CF-3 (J92500) cast stainless steel. CD-4MCuN (J93372) or CD-6MN (J93371). Cast duplex stainless steels are preferred for pumps due to abrasion from sand and grit loadings.

REFERENCES

4. **Digesters**

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**NOTES**


41. “Pressure Vessels,” American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code, Section VIII, Division 1.
4. Digesters

Other Useful References

At the end of each reaction in brown stock washing (cooking, oxygenation, or bleaching), there is dissolved organic and soluble inorganic material present in the pulp. The purpose of washing between stages in the fibreline is to economically remove the maximum amount of this dissolved organic and soluble inorganic material with the least amount of fresh or recycled water (i.e., with the lowest possible dilution). This is necessary because the dissolved solids present in the pulp as it is discharged from the washer will interfere with subsequent bleaching reactions and cause an increase in the use of bleaching chemicals to achieve the same degree of delignification and brightness. Final washing of bleached pulp is important to minimize the carry-over of corrosive ions to the paper mill.

A conventional brown stock washing system is illustrated in Figure 5-1. Brown stock washing systems normally include machinery such as knotters (2 stages), rotary drum vacuum or pressure washers (2 to 4 stages), foam breaker(s), centrifugal pumps, thick stock pump(s), and agitators. The knotters remove undesirable material from the pulp stream, such as knots, undercooked chips and tramp material. The accepted pulp slurry from the knotters is normally processed across each washer via intermediate stages for re-dilution and agitation. To maximize the removal of dissolved solids, most brown stock washing systems are arranged to process the washing liquor flow in a direction opposite to the pulp stream flow. This is termed “counter-current washing.” The fresh water or cleanest liquid is applied on the last washing stage and travels counter-currently through the intermediate stage(s) and to the first washing stage, where it exits to the recovery system at the highest solids concentration. The last stage of brown stock washing may be used to acidify the pulp with sulphuric or carbonic acid prior to bleaching.

In continuous digestion, the first stage of washing occurs in the digester itself (Figure 5-2). In this case, weak liquor from the first-stage vacuum washer is introduced into the digester in such a manner as to displace the cooking liquor out through stainless steel strainers. In the 1970s, prior to the recycling of wash waters, carbon steel was a common material chosen for brown stock washers. As recycling became common, minor constituents such as Stainless Steels and Specialty Alloys for Pulp and Paper
5. Brown Stock Washing

chlorides, thiosulphate, and polysulphides increased, requiring upgrading to Types 304L (S30403) and 316L (S31603). The buildup in chloride ion favours Type 316L over Type 304L and may require even higher molybdenum containing alloys, depending upon the chloride ion concentration. Type 316L is currently the preferred material for brown stock washing. Duplex alloys have been used successfully for some washers. Duplex alloys are preferred for the pumps, as there is considerable sand and grit carry-over in the white liquor.

Figure 5-2 Brown Stock Washing – Counter-Current Washing System Model

REFERENCES

The flow diagram of a typical kraft mill's chemical recovery system is shown in Figures 6-1 and 6-2. The cyclic recovery processes recover the inorganic chemicals (white liquor) used to cook or digest the wood chips. First, the black liquor is evaporated dry enough to be burned. Second, the reduced, molten smelt produced in the recovery boiler is dissolved in water to make green liquor. This is then causticized to produce the white liquor. Organic chemicals dissolved out of the wood are the fuel portion of the black liquor fired in the recovery furnace. This combustion also raises steam for energy generation and for process use.

### 6.1 BLACK LIQUOR

#### Black Liquor Evaporation

After separation from the pulp in brown stock washers, weak black liquor at a concentration of about 15% solids is pumped to a multiple-effect evaporator in which solids are concentrated to at least 50%. Further evaporation of the black liquor in a concentrator or direct contact evaporator increases solids content still higher so it has enough heat value to be the primary fuel in the recovery furnace.

Black liquor inorganic constituents are mostly sodium carbonate and sodium sulphide. Other inorganic constituents include sodium hydroxide, sodium sulphate, sodium thiosulphate, and sodium chloride. A typical composition for sulphate black liquor leaving the digester is shown in Table 6-1.

Pulp mills with a chemical recovery process utilize a series of multiple-effect evaporators (MEE) similar to that shown in Figure 6-3 to make the liquor concentrated enough for combustion in the recovery boiler. MEE systems vary as to the number of evaporators, concentrator systems, capacity, etc. Most evaporators are steam-heated, using either shell-and-tube or falling-film heat exchanger designs. Figure 6-4 shows a schematic of a falling film unit.

Some kraft mills concentrate the black liquor to around 80% solids, but most mills concentrate the liquor to somewhere in the 65-75% solids range. The high temperatures associated with evaporating the black liquor above about 40% solids make stainless steels essential for the liquor-wetted surfaces. Stainless steel heat exchanger surfaces are more or less universal in all evaporation stages.

Carbon steel may still provide satisfactory corrosion resistance in the bodies of the first two or three evaporation effects (these usually are the highest-numbered effects), especially where liquor temperatures are below 200°F (93°C). Although the exact mechanism for corrosion of carbon steel in black liquor is not fully understood, the tenacity of the self-protective passive film is a crucial factor.

Stainless steels, with their much more tenacious passivity, have a favourable history of resisting corrosion in all black liquor environments. As a result, stainless steels are used both to repair existing equipment where carbon steel has corroded, and in new equipment where corrosion of carbon steel might be expected.

MEEs from the third or fourth to the first effects and the concentrator are always made completely of stainless steel, most often Type 304L (S30403). Many mills have used sheet linings of duplex or austenitic stainless steel to protect carbon steel components against liquor corrosion. It is sometimes necessary to protect the carbon steel tube sheets and vapour zone target areas in MEEs. Corrosion barriers might be sheet linings of stainless steel (duplex versions are better) or thermal spray coatings.

In liquors concentrated to higher than about 70% dry solids, Type 304 and Type 316 concentrator tubing is subject to both significant general corrosion and to caustic stress corrosion cracking. Caustic cracking is believed to occur because temperatures and

<table>
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<tr>
<th>pH</th>
<th>Sodium Sulphide (at 23% solids; in gm/l)</th>
<th>Sodium Sulphide</th>
<th>Sodium Carbonate</th>
<th>Sodium Thiosulphate</th>
<th>Sodium Chloride</th>
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<td>11.6</td>
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<td>6.8</td>
<td>2.0</td>
<td>55.9</td>
<td>14.3</td>
</tr>
</tbody>
</table>
Figure 6-2 Flow Diagram of Black Liquor Recovery Boiler–Liquor Tanks–Lime Kiln

- Troughs in wet-bottom precipitators are lined with stainless steel.
- Seal water lines and condensate lines throughout can be stainless steel.

Stainless Steels and Specialty Alloys for Pulp and Paper
caustic concentrations are entering ranges where both Types 304 and 316 are subject to caustic stress corrosion cracking in these high dry solids environments. Duplex alloy S32205, ferritic stainless steels and nickel base alloys are preferred for tubing in high dry solids concentrators due to their better resistance to general corrosion and to caustic stress corrosion cracking.

There is also one report of stress corrosion cracking in the tidal zone of Type 304L tanks storing 72% solids black liquor. The tanks are located in a mill processing sea-water floated logs. In this same mill Type 304L tanks storing 50% solids black liquor have shown no signs of corrosion or stress corrosion cracking after more than 15 years.

Falling film evaporator elements are manufactured by spot welding two sheets of stainless steel [Types 304L, 2205 (S32205), or 6% molybdenum stainless steel] and pressurizing the space between the sheets. A bank of the dimpled sheets ready for installation in an evaporator is shown in Figure 6-5.

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**Figure 6-3 Typical Multiple-Effect Evaporator/Concentrator Design**

- **75% Product**
- **55%**
- **16% Feed**
- **Clean Condensate**
- **Foul Condensate**
6. CHEMICAL RECOVERY

Figure 6-4 Falling Film Black Liquor Evaporator and Concentrator Design

- Liquor Distributor
- Heating Element
- Steam
- Entrainment Separator
- Vapour Body
- Feed
- Recirculation Pump
- Vent
- Product
- Vapour
- Condensate
- Pump
Waste streams, such as sulphuric acid effluent from the tall oil plant and spent acid from chlorine dioxide operations - both are sources of sulphates for maintaining the sulphur balance - may be added to the evaporator black liquor stream before the first effect or concentrator. This sometimes makes liquors too corrosive for Type 304L stainless steel, especially if the residual alkalinity in the liquor is eliminated by these additions. Higher alloyed austenitic steels are generally adequate for handling black liquors.

Stainless steels perform well as pumps, piping, tube sheets, liquor boxes and surfaces subject to evaporator-related, black liquor flow turbulence or splashing perform well. Type 304L stainless steel also is widely used throughout the steam and condensate piping systems. This includes all vapour bodies, separators, condenser tubes, pumps and piping.

This discussion has concerned sulphate (kraft) and soda (i.e., alkaline) spent liquor evaporators. Evaporators for acid (i.e., sulphite) spent liquors require Type 316L (S31603) or higher molybdenum content stainless alloys for all liquor and vapour contacted surfaces. Evaporators for neutral pulping (sulphite semi-chemical (NSSC)), in which the liquors have lower but still alkaline pH and a higher concentration of sulphite ions, normally...

Figure 6-5  Dimpled Stainless Steel Plates - Falling Film Evaporator

Courtesy Ahlstrom
use Type 316 (S31608) stainless steels for heat exchanger tubing and other liquor contacted surfaces.

**Black Liquor Oxidation**

Black liquor oxidation is carried out in many mills as an odour-control measure. By oxidizing the liquor, hydrogen sulfide \((H_2S)\) and mercaptan levels in evaporator condensate and in the non-condensible phases are reduced. Oxidation of sulphides in the liquor to thiosulphate also reduces the hydrogen sulphide content of the boiler flue gas.

As with all liquor handling equipment at elevated temperatures, tanks piping and other components for black liquor oxidation are most often made of Type 304L stainless steel.

**Black Liquor Tanks**

Black liquor may be stored at 30% solids, which is a typical liquor concentration in soap separation tanks, as well as in the more concentrated “heavy black liquor” form, which may be stored before or after the liquor concentrator.

Black liquors must be kept hot for easier pumping. This makes corrosion of carbon steel in black liquor service unpredictable. Stainless steel construction, most commonly with Type 304L, can minimize corrosion in black liquor tanks and is essential to avoid flow-induced corrosion around agitators and in pumps and piping.

Stainless steel sheet linings can protect corroding surfaces in carbon steel tanks, provided the lining is properly designed to remain intact. Stainless steel linings also are used in carbon steel flash tanks on continuous digester systems.

A significant amount of welding is involved in properly installing a stainless steel lining because the dimensions of each lining panel must be small enough to minimize thermal expansion effects and avoid subsequent weld cracking. Another drawback of internal linings is the challenge of inspecting for corrosion behind the lining.

For new black liquor tanks it is generally more economical to specify solid stainless steel construction instead of using clad material or lining a carbon steel tank. Clad material at the thicknesses involved (less than 15 mm) is usually more expensive than solid stainless steel plate.

Storage tanks in a mill with high chloride levels in the heavy black liquor have experienced internal SCC and pitting in the wet-dry region of the walls. Testing showed that 6% Mo stainless steel adequately resisted the unusually aggressive environment in these tanks.

Appropriate inorganic corrosion-resistant linings can provide good chemical resistance to black liquor at all concentrations and temperatures.

**6.2 RECOVERY BOILER**

The reducing high temperature conditions in the smelt bed in the bottom of the recovery furnace convert sodium sulphate to sodium sulphide. Above the smelt bed oxidizing combustion conditions are required to avoid emissions of reduced sulphur gases like hydrogen sulphide. The combustion heat creates a molten, inorganic smelt rich in sodium sulphide and sodium carbonate. The red-hot, molten smelt is tapped from the boiler and dissolved in water in a tank outside the furnace – the dissolving tank – to form green liquor.

As described later, adding lime (from the lime kiln) causticizes the green liquor. The lime converts sodium carbonate to sodium hydroxide. Calcium carbonate is a by-product of this reaction. The hydroxide-rich, white liquor is clarified or filtered for use in the chip digesters. The calcium carbonate material is roasted to lime in the lime kiln.

**Recovery Boiler Tubing**

Stainless steels have superior corrosion resistance to carbon steels in the hot, sulphidic gas environments in the recovery boiler. As discussed above, both oxidizing and reducing sulphidic gas environments exist, with the latter
at the very bottom of the furnace. Carbon steel corrosion rates are low. However, they become unacceptably high in recovery boilers with steam pressures above 1000 psi (7 MPa), due to correspondingly higher tube temperatures.

A stainless steel or high alloy corrosion barrier can be applied to carbon steel tubes. In one case this is done in the form of “composite” tubes that have either a co-extruded, external stainless steel layer or a corrosion-resistant weld overlay around the entire tube. In another case it is either a thermal sprayed coating or corrosion-resistant weld overlay on the fireside only. These latter barriers can be applied on tubes in the boiler. Tubes with a chromium-rich, surface diffusion layer can be produced in a proprietary process termed “Chromizing™”.

Type 304L composite layers perform generally well on wall tubes, although they experience corrosion problems at wall openings. Figure 6-6 shows the floor and wall tubes with the smelt spout openings.

Type 304L composite layers can experience significant cracking in floor tubes and can crack at wall openings. The cracking may be due to SCC – possibly from environments arising during water-washing at outages – or from thermal fatigue. Thermal fatigue is more likely where smelt levels or smelt coverage of the tube surface fluctuate continually. Alloy 825 (N08825) is more resistant to cracking than Type 304L. Alloy 625 (N06625), whether co-extruded or weld overlaid, has the highest resistance to composite layer cracking.

Thermal sprayed coatings of stainless steel or Alloy 625, especially the impermeable coatings obtained with the high velocity oxygen fuel (HVOF) or high velocity air fuel (HVAF) processes, can provide excellent corrosion protection without the risk of SCC or thermal fatigue cracking.

Solid tubes of high-nickel alloys or Type 310 (S31000) stainless steel, or composite tubes with these materials as the outer layers, have been used for superheater tubing where the outlet steam temperature exceeds 900°F (482°C).

Recovery Boiler Precipitators

Most recovery boilers have electrostatic precipitators to remove particulates from the flue gases. The precipitator wall and plates and the inlet and outlet ducts are typically constructed of carbon steel, which generally performs acceptably in dry-bottom precipitators, ducting and stacks as long as metal temperatures are maintained above the dew point.
6. CHEMICAL RECOVERY

Carbon steel corrodes rapidly in the acidic conditions formed where the gases condense. This is called "dew-point corrosion" and is fairly inevitable at the bottom of wet-bottom precipitators. Accordingly, many wet-bottom troughs and hoppers are constructed or lined with stainless steel. The best grade to use should be determined by test. Some mills find Type 304 satisfactory, while others have used a higher-alloy stainless, such as Type 2205 or Type 316.

Stainless steel experiences slower dew-point corrosion than carbon steel. The austenitic stainless grades can experience chloride SCC, which can be avoided with high nickel alloys like Alloy 625 and C-276 (N10276) and with duplex stainless steels like Type 2205.

Type 2205 is a good material for recovery boiler stacks that experience dew-point corrosion. The 12% chromium stainless steels also significantly outlast carbon steel in precipitators, ducts and stacks. Alloy selection should depend on the condensate corrosiveness, which can be determined by corrosion testing.

The highly abrasive conditions in the salt cake mix tank, where boiler ash or dust is slurried in black liquor and
6. Chemical Recovery

Spent acid from the chlorine dioxide generator or other sulphur-bearing chemicals may be added, often, are too corrosive for carbon steel. Constructing or lining the salt cake mix tank with Type 304L stainless steel or, better still, Type 2205, is an increasingly common practice, as is the use of duplex stainless steels for pumps and piping in this system.

Smelt Spouts

Molten salt, known as “smelt”, runs out of the recovery boiler and into the water-filled dissolving tank via the smelt spouts. These are water-cooled troughs, with cooling water temperatures typically around 176°F (80°C). As already mentioned, the smelt is mostly molten sodium carbonate and sodium sulphide, with a temperature around 1500°F (815°C).

There are several different spout designs. Spouts usually are made of carbon steel, although stainless steel spouts are common outside North America. The trough of a new carbon steel spout can be weld overlaid to improve its durability, using Type 309 (S30900) stainless steel or a nickel alloy like Alloy 625.

The piping used to spray steam or weak green liquor (wash water) directly onto the smelt flow to break it into drops is most often Type 304L stainless steel. However, this can experience SCC where wash water evaporatively concentrates on the piping exterior. Duplex stainless steel is more resistant to this corrosion.

6.3 Chemical Recovery Tanks

Smelt Dissolving Tank

The molten smelt is quenched and dissolved in a large tank with internal agitators – the smelt dissolving tank – to produce green liquor. This tank rumbles continuously and the heat produced by heavy smelt inflows can cause significant hydraulic pulses. Most dissolving tanks have extra-thick walls and are made of carbon steel.

Internal corrosion protection is usually required because the agitated contents have a high content of abrasive, suspended solids. The continuous flows around agitators and the hydraulic pulsing help the heavy suspended solids content cause erratic, localized erosion-corrosion of carbon steel. Erosion, corrosion of carbon steel can also occur behind linings that are breached and are not sufficiently tightly attached.
There are three general ways to prevent corrosion in dissolving tanks:

- stainless steel construction with weldable 12% chromium steel, Type 304 or Type 2205 stainless steel;
- sheet lining with Type 430 (S43000), Type 304 or Type 2205 stainless steel and proper lining design, or
- lining with a reinforced, inorganic cementitious material.

All stainless steels have good corrosion resistance in green liquor immersion. Duplex and ferritic stainless steels resist SCC above the liquid level better than Types 304L or 316L. Solid stainless steel dissolving tanks are increasingly common. Pumps, agitators and nozzles that regularly see flow conditions are made of stainless steel. Duplex stainless steels are more resistant than austenitic grades to abrasive erosion-corrosion, such as experienced by agitator blades, due in part to the higher hardness of duplex stainless steel.

Green Liquor Tanks

Carbon steel green liquor tankage corrodes most rapidly where air dissolved in the green liquor produces thiosulphate ions. This usually occurs – and limits the worst corrosion to – half a metre or so immediately below the liquor level. Fluctuating levels reduce thinning rates by spreading the corrosion over a wider area.

Stainless steels like Type 304L austenitic, Type 2304 (S32304) or Type 2205 duplex grades have excellent corrosion resistance in all green liquor service conditions, including pumps and piping. 12% chromium stainless steel also is suitable for green liquor tank construction. Use of muriatic (hydrochloric) acid to remove carbonate scale buildup can harm these stainless steels, even if the acid is inhibited. More information on problems with inhibited hydrochloric acid cleaning are provided in section 20 “Corrosion”.

Many carbon steel clarifiers and tanks in green liquor service have internal stainless steel linings or solid plate inserts to prevent corrosion. Solid Type 304L stainless steel also is widely used for rakes, internal piping and nozzles.

Slakers and Causticizers

Slakers are tanks in which calcined lime is converted to calcium hydroxide, or a lime solution. The lime solution is added to the green liquor in the causticizer tanks to convert the sodium carbonate to sodium hydroxide, making white liquor from green liquor.

Slaker and causticizer environments are strongly alkaline and have high levels of suspended particles. The abrasion-erosion effects of the suspended materials can cause rapid corrosion of carbon steel where protective scales or deposits do not form. The abrasion from these suspended materials normally has an aggressive “polishing” effect on stainless steels. Harder stainless steels like the duplex grades or work-hardened austenitic grades are significantly more resistant to this abrasive, “polishing” mechanism.

Slaking and causticizing tanks are typically constructed of stainless steel or of carbon steel with an inorganic lining, commonly a gunned, sulphate-resistant, portland cement-based material. Pumps and piping are the standard grades of stainless steel, or duplex grades to better resist the abrasive conditions.

White Liquor Tanks

White liquor is clarified or filtered and then stored in tanks. Onset and rates of carbon steel corrosion are very unpredictable in white liquors. Aeration of white liquor produces intermediate, oxidized sulphur species like thiosulphate or polysulphide. These chemical species affect the passivity of carbon steel and can increase corrosion, although polysulphide levels higher than about 2 percent help stabilize the passive layer, thereby reducing carbon steel corrosion.

Stainless steel is fully corrosion resistant to white liquor due to its significantly more tenacious passive film. Types 304 and 316 are subject to intergranular cracking when sensitized by welding in white liquor at temperatures above 160°F (70°C). Sensitization can be avoided by specifying the low carbon grades, e.g., Type 304L, or a duplex stainless steel.
Molybdenum-containing stainless steels like Types 316L and 317L (S31703) have measurably poorer corrosion resistance than 304L in white liquor environments. Duplex stainless steels, with their higher chromium content, have better corrosion resistance than 304L. They also perform better under erosion-corrosion conditions, where the higher hardness of the duplex stainless steels contributes to their superiority.

Replacing the corroded part of the carbon steel wall with stainless steel has successfully repaired many white liquor clarifiers. Figure 6-7 shows schematically how this can be done. (This method of repair applies to white, green and black liquor tanks.)

For liquor heaters, tubes of Type 2205 stainless steel, 26-chromium ferritic stainless steel (e.g., S44660), and nickel (or nickel alloys) all outperform Type 304, which can experience internal corrosion at temperatures above 300°F (150°C) and also experience SCC, especially from the steam side.

As mentioned earlier for green liquor piping, acid cleaning austenitic stainless steel tubes in white liquor heaters with hydrochloric (muriatic) acid can damage the tubes. Pitting and SCC can occur with even short exposure to hot hydrochloric or muriatic acid, even if the acid is inhibited.

Clarifier rakes, piping, pumps, valves, nozzles, etc. for white liquor service are Type 304L or Type 2205 wrought stainless steel, or CF-3 (J92500) or CD-4MCuN (J93372) castings. As with wrought materials, duplex stainless steel castings have higher resistance to erosion-corrosion than austenitic stainless steel castings.

Additional Considerations for Tanks Wholly or Partially Made of Stainless Steel in Black Liquor, Green Liquor and White Liquor Service

As stainless steel replaces carbon steel for these chemical recovery tanks, two important precautions are sometimes overlooked.

First, when hydrotesting newly installed stainless steel tanks, it is necessary to drain the water used for hydrotesting or place the tank in service promptly to avoid microbiological influenced corrosion (MIC). MIC has been reported in Type 304L (and 316L) tanks in a number of cases where water used for hydrotesting was left in the tank for a month or more. It is important to drain the water completely since MIC can also occur in water left in the bottom of incompletely drained tanks. MIC has not been reported when tanks are placed in service within a few days of hydrotesting.
Two methods for replacing courses in carbon steel tank walls. The double-lap method on the right allows new plate to be positioned while the tank is in service. The corroded carbon steel portion is removed and the internal lap welds are made during an outage.
Second, the exterior of insulated Type 304L tanks is subject to SCC under the insulation, especially when the insulation is regularly wetted, e.g., by rain or leakage from nearby lines. Under-insulation SCC has been such a frequent occurrence that NACE developed a Standard Recommended Practice: “The Control of Corrosion Under Thermal Insulation and Fireproofing Materials” (RPO 198-98). This document outlines good practices to prevent under-insulation SCC.

Duplex and more highly alloyed stainless steels are far less susceptible to MIC and chloride SCC. However, both draining promptly after hydrotesting and keeping the insulation dry are good, anti-corrosion practices to follow, regardless of the material of construction. More information on these subjects is in the section on “Corrosion”.

6.4 LIME KILN

Lime mud from the white liquor clarifier is washed and fed to the lime kiln, where moisture is driven off and calcium oxide is formed. This is added to the green liquor to make white liquor. The lime mud is conveyed into the chain section of the kiln by a short section of spiral flights welded to the kiln shell. The kiln shell and the flights in this conveying section are subject to moderate abrasive corrosion. Type 2205 duplex stainless steel has been used for the flights and to line the kiln shell to better resist the abrasion in Zones 1 and 2 in Table 6-2.

Lime kiln chain

Heavy chains are used to collect heat from the hot exit gases and transfer the heat to the lime mud to evaporate the moisture from the mud. The chain section in the kiln can be 50 ft (15 m) or more long; so the chain nearest the burner is subject to both convective and radiative heat transfer. Progressing into the kiln from the feed end, four zones of the chain section can be defined, as in Table 6-2.

Carbon steel and low alloy steels can be used for the first two zones of chain if the metal temperature does not exceed 930°F (400°C). Cast or wrought stainless steel chain is required in the hotter zones where chain life is determined by scaling rather than by wear. Both austenitic and ferritic stainless steels are used. Selection is based on experience in a particular kiln and cost.

Austenitic stainless steels are considerably stronger than the ferritic stainless steels above about 1000°F (540°C). Type 304 stainless steel
or its cast equivalent CF 8 can be used in Zones 2, 3 or 4. Special heat-resisting grades are also available for Zone 4.

Type 304 stainless steel chain:
• has reasonable oxidation resistance up to 1500˚F (815˚C)
• can be exposed for 10,000 hours at 1200˚F (650˚C) and still retain adequate room temperature ductility
• has a reasonable creep rate at 1200˚F (650˚C).

While Type 304 is the basic alloy used for lime kiln chain, other alloys with better resistance to high temperatures are also used. Table 6-3 shows some aluminum and silicon alloyed, ferritic stainless steels used for lime kiln chain.

The calcined lime discharged from the kiln passes through lump-crushers and grizzlies and is conveyed away from the lime kiln by a drag chain. Since the calcined lime is discharged at a temperature of about 2200˚F (1200˚C), heat-resisting austenitic stainless steel is used for components handling hot lime. Typically HH (J93503) and HN (J94213) cast stainless steels are used for grizzlies and chain links, while Type 310 austenitic stainless steel is used for chain pins. Table 6-4 gives the composition of these stainless steels.

At the service temperatures encountered, the HH and HN cast steels are subject to precipitation of secondary phases that significantly reduce the ambient temperature toughness. Drag chain failures have occurred during startup when the chain is cold and jammed with hard deposits of calcined lime. Failures can be avoided by appropriate design and startup procedures.

The higher chromium content provides better oxidation resistance at temperatures above 1200˚F (650˚C). However, the higher chromium content makes these alloys more susceptible to sigma formation than Type 304. A careful review with a materials specialist is suggested when selecting alloys for the higher temperature services.
6. Chemical Recovery

SUGGESTED READING


Tall oil is a mixture of rosin and fatty acids with unsaponifiables in the black liquor from the digesters. It is removed from the black liquor by skimmers and sent to a storage tank for processing with sulphuric acid in the tall oil plant. Mappin provides flow diagrams for the batch and continuous acidulation processes. Conventional materials are noted in Figures 7-1 and 7-2.¹

Batch acidulation is the most prevalent process method. Most batch reactors are constructed of carbon steel with membrane and acid brick linings. However, Ketchum reported in 1990 that a batch reactor constructed of Alloy 20 (N08020) was free of significant corrosion wastage after 24 months in service.² The cost of the Alloy 20 reactor was only 60% of the cost of a membrane, acid brick lined reactor. Ketchum recently reported that the Alloy 20 reactor operated for 15 years without significant maintenance before it was shut down when the mill discontinued tall oil processing.¹ The reactor for the continuous process is either FRP, Alloy 20 or Alloy 904L (N08904). Older lead-lined reactors have been discontinued.

Sulphuric acid is the principal corrodenent in tall oil plants. Carbon steel has good resistance to strong 98% sulphuric acid and is the principal material used for strong acid storage tanks. Flow disturbs the protective sulphate film that protects carbon steel; therefore Type 316L (S31603) is normally used for piping. Type 316L is also useful in weak sulphuric acid at low temperatures. Copper additions to stainless steel improve corrosion resistance to sulphuric acid. Alloy 20, which was developed for sulphuric acid service and has 3.5% Cu, is the principal upgrade in North America. Alloy 904L, which has 1.5% Cu, is the principal upgrade in Europe when concentrations and temperatures are too high for satisfactory performance for Type 316L. In the mid range of concentrations at elevated temperatures, Ni Mo Alloy B (N10665) is one of the few metallic materials – other than tantalum and 12% silicon cast iron – that has useful corrosion resistance.

CN-7M (N08007) is the basic cast alloy used for pumps, valves and other cast components in sulphuric acid service. Alloy 20 is its wrought counterpart.

Isocorrosion charts provide useful estimates of probable performance of the large number of alloys used, and promoted for use, in sulphuric acid. Figure 7-3 shows the isocorrosion chart for Type 316L.³ The principal regions of useful corrosion resistance are below the 5 mpy (0.13 mm/y) line, at both low and high concentrations of sulphuric acid. Figure 7-4 shows the isocorrosion chart for Alloy 20.³ Alloy 20 is most useful at moderate temperatures up to about 30% concentration of sulphuric acid. Figure 7-5 shows the isocorrosion chart for Ni Mo Alloy B2 (N10665), which has useful resistance up to the boiling point of sulphuric acid in the mid concentration range, where so few materials are useful.⁴ (Refer to Table 7-1 for the composition of these alloys.) Ni Mo Alloy B2 should not be confused with Alloy C276 (N10276), which has much poorer corrosion resistance in sulphuric acid. Figure 7-6 shows the isocorrosion curves for a number of common alloys, including 904L and 6% Mo.⁵ Figure 7-7 shows the adverse effect on corrosion behaviour of even a small amount (200 ppm) of chlorides on the alloys shown in Figure 7-6.⁵

Chemical species, other than chlorides, including organic species, often present in sulphuric acid can have a significant effect on corrosivity. The positive or negative impact of other species present on corrosivity, and the nature of sulphuric acid itself, tend to make alloy selection site specific. Most of the isocorrosion charts in this section are for sulphuric acid, free of other chemical species. Figure 7-5 demonstrates the major adverse effect of chlorides. The isocorrosion charts, Figures 7-2 to 7-7 are very useful in selecting alloys for evaluation at individual sites in an operating plant. However, they provide only very general information on probable performance, as other species present can have such a profound effect on corrosion behaviour. It is best to expose coupons of candidate alloys in actual operating equipment before materials selection or upgrading decisions are undertaken.
Figure 7-1 Typical Materials of Construction in the Batch Acidulation Process

- Soap Storage: 200,000 gal (CS)
- Sulphuric Acid (93%)
- Steam Sparge (AL20)
- Reactor: 40,000 gal (Acid Brick-lined)
- Wet CTO Settling Tanks (2) 200,000 gal (FRP or SS or SS-lined)
- Spent Acid/Brine Vat (FRP)
- Truck Loading

Figure 7-2 Typical Materials of Construction in the Continuous Acidulation Process

- Soap Feed (CS)
- H₂O (CS)
- Fresh Acid (CS)
- Alternative: Waste Acid (30%) from Bleach
- In-line Mixer (AL20 or PLSP)
- Reactor (FRP, SS, or Lead-lined)
- Sparged Steam (SS)
- Centrifuge Feed Tank 300 gal (FRP)
- Centrifuge (SS)
- Spent Acid/Brine Neutralizing Tank 200,000 gal (FRP or SS)
- To Recovery or Weak Liquor (CS)

Materials of Construction:
- Crude Tall Oil (CTO)
- Fibreglass-reinforced Polyester (FRP)
- Carbon Steel (CS)
- Stainless Steel (usually 316L) (SS)
- Alloy such as Carpenter 20Cb-3 (AL20)
- Plastic or Plastic-lined Steel Pipe (PLSP)
Figure 7-3 Sulphuric Acid Isocorrosion Chart - S31603

Corrosion rates in parentheses are in mils per year

Figure 7-4 Sulphuric Acid Isocorrosion Chart - N08020

Corrosion rates in parentheses are in mils per year
NOTES

7. Tall Oil

Figure 7-5 Sulphuric Acid Isocorrosion Chart - N10665

Figure 7-6 Sulphuric Acid
Isocorrosion Diagram, 0.1 mm/year, for Austenitic Stainless Steels in Naturally Aerated Sulphuric Acid of Chemical Purity. Broken-line Curve Represents the Boiling Point.
7. TALL OIL

Figure 7-7 Sulphuric Acid with Chlorides
Isocorrosion Diagram, 0.1 mm/year, in Sulphuric Acid with an Addition of 200 ppm Chlorides.

Table 7-1 Composition of Alloys Used for Sulfuric Acid Service

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common 316L S31603</td>
<td>1.4404 C 0.03 Cr 17 Ni 11 Mo 2.2 N — Cu — Other</td>
</tr>
<tr>
<td>Alloy 20 N08020</td>
<td>(2.4660)* Cr 0.06 Cr 20 Ni 34 Mo 2.5 N — Cu 3.5 Other</td>
</tr>
<tr>
<td>Alloy 904L N08904</td>
<td>1.4539 Cr 0.02 Cr 21 Ni 26.5 Mo 4.5 N — Cu 1.5 Other</td>
</tr>
<tr>
<td>Ni Mo Alloy B2 N10655</td>
<td>— Cr 0.01 Cr 1.0 Ni 70 Mo 26 N — Cu 1.0 Co 2.0 Fe Other</td>
</tr>
</tbody>
</table>

* 2.4660 is a tentative EN designation.

REFERENCES

For many years kraft pulp mills have collected and disposed of “foul” condensates and odorous non-condensable gases (NCGs) containing hydrogen sulphide and reduced organic sulphur compounds in order to reduce the impact of emissions on neighbouring communities and the environment. These compounds are collectively described as Total Reduced Sulphur or TRS. Typically low volume high concentration (LVHC) gases and off gases from the stripping of foul condensates are collected at concentrations above their upper explosive limit (UEL) and incinerated in the lime kiln, recovery boiler, power boiler, or dedicated thermal oxidizer. The stripped condensate is recycled within the process and/or sent to the mill’s effluent treatment system. Heat recovered from the gases and condensates is used to heat process water. Some high volume low concentration (HVLC) gases are collected below their lower explosive limit (LEL) and incinerated, while others are released to the atmosphere.

Over the last several years environmental regulations have progressively restricted the release of TRS and other compounds in NCGs and foul condensates. Accordingly, there has been continuous evolution of processes and process equipment for collection and disposal of NCGs and foul condensates. Process evolution up to 1998 is described in textbooks and selected technical articles listed in the references at the end of this section.

On November 14, 1997 the U.S. Environmental Protection Agency promulgated the National Emissions Standards for Hazardous Air Pollutants (NESHAP) for selected pulp and paper categories. These new regulations required the collection and disposal of dilute NCGs and condensates from sources that previously were released to the environment by most mills. Depending on a mill’s age and process configuration, these sources may include:

- LVHC vents
- Knotting and screening
- Brown stock washing
- Brown stock decker
- Oxygen delignification
- Weak black liquor storage tank vents.

Existing mills can thus end up with two or more parallel systems to collect and dispose of NCGs and strip and recycle foul condensates. It is also apparent that process evolution will continue. Table 8-1 summarizes sources of odours and odour removal uses.

Carbon steel is not suitable for NCG collection systems. Concentrated NCGs are saturated in water and thus condensation occurs in the collection system. Dissolved NCGs in this condensed make it corrosive to carbon steel. Fiberglass Reinforced Plastic (FRP) is generally not recommended for...
NCG collection systems because of attack on the resin by turpentine and methanol in the NCG system. FRP resins are also subject to failure should NCG ignite.

Types 304L (S30403) and 316L (S31603) stainless steels have been the materials of choice for process equipment and piping handling NCGs and foul condensates. They do not experience general corrosion and remain free of fouling, which is beneficial for heat transfer equipment. Figure 8-1 shows a stainless steel steam stripping column.

Design of collection systems is important. Pipe networks should be properly grounded and potential sparking sources eliminated. Provisions should be made to prevent carry-over of black liquor droplets into the NCG piping especially where the black liquor has significant chloride ion content. Pipe slope should be adequate to ensure rapid condensate flow and condensate separators should be installed at the low points of the lines. It may also be necessary to purge some lines and equipment on startup and/or shutdown.

The pH of foul condensates is generally above 8, but in vapour space condensates the pH can be acidic due to dissolved NCGs. Depending on the mill and processes involved, chloride ions may be present. Preferential corrosion of weld metal may occur in the presence of some condensates if they are allowed to collect in “dead” zones. For example, Figures 8-2 and 8-3 show corrosion of ferrite in Type 316L weld metal after 20 years of service. Depending on temperature, stress corrosion cracking of Types 304L and 316L has also occurred.

It is not known if sulphur compounds have played a role in the instances of weld metal corrosion or stress corrosion cracking. Further, the collection and analysis of NCGs and condensates for diagnosis of corrosion problems is not straightforward and results may vary depending on sampling and analysis procedures. Thus it is not generally possible to predict which areas of process equipment, if any, may experience corrosion or stress corrosion cracking. Duplex stainless steel, higher alloy austenitic stainless steels, and nickel base alloys have been used in response to local occurrences of stress corrosion cracking.

Stainless steels and nickel base alloys suitable for high temperature service are commonly used for burner components for firing NCGs in lime kilns (refer to discussion of lime kilns in “Chemical Recovery”) and for some components of dedicated thermal oxidizers. Very aggressive environments from sulphur compounds in the non-condensable gases can develop in thermal oxidizers, which incorporate a quench chamber and scrubber for the combustion gases. Extensive use of nickel base alloys and Type 317L (S31703) stainless steel has been reported.

Because of the wide variety of processes and environments involved in collecting, processing, and incinerating NCGs, it is important when selecting equipment to review past performance and determine if process conditions will be outside the envelope of experience. In all cases it is desirable to ensure quality in welding to maximize the margin against corrosion or fatigue.

Table 8-1 Sources of Odours and Odour Removal Units

<table>
<thead>
<tr>
<th>Sources of Kraft Mill Odours</th>
<th>Digester Blow Tanks</th>
<th>Digester Blow Tanks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Digester</td>
<td>Digester Relief</td>
<td>Multi-Effect Evaporators</td>
</tr>
<tr>
<td>Accumulators</td>
<td>Sewer</td>
<td>Direct Contact Evaporators</td>
</tr>
<tr>
<td>Electrostatic Precipitators</td>
<td>Makeup</td>
<td>Sewer Outfall</td>
</tr>
<tr>
<td>Contaminated Hot Water</td>
<td>Slaking</td>
<td>Mud Filters</td>
</tr>
<tr>
<td>Dissolving Tanks</td>
<td>Causticizing</td>
<td>Knotters</td>
</tr>
<tr>
<td>Bleach Plant Towers</td>
<td>Screens</td>
<td>Driers</td>
</tr>
<tr>
<td>Washers</td>
<td>Foam Tanks</td>
<td>LVHC Vents</td>
</tr>
<tr>
<td>Tailings</td>
<td>Brown Stock Washers &amp; Decker</td>
<td>Liquor Storage Tanks</td>
</tr>
<tr>
<td>Oxygen Delignification</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Units Where Kraft Mill Odours Are Incinerated or Scrubbed

| Lime Kiln                           | Recovery Boiler              | Wet Scrubber        |
| Power Boiler                         | Thermal Oxidizer             |                     |

Stainless Steels and Specialty Alloys for Pulp and Paper
This is a typical stream stripping column for stripping the odour-bearing compounds from various waste streams originating at different odour-control condensers in the mill. Stainless steel is required to prevent corrosion and the accumulation of corrosion products around the bubble caps in the column, which could reduce the unit's efficiency.
Figure 8-2 Preferential Corrosion of Type 316L Weld Metal Where Aggressive Condensate Collected in a Vapour Line

Figure 8-3 Closer View of Corrosion of Ferrite in Type 316L Weld Metal (400X)
8. Air Quality Control

REFERENCES


Once the principal method for producing chemical pulp, the sulphite process has lost ground to the kraft and chemical-mechanical pulping methods. Nevertheless, sulphite pulping remains an important process.

Many similarities can be seen between Kraft and sulphite mills, although chemistries are quite different. Each has batch or continuous digestion, and some sulphite operations have chemical recovery. Following digestion, processes for washing, bleaching and papermaking can be identical. Consequently, the following discussion is limited to liquor preparation, digestion and chemical recovery. Figure 9-1 is a flow diagram of a typical magnesium base pulping and recovery operation.

9.1 THE ENVIRONMENT

Sulphite cooking liquor consists of free sulphur dioxide dissolved in water together with sulphur dioxide in the

---

Figure 9-1 Flow Diagram of Magnesium Base Mill and Recovery System

Stainless Steels and Specialty Alloys for Pulp and Paper
form of bisulphite. Until about 1950, sulphite pulping was an acid process using calcium as the base. Because the acid process was limited to only certain wood species, other base materials were introduced. These soluble bases are sodium, magnesium and ammonium, and their use has broadened sulphite pulping for all wood species. Subsequent to the introduction and application of magnesium and sodium bases, several two-stage sulphite pulping methods using these bases have been developed and utilized commercially. These methods are generally characterized by a dramatic change in cooking pH between the initial stage (for penetration and sulphonation) and the second stage (for dissolution and removal of the lignin).²

Depending upon the process, the pH of the cooking liquor can range from acid to neutral to alkaline. In acid bisulphite pulping, any pH within the range of 1.5 to 4.0 can be achieved by controlling the ratio of free and combined SO₂. True bisulphite pulping, with equal amounts of free and combined SO₂, would be carried out at a pH of 4.0 to 5.0. Another important sulphite pulping process is neutral sulphite semichemical pulping discussed in the following section.

Sulphuric acid is the principal aggressor in an acid sulphite mill. It can be generated in any number of unit operations. The environment usually contains chlorides that are often present in other chemicals used and are always present in logs that have been floated to coastal mills. Chlorides increase the aggressiveness of sulphuric acid. Refer to Figures 7-6 & 7-7 in the “Tall Oil” section.

9.2 CONSTRUCTION MATERIALS

It can be said that stainless steels and sulphite pulping grew up together. In fact many new alloys were tested in acid sulphite mills. Type 316 (S31600) stainless steel became the principal material of construction for sulphite mills, although more highly alloyed materials are required in a number of applications. Type 317L (S31703) and the higher molybdenum stainless steels are finding wider application, especially in the higher chloride environments. More recently, duplex stainless steels have been specified, due to their excellent resistance to pitting and stress corrosion cracking. There are also a number of applications where specialty alloys such as Alloy 20, (N 08020), 6% Mo alloys, G30 (N 06030), and C276 (N 10276) are advantageous.
9. SULPHITE PROCESS

9.3 SULPHUR DIOXIDE PRODUCTION

The principal method for producing sulphur dioxide is the burning of elemental sulphur, although some Canadian mills roast iron pyrites. The steps for preparing a sulphite cooking liquor are as follows:

1. Burning of sulphur.
2. Rapid cooling (to prevent sulphur trioxide).
3. Absorption of sulphur dioxide in a weak alkaline solution.
4. Fortifying the raw acid.

Mild steel is satisfactory for sulphur burners and combustion chambers. This is not a good environment for austenitic stainless steels because of the formation of low-melting-point nickel sulphide scale.

The hot sulphur dioxide is cooled rapidly in either heat exchangers or direct-contact water spray towers. The heat exchangers, or pond coolers, are lead lined steel pipe. Cooling towers are commonly acid brick lined but are occasionally Type 316L stainless steel. When stainless steel is used, walls should receive a constant supply of wash water. Figure 9-2 shows one design for a sulphur dioxide cooler. In this case the first section is lead or acid-brick lined, and the second section is stainless steel. Emergency water is available in case there is an excursion in temperature.

Piping from the cooling tower to the absorption tower can be exposed to sulphuric acid. Piping has been Type 316L or 317L, although some mills use FRP.

The sulphur dioxide compressors can be lined with lead or rubber (Alloy 20), or more commonly, with Type 316L or 317L construction. A better choice would be Alloy 20 or 904L (N08904), as this equipment is prone to accumulation of carry-over sulphur and attack by the small amounts of sulphuric acid which are inadvertently formed in the burner.

Atmospheric absorption towers can be Type 316L or 317L or FRP.

With FRP construction, all internals would be Type 316L or 317L stainless. Both the body and internals of pressure towers can be of stainless steel construction.

Acid tanks are usually acid-brick lined, although Types 316L and 2205 (S32205) duplex stainless steel have been used. However, sulphuric acid can be present, and if the temperature exceeds 185°F (85°C), acid-brick lined tanks are preferred.

9.4 DIGESTERS

Older batch digesters were acid-brick lined. However, digesters have more recently been constructed from Types 317L, 904L, 317LMN (S31726), and 2205 duplex stainless steels. Duplex stainless steel alloys offer better protection against chloride stress corrosion cracking compared to austenitic stainless steels. In brick-lined digesters, most fittings, screens, sleeves, and man-way hatches are Type 316L or 317L stainless steel.

Continuous digesters for sulphite pulping are very similar to kraft continuous digesters in design. For the sulphite process, continuous digesters are all stainless steel construction using Type 316L (with a minimum of 2.75% molybdenum) or 317L. Duplex stainless steel has also been used in several continuous digesters.
Figure 9-2 Spray-Type Sulphur Dioxide Cooler

- Emergency Water
- Hot Gas
- Lead and Acid Brick Lining
- Makeup Water
- Weir Box
- Primary Tower
- Secondary Tower
- Heat Exchange
- Cooled Gas
- Makeup Water
9. SULPHITE PROCESS

9.5 WASHING AND SCREENING

Pumps, piping, screens, knotters, washers and deckers may all be exposed to small amounts of bisulphite in the spent liquor, so stainless steel construction is still necessary for corrosion protection. Type 316L stainless is almost standard. However, crevice corrosion may occur under pulp deposits; so the choice may be for Types 317L, 2205 duplex or higher alloyed materials.

9.6 CHEMICAL RECOVERY

A number of sulphite mills operate liquor recovery systems. However, there appears to be considerable variation in operating conditions. Sulphite recovery boilers are primarily of carbon steel construction, with significant corrosion allowances in critical areas such as screens, superheaters, and waterwall tubes. More recent construction has incorporated composite Type 304L with SA210 steel tubes in the lower furnace waterwalls. Carbon steel remains the choice for floor tubes. The SO₂ content of sulphite recovery flue gas is much higher than in kraft systems, increasing the potential for SO₂ formation.

Scrubbing systems are usually of FRP and/or Type 316L/317L stainless steel. Where high levels of chlorides and/or SO₂ are present, high molybdenum stainless steels or nickel base alloys give better service. The magnesium sulphite operation presents a special case in scrubber corrosion, where the MgO slurry in water is combined with hot SO₂ gas. In this case the SO₂ gas enters the top of one leg of the scrubber and is combined with the MgO slurry shower. Problems of severe stress corrosion cracking and crevice corrosion under wet salt have occurred in Type 317L stainless steel scrubber walls. One solution has been to replace the affected components with Ni-Cr-Mo-W (e.g. C-276) alloy. Consideration could be given to use of duplex stainless steels in this application given those alloys' excellent resistance to pitting and stress corrosion cracking.

Jonsson reported that a steel corresponding to Type 316L is suitable material for all components in the evaporators such as tubes, vapour bodies, liquid flash tanks, vapour pipes, condenser pipes, liquor pipes, valves, pumps, and condensers where calcium bisulphite is evaporated. For evaporation of magnesium base cooking liquor, Type 316L with 2.75% molybdenum or Type 317L is often prescribed, since the corrosive conditions are considered to be somewhat more severe than for calcium bisulphite. For sodium base cooking liquor, the conditions are not so corrosive and therefore Type 316L is used for the first effect and Type 304L or mild steel for the weak liquor effects in the evaporator train. Carbon steels in the weak liquor stages have sometimes been replaced by stainless steels, primarily to reduce fouling and secondarily to reduce corrosion. The corrosion problems are less severe for cooking liquor using ammonium base.

9.7 CHLORIDE CONTROL

Chloride ions entering the pulp mill cycle from salt water wood storage can cause serious corrosion of stainless steel equipment throughout the liquor cycle. A control system conceived for the magnesium oxide recovery process can greatly reduce corrosion by maintaining a low chloride ion level. The system is based on the knowledge that the chlorides leave the recovery boiler as hydrochloric acid and can be readily removed from the flue gas by a venturi absorber.
9. Sulphite Process

REFERENCES

In neutral sulphite semichemical (NSSC) pulping, hardwood chips are cooked in a liquor solution consisting of sodium sulphite with a small quantity of sodium carbonate, bicarbonate, or hydroxide. A typical strong liquor contains 120–200 g/l of sodium sulphite and 30–50 g/l of sodium carbonate. The liquor is generally prepared by burning sulphur to form sulphur dioxide, and then absorbing the gas in a solution of sodium carbonate (soda ash), although small mills may purchase chemicals if readily available from a nearby source.

Cooking is done in digesters similar to those used in the kraft process, except that the continuous digesters are of a different design. Typical continuous digesters include horizontal multiple-tube units or inclined tube digesters.

The cooking occurs in either the liquid or the vapour phase. For vapour phase cooking the chips must pass through a press impregnator before entering the digester. The flow diagram for a typical NSSC mill is illustrated in Figure 10-1. Cooking temperatures range from approximately 355 to 380°F (180–195°C); the pH range is from 7.2 to 9. Heating is either directly by steam injection or indirectly with an external heat exchanger.

A number of mills are combined kraft/NSSC operations because both are used in the manufacture of corrugated cardboard. Consequently the sulphur and soda obtained from NSSC spent cooking liquors are introduced into the kraft chemical recovery system to replace the salt cake lost in the kraft mill. During carbonation of the smelt,
10. NSSC

**NOTES**

Hydrogen sulphide is released. This is burned to sulphur dioxide in a separate reactor or in the oxidation zone of the recovery boiler.

Because NSSC spent liquors are more corrosive than kraft liquors, stainless steels are generally used in all equipment. While Type 304 (S30400) has been used successfully, Type 316 (S31600) is generally preferred because of its better resistance to corrosion. When welding is involved, the low carbon variations, Types 304L (S30403) and 316L (S31603) are used to prevent problems with intergranular corrosion. While NSSC pulp can be bleached, using chlorine, caustic soda, or hypochlorite, bleaching is not usually required.

In a related process, pulping is done at more acidic pH levels, using bisulphite rather than sulphite as the active chemical. In some instances, this has caused rapid attack of the vapour phase region of the digester, due to the formation of sulphuric acid vapour. The conditions that promote the formation of acid vapours are the presence of air and a low cooking liquor pH. Digesters for use in semichemical bisulphite pulping have been made from a range of materials, including carbon steel and austenitic stainless steels. The accelerated corrosion of a Type 317L (S31703) continuous bisulphite semichemical digester has been described by Murarka. Formation of acid vapours was minimized by raising the liquor pH from 4 to 6, and by using a plug screw feeder to reduce the entry of oxygen with the incoming chips. Additional precautions taken were feeding the chips into the digester below the liquor level, and preheating the water in the blow tank to lower its dissolved oxygen content. The vapour space of the digester was clad in 904L (N08904) stainless steel. Presteaming the chips and replacing the air in the digester with steam prior to startup have also been advocated to minimize the possibility of acidic corrosion.

**REFERENCES**

High yield mechanical pulping is the generic name for producing pulps mechanically, using either disc refiners or grindstones (also called “pulpstones”). Today, high yield mechanical pulping is dominated by disc refiner technology and, in North America, stone groundwood technology is rapidly disappearing from the scene. Newsprint and groundwood specialties typically contain high amounts of refiner pulps, sometimes as much as 100%.

A large number of refiner pulping processes have been developed, primarily as a result of the need to produce tailor-made pulps and to decrease energy requirements. The simplest process is refiner mechanical pulping (RMP), in which the chips are refined at atmospheric pressure with no prior use of heat or chemical action. For newsprint production, the dominant methods of refiner pulping are thermo-mechanical pulping (TMP), in which the chips are softened by heating in a steaming tube before entry into the primary refiner, and chemi-thermo mechanical pulping (CTMP), in which the chips are also impregnated with a cooking chemical such as sodium sulphite. In both TMP and CTMP systems, chip steaming and refining take place at temperatures above 212°F (100°C), so that the steaming vessel and the first stage refiner are pressurized. In the secondary refiner, the pulp is usually discharged at atmospheric pressure. The distinction between TMP and CTMP can be blurred, as TMP facilities sometimes add sulphite solution to the chips before refining. A schematic illustration of a TMP system is shown in Figure 11-1.
Modern refiners are large and powerful, with disc diameters up to 1.8 m (70 inches) and motor powers of 11 MW (15,000 HP) and higher. In operation, pulping is achieved by passing wood chips between two or more closely spaced sets of serrated refiner plates, at least one set of which is rotating. Each set of plates is made by bolting individual plates onto a backing disc. Refiner plates are made from abrasion resistant cast irons, such as 25% Cr, Ni-HiCr Type D (ASTM specification A532) or high carbon cast stainless steels, and are treated as consumables. For more information on the wear and corrosion of refiner plates, see Reference 1.

Relatively little information exists in the literature regarding corrosion in high yield pulping environments. A recent review is given in Reference 2. A survey of materials problems and inspection procedures for refiner systems is reported in Reference 3. A nagging concern is stress corrosion and corrosion fatigue, particularly with regard to pressurized steaming tubes, refiner discs, and refiner drive shafts. Many of the most severe problems reported to date have occurred in coastal mills, where high chloride levels have been encountered. However, chlorides are often a problem for inland mills as well. Chlorides can be introduced from deicing salts spilled on wood in the yard. Caustic used in the mill often contains chlorides. Even if chlorides are low, they can concentrate in crevices, under deposits, and just above the waterline in the vapour phase. Mills reducing their fresh water usage can also be vulnerable to unexpected attack, as contaminated white water from the paper mill may be fed back to the mechanical pulp mill.

The combination of the presence of chloride ions, the use of chemical pulping or bleaching agents, and the release of volatile wood acids can result in the localized buildup of highly aggressive conditions, even when nominal white water conditions are considered to be relatively innocuous. In some of the cases mentioned in Reference 2, corrosion was initiated under deposits or in dead zones where the local environment was considerably more aggressive than the nominal environment. For example, deposit analyses from a coastal presteaming vessel showed pH values of 1.9 and chloride levels of about 13,000 ppm (compared to a nominal chloride level in the TMP white water of about 200 ppm). One mill has reported replacement of two Type 904L (N08904) steaming vessels with Alloy C276 (N10276) and Alloy C22 (N06022), on account of serious chloride stress corrosion cracking (SCC) of 904L, an alloy that is normally resistant to chloride SCC.

Type 316L (S31603) is the standard alloy used by manufacturers for the major components of refiner systems. Exceptions are where high strength is required (e.g., for drive shafts and refiner backing disks) and in areas where corrosion is considered to be a particular concern. Upgrading to 904L or 2205 (S32205) has been suggested for high...
chloride environments. Alloy C276 or Alloy C22 has been used for particularly aggressive and acidic conditions in steaming tubes. For cavitation resistance, 2205 clad plate has been suggested for some applications. The metallurgy used for refiner backing discs, drive shafts, and casings varies with the manufacturer and specific process conditions. Alloys that have been used include forged 15-5PH (S15500), CA6-N M (J91540) and 16Cr 5N i 1Mo (C B-6, U N S designation J91804). Refiner casing alloys include 316L, 904L, CA-15 (J91150), CA6-N M, and 2205 clad carbon steel, the exact choice depending on the anticipated service conditions. Chloride SCC is reported to be such a serious problem that the use of Type 316L for pressurized components has been discontinued. Chloride SCC of CB-6 refiner cases in less than two years has also been reported. Drive shafts are not designed to be exposed to the process, and have typically been made from alloy steels such as 4140 or 4340; some use of martensitic stainless steel and the duplex stainless steel 2507 (S32750) has been reported.

REFERENCES

Recycling of waste paper reduces the need for new wood from forests; it is becoming a major part of the pulp and paper industry. There are a growing number of mills whose sole feed is waste paper. Recovered waste paper is introduced into large diameter rotary drum repulpers, where the paper is shredded and a clean water recycle stream is introduced, resulting in a 5-8% consistency pulp. After screening and washing, the pulp is sent to a single-stage or two-stage bleaching operation. Hydrogen peroxide or hypochlorite are the usual bleaching agents. After bleaching, the pulp is washed and sent on to pulp preparation. The filtrate is recycled to the holding tanks ahead of the screens. Type 316L (S31603) and its cast counterpart CF-3M (J92800) are the principal materials of construction for the equipment. A waste paper flow diagram is shown in Figure 12-1. There are many variations in flow details depending upon the waste paper sources and individual mill preferences.

The alkaline environment in the repulper is conducive to microbiological influenced corrosion (MIC) beneath the pulp pads that adhere to the stainless steel lifter plates in the repulper. These lifter plates are designed to do the shredding. Residual chlorine from bleaching and chlorides in the white water contribute to the aggressiveness of the environment. In a few cases, upgrading of the lifter plates to 6% Mo stainless steel has been required to resist the most aggressive conditions. While Type 316L piping is standard, problems with corrosion under adherent pulp pads have been reported in a few mills, which required upgrading to 6% Mo or FRP. It is expected that mills dedicated to waste paper recycling will continue to grow in importance.
12. Waste Paper Recycling

Figure 12-1 Flow Diagram for Waste Paper Recycling
13. BLEACH PLANT

13.1 STAGES OF BLEACHING

The oxygen delignification and bleach plant sequence is a continuation of lignin removal following the digester cooking process. Bleaching takes place in these sequences in 3 to 5 steps, each step referred to as a stage. Each stage of a bleach sequence is comprised of four basic equipment components:
1. A pump to move the pulp through the stage at the desired consistency.
2. A mixer to blend the pulp, chemicals and steam.
3. A reaction tower or vessel (atmospheric or pressurized) with dilution and agitation equipment for discharge consistency control.
4. A washer to separate residual chemicals and reaction by-products from the pulp.

These four components are shown in Figure 13-1 for an atmospheric bleaching stage ($\text{Cl}_2$, $\text{ClO}_2$, $\text{E}_o$) and a pressurized stage ($\text{O}_2$, $\text{O}_3$, $\text{P}_O$). (See Table 13-1 for definitions.) The upflow section of the atmospheric stage can also be pressurized ($\text{E}_e$, $\text{E}_{op}$, $\text{P}_{HT}$). These stages are divided into two process categories within each bleaching sequence: delignification and brightening. There are a large number of different bleaching stages in use in various combinations. The designations as they are commonly used in the literature are shown in Table 13-1.
13. **Bleach Plant**

### Delignification

Immediately following the cooking process, the delignification stages selectively continue the bulk removal of lignin from the fibre. Inclusive in this group of bleaching stages are oxygen delignification (O), chlorination (C), or chlorine dioxide (D) stages, and oxidative extraction (E) or peroxide reinforced extraction stages (Eo). In a bleaching sequence, the delignification stages are typically grouped as Dc, Eo, Dn, and OD.

### Brightening

Following the delignification stages are the brightening stages. These stages are most effective when the lignin level in the pulp has been reduced to less than 1% by weight. Permanent brightness development occurs as this remaining lignin is removed or modified in the brightening stages. These are typically chlorine dioxide stages (D), with intermediate caustic neutralization steps (n) or mild caustic extraction stages (E). In a bleaching sequence, the brightening stages are typically grouped as D, DED, DD or DnD.

### Bleaching Sequences

The final brightness target and environmental constraints define the combination of delignification and brightening stages in a bleach plant design. The most typical sequences are:

- **DcEoDnD** to achieve 88–90% International Standard Organization (ISO) target brightness
- **ODEoD** to achieve 85–88% International Standard Organization (ISO) target brightness

These sequences were selected to encompass the scope of bleach stage design parameters currently utilized in bleach plants. The ODEo sequence, with no elemental chlorine utilized, is referred to as an elemental chlorine-free (ECF) sequence. Figure 13-2 schematically outlines the DcEoDn bleaching sequence.

Table 13-2 summarizes the typical operating and design parameters for DcEoDnD and ODEoD sequences to achieve 88–90% ISO and 85–88% ISO target brightness, respectively, on softwood pulp. The Oc delignification stage in the ODEo sequence is designed to reduce the brown stock kappa to 18.0.
### Table 13-2 Typical Operating and Design Parameters for Conventional and ECF Bleaching Sequences

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>ECF</th>
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<tbody>
<tr>
<td><strong>Bleaching Sequence</strong></td>
<td>D, E, D, D</td>
<td>O(E)D, D</td>
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<tr>
<td><strong>Brown Stock Kappa #</strong></td>
<td>30</td>
<td>30</td>
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<tr>
<td><strong>Target Brightness (% ISO)</strong></td>
<td>88–90</td>
<td>85–88</td>
</tr>
<tr>
<td><strong>Stage</strong></td>
<td>NA</td>
<td>Oxygen</td>
</tr>
<tr>
<td>% NaOH (on pulp)</td>
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<td>1.5–2.0</td>
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<tr>
<td>% O₂</td>
<td>NA</td>
<td>1.5–2.0</td>
</tr>
<tr>
<td>Temperature</td>
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<tr>
<td>Final pH</td>
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<td>10.0–12.0</td>
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<td>Bleach Tower</td>
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<td>Cone top &amp; bottom (100 psig at bottom, pressurized)</td>
</tr>
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<td>Retention Time (min)</td>
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<td>60</td>
</tr>
<tr>
<td><strong>Stage</strong></td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>% Cl₂ Substitution</td>
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<td>3.6–4.7</td>
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<td>% Active Cl₂ (on pulp)</td>
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<td>Final pH</td>
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</tr>
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<td>Consistency, %</td>
<td>3–4</td>
<td>3–12</td>
</tr>
<tr>
<td>Bleach Tower</td>
<td>Upflow (atm)/Downflow</td>
<td>Upflow (atm)/Downflow</td>
</tr>
<tr>
<td>Retention Time (min)</td>
<td>60 (15/45)</td>
<td>45 (15/30)</td>
</tr>
<tr>
<td><strong>Stage</strong></td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>% O₂ (on pulp)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>% H₂O₂ (on pulp)</td>
<td>NA</td>
<td>0.5</td>
</tr>
<tr>
<td>Final pH</td>
<td>10.5–12.0</td>
<td>10.5–12.0</td>
</tr>
<tr>
<td>Temperature</td>
<td>165–185°F (74-85°C)</td>
<td>165–195°F (74-90°C)</td>
</tr>
<tr>
<td>Bleach Tower</td>
<td>Upflow (atm)/Downflow</td>
<td>Upflow (pressurized)/Downflow</td>
</tr>
<tr>
<td>Retention Time (min)</td>
<td>45 (5 min at 20 psig/40 min)</td>
<td>45 (15 min at 60 psig/30 min)</td>
</tr>
<tr>
<td><strong>Stage</strong></td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>% Cl₂ (on pulp)</td>
<td>0.8–1.2</td>
<td>1.0–1.4</td>
</tr>
<tr>
<td>pH</td>
<td>3.5–4.5 (dilution zone is neutralized to 7.0–9.0 pH)</td>
<td>3.0–4.5</td>
</tr>
<tr>
<td>Consistency, %</td>
<td>10–12</td>
<td>10–12</td>
</tr>
<tr>
<td>Temperature</td>
<td>160–175°F (70-80°C)</td>
<td>160–175°F (70-80°C)</td>
</tr>
<tr>
<td>Bleach Tower</td>
<td>Upflow (atm)/Downflow</td>
<td>Upflow (atm)/Downflow</td>
</tr>
<tr>
<td>Retention Time (min)</td>
<td>180 (45/135)</td>
<td>240 (45/195)</td>
</tr>
<tr>
<td>Brightness (% ISO)</td>
<td>87.0–88.0</td>
<td>85.0–88.0</td>
</tr>
<tr>
<td><strong>Stage</strong></td>
<td>D</td>
<td>-</td>
</tr>
<tr>
<td>% Cl₂ (on pulp)</td>
<td>0.1–0.3</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>4.5–5.0</td>
<td>-</td>
</tr>
<tr>
<td>Temperature</td>
<td>160–175°F (70-80°C)</td>
<td>-</td>
</tr>
<tr>
<td>Consistency, %</td>
<td>10–12</td>
<td>-</td>
</tr>
<tr>
<td>Bleach Tower</td>
<td>Upflow (atm)/Downflow</td>
<td>-</td>
</tr>
<tr>
<td>Retention Time (min)</td>
<td>180 (45/135)</td>
<td>-</td>
</tr>
<tr>
<td>Brightness (% ISO)</td>
<td>88–90.0</td>
<td>-</td>
</tr>
</tbody>
</table>
13. BLEACH PLANT

13.2 NON-CHLORINE BLEACHING STAGES

Non-chlorine bleaching stages, utilized in both the delignification and brightening stages of a bleaching sequence, are designed to reduce or eliminate the usage of chlorine-based (\(\text{ClO}_2\)) bleaching chemicals. These stages are the building blocks for the totally chlorine-free (TCF) bleaching sequences.

Delignification

The function of the stages is identical to the description above, entitled “Delignification.” Inclusive in this category for non-chlorine bleaching stages, the bleaching stages utilized are oxygen delignification (O); ozone (Z); and pressurized, hydrogen peroxide reinforced, oxidative extraction stages (E_{op}).

Brightening

Following the delignification stages are the brightening stages, as previously described. For non-chlorine bleaching the brightening stages are typically pressurized, oxidative hydrogen peroxide stages (\(P_{\text{ht}}, P_{O}, P\)).

Bleaching Sequences

Non-chlorine bleaching stages in ECF sequences are used primarily to maintain final brightness targets while lowering active chlorine demand. The non-chlorine stages can be utilized to reduce active chlorine in both the delignification and brightening stages.

The final brightness target and environmental constraints define the combination of non-chlorine delignification and brightening stages in an ECF bleach plant design. For example purposes only, a proposed \(D_{Q}(ZE_{op})DP_{HT}\) bleaching sequence is shown schematically in Figure 13-3. The purpose of this figure is to illustrate how a plant might apply an ozone (Z) delignification stage and/or a \(P_{HT}\) brightening stage.

Figure 13-3  \(D_{Q}(ZE_{op})DP_{HT}\)* for ECF Bleaching Sequence

*Stages in parentheses ( ) denotes no wash between stages. In some instances a chelation or acid rinse step followed by a washer may be required prior to the \(P_{HT}\) and \(P_{O}\) stages.
13. BLEACH PLANT

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Bleaching Stages

The range of operating conditions for non-chlorine bleaching stages are outlined in Table 13-3. These conditions are used to optimize the displacement of active chlorine in the delignification and brightening stages while maintaining pulp quality.

| **Table 13-3 Typical Operating and Design Parameters for Non-Chlorine Bleaching Stages** |
|-----------------------------------------------|----------------|----------------|
| **Bleach Stage** | Reinforced oxidative extraction, $E_{\text{up}}$ | Ozone, $Z$ | Pressurized peroxide, $P_{\text{in, PO}}$ |
| % Chemical (on pulp) | 0.5–1.0 (H$_2$O$_2$), 0.5 (O$_2$) | 0.2–0.5 (O$_2$) | 1.0–3.0 (H$_2$O$_2$), 0.5 (O$_2$) |
| Temperature | 185–200°F (85–105°C) | 120–140°F (49–60°C) | 185–210°F (85–99°C) |
| Final pH | 10.0–10.5 | 2.5–3.0 | 10.0–10.5 |
| Consistency, % | 12–14 | 12–14 | 12–14 |
| Bleach Tower | Upflow (press)/downflow | upflow (press) | upflow (press)/downflow or pressurized upflow |
| Retention time (min)* | 60 (15@ 60 psig/45 atm) | 5–10@ 150 psig | 180 (15 @ 60 psig/165 atm), 120@ 60–100 psig |

* Pressures noted at tower bottom inlet.

13.3 PROCESS WATER REUSE FOR ECF AND NON-CHLORINE BLEACHING STAGES

Many bleach plants today recycle filtrates counter-currently to accomplish at least partial closure (see Figures 13-4 and 13-5). The bleach plant effluent, which flows to the waste treatment plant, is primarily overflow from the $D_1/D_{100}$ and $E_{\text{ip}}$ stages.

There are several benefits to recycling filtrates, such as:

- Reduction in water consumption and effluent flow.
- Reduction in chemical consumption ($NaOH$ and $H_2SO_4$).
- Reduction in heating requirements.

In cases where bleach stage residual is high, filtrate recycle can also lead to corrosion in certain parts of the bleach plant.

The effluents from the bleaching operation contribute a significant portion of the $\text{COD}$ (chemical oxygen demand), colour, and $\text{AOX}$ (absorbable organic halide) to the overall effluent stream. Environmental regulations have put limitations on the levels of these components discharged with bleach plant mill effluent. This has led to a decrease in the use of chlorine and chlorine-containing compounds and to the trend...
Recent bleach plant design is also focusing on reducing the effluent flows by increasing the level of filtrate recycling. Reevaluation and increased monitoring of the construction materials used throughout the bleach plant are becoming more critical as new bleaching processes and increased filtrate recycle are utilized in bleach sequences.3
13. BLEACH PLANT

13.4 SELECTION OF MATERIALS FOR BLEACHING EQUIPMENT

Materials for bleach plant equipment have undergone major changes over the past 30 years. In the 1970s recycling of wash water and approaches to closure of the wash water cycle increased corrosivity. Changes in bleaching processes and reduction in time available for maintenance, together with recycling of wash water, required upgrading to more highly alloyed, more corrosion resistant materials in the late 1970s and 1980s. More recently, the need to reduce dioxins has resulted in replacing chlorine with chlorine dioxide. Substituting chlorine dioxide for elemental chlorine is known as elemental chlorine-free (ECF) bleaching. Substituting oxygen and hydrogen peroxide for both chlorine and chlorine dioxide, as some mills have done, is known as totally chlorine-free (TCF) bleaching. TCF bleaching requires less highly alloyed materials than ECF bleaching. Types 316L (S31603), CF-3M (J92800) and CF-8M (J92900) are quite adequate for most applications in TCF bleaching.

For environmental reasons, a number of mills have eliminated the chlorination stage. Only a few continue their use of chlorine and these are expected to discontinue use of chlorine within the next few years. In ECF bleaching where elemental chlorine has been eliminated, the bleaching sequence is normally comprised of two to three chlorine dioxide stages. The use of ECF bleaching is expected to continue to grow in North American mills. Only a few mills have adopted TCF bleaching because it lacks economic appeal. The hypochlorite stage, which was very popular half a century ago, has been largely abandoned in North America and Europe, but is still in use in South America and the Far East.

Some of the more common materials used in the older chlorine (C), chlorine dioxide (D), and hypochlorite (H) stages are shown in the first three columns of Table 13-4. Piping which leads to the chlorine or chlorine dioxide tower is FRP. The tower itself is steel with a membrane, acid brick lining, or solid FRP. Piping from the towers is either 6% Mo stainless steel or FRP. Cast alloys CW-2M and CX-2MW performed well in chlorine stage chemical mixers. In both the chlorine stage with chlorine dioxide substitution and the chlorine dioxide stage, these nickel-base alloys have suffered substantial corrosion. Titanium is the preferred material for both the chemical and high shear mixers in D stage. In the old C stage, precautions must be taken to prevent dry chlorine from entering the titanium mixer in order to avoid a pyrophoric reaction. 6% Mo stainless steels have become standard for the C and D stage washers.
During ECF bleaching when countercurrent washing is utilized in the bleach plant, caustic filtrate is applied as shower water on the first stage chlorine dioxide bleach filter to displace the chlorine dioxide in the pulp mat. Residual chlorine dioxide in the pulp mat combines with the caustic, resulting in the formation of sodium chlorate and sodium chlorite in the following reaction:

\[ 2\text{ClO}_2 + 2\text{NaOH} \rightarrow \text{NaClO}_3 + \text{NaClO}_2 + \text{H}_2\text{O} \]

The resulting condition is known as near neutral chlorine dioxide with a pH of 6 to 7.

Super-austenitic, 6% molybdenum stainless steels have adequate resistance to near neutral chlorine dioxide. However, the nickel base alloy filler metals, AWS ERNiCrMo-4 and AWS ERNiCrMo-10, normally used for fabrication, are subject to what has been termed transpassive corrosion in this near neutral chlorine dioxide environment. These nickel base filler metals undergo molybdenum dissolution, which renders them unsuitable for this near neutral chlorine dioxide environment. After some investigation it was found that AWS ERNiCrMo-11 with higher chromium and lower molybdenum had much better corrosion resistance in the near neutral chlorine dioxide environment while still maintaining good resistance to acid chloride environments. ERNiCrMo-11 has become the preferred filler metal for fabricating 6% molybdenum stainless steel washers for near neutral chlorine dioxide stage service.

### Table 13-4 Materials for Bleaching Plant Equipment

<table>
<thead>
<tr>
<th>Bleaching Stage</th>
<th>Chlorination C</th>
<th>Chlorine Dioxide D</th>
<th>Hypochlorite H</th>
<th>Caustic Extraction E</th>
<th>Caustic/Oxygen EO</th>
<th>Peroxide P</th>
<th>Ozone Z</th>
<th>Oxygen O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tower shell - lining</td>
<td>mild steel</td>
<td>mild steel</td>
<td>316L(1)</td>
<td>316L(1)</td>
<td>316L(1)</td>
<td>316L(1)</td>
<td>316L(1)</td>
<td>316L(1)</td>
</tr>
<tr>
<td>Tower agitators - casing</td>
<td>C-276/CW-2M</td>
<td>titanium</td>
<td>C276/CW-2M</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
</tr>
<tr>
<td>Line or radial chemical mixers - casing</td>
<td>C-276/CW-2M</td>
<td>titanium</td>
<td>C276/CW-2M</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
</tr>
<tr>
<td>Steam mixers - casing</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
</tr>
<tr>
<td>High-shear mixers - casing</td>
<td>titanium(2)/ CW-2M</td>
<td>titanium</td>
<td>CF-3M</td>
<td>CF-3M</td>
<td>CF-3M</td>
<td>CF-3M</td>
<td>CF-3M</td>
<td>CF-3M</td>
</tr>
<tr>
<td>Pumps - low density stock filter</td>
<td>CG-3M</td>
<td>CG-3M</td>
<td>CG-3M</td>
<td>CG-3M</td>
<td>CG-3M</td>
<td>CG-3M</td>
<td>CG-3M</td>
<td>CG-3M</td>
</tr>
<tr>
<td>Filtrate tanks</td>
<td>Tile or FRP</td>
<td>Tile or FRP</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
</tr>
<tr>
<td>Sewer lines</td>
<td>FRP</td>
<td>FRP</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
</tr>
</tbody>
</table>

(1) To prevent external stress corrosion cracking, special care in insulation of Type 316 is required.
(2) Heat tint and embedded iron must be removed from all wetted surfaces to reduce decomposition of hydrogen peroxide.
(3) Titanium must be protected from contact with dry chlorine by interlocks to avoid pyrophoric reactions.
(4) Zr is used for the high temperature (>100°C), more aggressive applications.
13. BLEACH PLANT

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stages (shown in the remaining columns of Table 13-4), Type 316L and its cast counterpart CF-3M are the principal materials used for the towers, pumps and mixers. For Type 316L towers, it is necessary to protect the outside from chloride stress corrosion cracking (SCC) beneath the insulation, as described below and in Section 20, “Corrosion.” Some mills have selected duplex stainless steel for the oxygen towers because of its better resistance to chloride SCC. Zirconium is used for the high shear mixer in the hot alkaline peroxide stage.

For bleach plant service, it is desirable that all wetted surfaces be clean and free of embedded iron and other fabrication-related defects. It is essential that Type 316L hydrogen peroxide towers and other peroxide wetted surfaces are free of embedded iron, as embedded iron degrades hydrogen peroxide. ASTM A380 and A967 provide the guidelines for detection and removal of embedded iron and other fabrication defects using mechanical, chemical, and electrochemical methods described in some detail in Section 20, “Corrosion.”

13.5 OXYGEN BLEACHING

Oxygen has become a principal technology to replace chlorine based chemicals for bleaching pulp. Oxygen usage is expected to continue growing as chlorine usage declines. Initially, oxygen bleaching was done on high consistency pulp, leaving a gas phase at the top of the vessel. Pressures were as high as 120 psig (0.8 MPa) and temperatures as high as 275°F (135°C), conditions that are conducive to internal chloride SCC. The interface between liquid and vapour in high consistency bleaching provided a “hot wall” effect, where chlorides could concentrate just above the liquid level, increasing the probability of internal chloride SCC.

In order to prevent internal chloride SCC of Type 316L when gas phase oxygen bleaching began in the early 1970s, Scandinavian mills “cold stretched” Type 316L oxygen reactors. Cold stretching was done by over-pressuring the vessel sufficiently so that, at operating pressures, the inside surface remained in compression and resistant to chloride SCC. Cold stretching also allowed a reduction in wall thickness under Scandinavian pressure vessel codes. In North America, where codes did not allow a reduction in wall thickness for cold stretching, upgrading to solid or clad Alloy 20 (N08020) became the practice to resist chloride SCC in oxygen reactors.

The initial process was changed to treat medium consistency pulp in an upflow mode instead of downflow mode, eliminating
the vapour space to the top of the vessel, where chlorides could concentrate and initiate chloride SCC. This reduced the potential for internal chloride SCC of Type 316L without the need for cold stretching. Most of the oxygen reactors treating medium consistency pulp in the upflow mode have been Type 316L. Recently some have been fabricated from Alloy 2205, which is resistant to chloride SCC. An oxygen delignification vessel of Alloy 2205 ready for shipment is shown in Figure 13-6.

Type 316L is quite susceptible to external stress corrosion cracking under insulation when the insulation becomes wet from rain or even high humidity. NACE Publication RPO 198-98 Item 21084 “Standard Recommended Practice – The Control of Corrosion Under Thermal Insulation and Fireproofing Materials” provides the necessary information for keeping the outside surface of Type 316L reactors, and other Type 304L (S30403) and 316L vessels and towers, dry and resistant to SCC. More information is provided in Section 20, “Corrosion.”

Although internal chloride SCC has not been reported in vessels where pulp is treated with oxygen in the upflow mode with no vapour space at the top, a number of mills have elected to upgrade to Alloy 2205 for better resistance to both internal and external chloride SCC.

Types 316L and CF-3M are satisfactory for other components in the oxygen and hydrogen peroxide bleaching stages.

13.6 PUMPS, VALVES, AND THE GROWING USE OF DUPLEX

Since conditions vary considerably from mill to mill, individual mill site experience generally provides the best guide for alloy selection and upgrading. The PREN (pitting resistance equivalent number) – shown in Table 2-2 for

Figure 13-6 Alloy 2205 Oxygen Delignification Vessel - Canada

Courtesy Enterprise Steel
The earlier practice of upgrading to 317L (S31703) in North America, and to 904L in Europe, when 316L proved marginal or inadequate, is being supplemented, and to an extent superseded, by the current trend of upgrading to a duplex alloy, usually Alloy 2205. Alloy 2205 is becoming the preferred upgrade whenever higher strength, better resistance to chloride SCC or better resistance to abrasion is needed. Alloy 2205 is also often the choice for large field-erected vessels, where its higher strength can be used to offset much of the higher material cost.

The cast 317L Alloy, CG-3M, and 6% Mo Alloys, CN-3MN and CK-3MCuN, have become standard for filtrate pumps in the chlorine and chlorine dioxide stages. CF-3M, CG-3M and the duplex grade CD-3MN are used for pulp stock feed pumps in these two stages. CF-3M and CG-3M and the cast duplex grades are the principal stock pump materials in the six less corrosive stages. Duplex is preferred wherever there is abrasive wear. CK-3MCuN and CN-3MN are preferred for valves in the chlorine stages. CG-3M, CG-8M and CN-7M are used for valves in the six less corrosive services. CN-7M is preferred for control valves.

Titanium is the only material that has been used for continuous bleaching towers, despite the considerable maintenance required.
13. Bleach Plant

REFERENCES

11. TAPPI TIP 0402-20 “GTAW root pass welding of 6% molybdenum austenitic stainless steel pipe – open root joint with hand fed filler.”
Pulpers

There is a wide variety in the design of pulpers and in the materials used in their construction. The material choice depends largely on the operating conditions. For the most part, stainless steels are preferred, since they minimize corrosion and possible contamination or discoloration of the stock. If the pulper is used for chemical or filler addition, the potential increase in corrosion or abrasion (erosion) due to the additives needs to be considered.

One pulper manufacturer offers two levels of protection: “corrosion resistant” and “super corrosion resistant.” A corrosion resistant pulper used Type 304 (S30400) for the tank and extraction chamber, and Type 410 (S41000) for the main rotor, impeller, deflaking elements, and extractor grate. Type 410 offers high hardness with a minimum corrosion resistance. For superior corrosion resistance, tanks, extraction chambers, and rotors are Type 316 (S31600), while other components are 17-4PH (S17400) precipitation hardened stainless steel which has superior abrasion resistance.

Tanks

Stainless steels are normally used for stock tanks. Type 304L (S30403) is usually adequate, but materials should be selected based on mill experience or tests. The agitator shaft and impellers will typically be made from Type 316 (S31600).

Refiners

In a typical double-disc refiner, rotating heads, casing connections and packing boxes are either Type 304 or Type 316, depending upon service requirements. The discs used for developing the fibres range from Ni-HiCr Type D (ASTM A532), 17-4PH or modifications of these two materials.

Screens

A wide variety of screens are used throughout the paper mill, including pressure screens and vibrating screens. Virtually all are constructed, as a matter of routine, with Type 316 stainless steel for wetted parts. Pressure screens are equipped with rotors that use hydrofoils to provide pulsation, which prevents plugging over the perforations or slots in the screen. The screen is either slotted or drilled, depending upon production requirements. Stainless steel construction provides good resistance to
corrosion and abrasion. The stainless surfaces are usually highly polished, sometimes by electropolishing.

**Vibrating Screens**

This is another screen application in which all wetted parts are of Type 316 stainless steel construction. Vibrating screens use a perforated plate available in a range of hole sizes. They are generally used for handling tailings from primary screens; scalping ahead of pressure screens to help minimize plugging; or in processing liner stock, repulped broke, or virgin pulp purchased in bales, to remove gross contamination.

**Cleaners**

Most cleaners today are of a cyclone design and are made from a polymeric material. However, there are still some designs that are constructed of stainless steel, usually Type 316. The stainless steel is cold worked and highly polished to provide a uniformly smooth, tough, abrasion-resistant surface. Cleaners are generally used in multiple stages. Some units are designed to remove both heavy speck rejects and light shive rejects. Ceramics can be used in high-velocity, high-wear areas of the cleaner. The stands that hold the cleaners are often made from stainless steel, either Type 304 or Type 316 stainless steel.

*Figure 14-1 Disc Filter*

![Disc Filter](image-url)

*Courtesy of Alberta-Pacific Forest Industries Inc.*
Savealls

As with everything else in stock preparation, stainless steels and nonmetallic materials are preferred for equipment exposed to stock.

Deflakers

Deflakers are generally used to separate fibre bundles following a stock preparation pulper or machine broke pulper, thus reducing the requirement for refining. Rotors and stators are usually stainless steel, as are most of the wetted parts. One design, for example, utilizes a cast precipitation hardening stainless steel CB-7Cu-1 (the cast equivalent of wrought 17-4 PH) for the rotor and stator.
Figure 14-3  M-Screens

Figure 14-4  DD 4500 Refiner
14. Stock Preparation

Figure 14-5 Vortex Agitator

Courtesy GL&V USA Inc.
Figure 14-6  Vertical Barracuda and Shark Pulper

Courtesy GL&V USA Inc.
15. PAPER MACHINE

15.1 INTRODUCTION

Wet environments such as the stock approach piping, and headbox, and forming section are usually manufactured out of Types 316 (S31600) and 316L (S31603) stainless steel. Heavy strength components are fabricated out of mild steel and clad or wrapped in 316L stainless steel.

The press section of the machine is primarily fabricated out of steel and either painted or clad in Type 316L stainless steel for corrosion protection. The remainder of the machine frame is manufactured primarily from painted steel components, with the exception of specialized component applications.

Paper machine environments are as diverse as the paper products made. Some generalizations can be made with respect to paper product and machine environment. Table 15-1 lists three general categories of paper production and typical environments. The extent of mill closure, pulping, bleaching, and brightening processes will affect the presence and concentrations of corrosive ions. The recent move away from chlorine bleaching compounds to reduce chlorinated organic compounds in pulp mill and paper machine effluents has been a positive step in the reduction of corrosion problems on the paper machine as well. A few mills have upgraded building roofing to Types 304 (S30400) and 316.

The remainder of this section will walk through a typical twin wire paper machine, from stock approach piping to the reel, covering typical and exceptional materials of construction and, where appropriate, surface finish requirements. Discussion of tissue machines will be interjected where appropriate. Paper machine rolls will be covered in Section 16.

<table>
<thead>
<tr>
<th>Table 15-1 Typical Corrosive White Water Compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper Making Environments</td>
</tr>
<tr>
<td>Acid-Alum with Sulphur</td>
</tr>
<tr>
<td>Newsprint, Linerboard, SC</td>
</tr>
<tr>
<td>pH 4.0</td>
</tr>
<tr>
<td>Temperature (°C) 55</td>
</tr>
<tr>
<td>Temperature (°F) 130</td>
</tr>
<tr>
<td>Conductivity (microsiemens) 4300</td>
</tr>
<tr>
<td>Chloride Ion (mg/L) 400</td>
</tr>
<tr>
<td>Sulphate Ion (mg/L) 4000</td>
</tr>
<tr>
<td>Thiosulphate Ion (mg/L) 40</td>
</tr>
<tr>
<td>Sulphite Ion (mg/L) 80</td>
</tr>
<tr>
<td>Acid-Alum</td>
</tr>
<tr>
<td>Fine Paper, Bleached Board, Wood Free Grades</td>
</tr>
<tr>
<td>pH 4.0</td>
</tr>
<tr>
<td>Temperature (°C) 43</td>
</tr>
<tr>
<td>Temperature (°F) 110</td>
</tr>
<tr>
<td>Conductivity (microsiemens) 2100</td>
</tr>
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<td>Chloride Ion (mg/L) 300</td>
</tr>
<tr>
<td>Sulphate Ion (mg/L) 800</td>
</tr>
<tr>
<td>Thiosulphate Ion (mg/L) 40</td>
</tr>
<tr>
<td>Sulphite Ion (mg/L) 80</td>
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<tr>
<td>Alkaline</td>
</tr>
<tr>
<td>Fine Paper, Bleached Board</td>
</tr>
<tr>
<td>pH 8.0</td>
</tr>
<tr>
<td>Temperature (°C) 45</td>
</tr>
<tr>
<td>Temperature (°F) 112</td>
</tr>
<tr>
<td>Conductivity (microsiemens) 1100</td>
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<tr>
<td>Chloride Ion (mg/L) 250</td>
</tr>
<tr>
<td>Sulphate Ion (mg/L) 750</td>
</tr>
<tr>
<td>Thiosulphate Ion (mg/L) —</td>
</tr>
<tr>
<td>Sulphite Ion (mg/L) —</td>
</tr>
</tbody>
</table>
15. PAPER MACHINE

15.2 THE WET END

The wet end starts with the approach piping carrying the treated pulp to the paper machine and continues to the dryer section Figure 15-1.

Stock Approach System

The typical material used for all types of paper production is Type 316L stainless steel. Occasionally in highly closed or poorly controlled process mills, Type 317L (S31703) stainless steel is used. Type 304L stainless steel can be used with success in open mills, with reduced chemical usage and concentration.

Outside surfaces have the usual pipe cold finish. Inside surfaces are at a minimum 0.75 micrometre $R_a$ ($R_a =$ Arithmetic mean of peak to valley height of surface roughness.) This finish will pass a cotton ball test (a simple test where a cotton ball is dragged across the surface - to pass means no fibres are pulled from the surface). More highly polished finishes of 0.25 $R_a$ are sometimes specified. The inside surfaces are normally electropolished to reduce deposits and fibre buildup.

Electropolishing, which is the controlled dissolution of

Figure 15-1 Refiner Section Leading to Headbox Approach Piping

Courtesy Beloit Corporation
metal from the surface, is the reverse of electroplating. A current is applied to the surface through a suitable conducting medium. The stainless steel is made the cathode. The current concentrates at high points on the surface, resulting in selective dissolution of the high points. An extremely smooth surface results. Even fine mechanical polishing results in torn and raised metal. Electropolishing also removes common metal inclusions such as calcium and manganese sulphides which are not removed by the best mechanical polishing. Sufficient electropolishing time can remove work hardened surfaces. This results in an extremely clean and corrosion resistant surface, in an excellent “passive” condition.

Headbox

Modern headboxes are hydraulic in design with the elimination of air pads and other components as shown in Figure 15-2. Since air-water interfaces are eliminated, the associated corrosion problems are also attenuated. Common headbox construction is of Type 316L or 316L with a specified minimum 2.5% molybdenum. Headbox orientation can lead to specific corrosion problems. Horizontally positioned headboxes for Fourdriniers and horizontal twin wire formers can have stock deposits on the apron. This can promote crevice attack. Higher alloyed stainless steels are applied to prevent or reduce crevice attack. Typically the 6% molybdenum austenitic alloys are used. Nickel based alloys such as Type C276 (N10276) or C22 (N06022) have also been used in a few cases. In vertically oriented headboxes, the apron tip and slice lip can be subject to stock deposits and concentration of corrosives due to continued wet/dry operation of the deposit. The above materials have been applied to both the apron tip and slice lip. The remaining parts of the headbox are designed to reduce or eliminate the horizontal surfaces that are prone to stock deposits.

Type 317L stainless steel and more highly alloyed materials have been used occasionally in headboxes to reduce or eliminate potential corrosion problems in more corrosive mills.

The paper machine atmospheric environment is summarized below:
1. Temperature 77 to 120°F (25 to 50°C).
2. Very high humidity.
3. Traces of residual chlorine and other oxidants from bleaching stages.
4. 150 psi (1035 kPa) water and chemical spray cleaning.
5. Unintentional but occasional release of white water, usually as a spray.

Carbon steel and galvanized steel bolting and ferritic stainless steel components rust readily in the high humidity paper machine environment. Types 304 and 316 will develop rust spots and rust streaks unless they
have been thoroughly cleaned and are free of embedded iron. Electropolishing is a good means of cleaning and deburring bolt threads, reducing the tendency to gall.

**Former**

The forming zone or wet end of the paper machine is generally constructed of solid Type 316L stainless steel. For large sections such as the framework, mild steel is used and Type 316L sheet is applied as a cladding to protect the steel from the environment. Due to mist and spray acting to concentrate corrosives, all materials are stainless steel Type 316 or more highly alloyed materials. Duplex stainless steels are useful where higher strengths are necessary.

Doctor blades which level the pulp on the Fourdrinier screen must retain a clean, straight edge. They are made from NiCu Alloy K500 (N05500).

**Press**

The press section tends to be a gray area of materials selection, see Figure 15-3. Less corrosive mills employ painted steel framework and lower alloyed martensitic and ferritic stainless steels where some corrosion resistance and higher strength is required. Successful application of coatings and electroplating as well as aluminum alloys are common in the press section, even when premature failure of these materials occurs in the forming section. Increased use of recycled fibre sources

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**Figure 15-2 Fourdrinier Wet End Showing Headbox**

![Fourdrinier Wet End Showing Headbox](image)
and reduced mill effluent have led to increased use of harsh chemical cleaners on the press felts. These harsh cleaners can attack the paint protecting the steel. Type 316L stainless steel cladding is increasingly used in press sections.

Roll Journals

Wet end paper roll journals are being made increasingly from Types 17-4 PH (S17400) and 2205 (S32205) duplex stainless steel. These materials replace carbon steel, low alloy steel, cast iron, and 304L/316L journals. Type 17-4 PH is readily pitted in most paper machine wet end environments, leading to corrosion fatigue; so the trend is toward the pit-resistant duplex stainless alloys for journals. Large heads with integral journals, such as for press rolls, continue to be cast from ductile (spheroidal graphite) and gray (flake graphite) cast iron. These heads are painted to resist corrosion.

Figure 15-3 Typical Modern Press Section
15.3 THE DRY END

As the wet paper leaves the Foudrinier wire moisture is removed over suction rolls, which are discussed in the next section, and over drying rolls (Figure 15-4).

Dryer

The common materials in the dryer section are painted steel and bare cast iron. Copper based alloys are also used in this section. The environment is considerably dryer than previous sections of the machine. High humidity can lead to corrosion of unprotected steel. Zinc coatings (galvanized) are not recommended due to temperature reversal of the iron and zinc galvanic couple above about 190F (90C), (Iron corrodes to protect zinc instead of zinc corroding to protect iron.) Typical dryer environments are as follows:

1. Temperature range = 75 to 250°F (25 to 120°C).
2. High humidity.
3. Equipment collects paper dust between cleaning intervals.
Calender

Calenders consist almost exclusively of painted mild steel. (See Figure 15-5) Cast spheroidal and flake graphite irons are commonly used. Unique to the calender section is the use of chilled and white irons, along with hard ceramic coatings. Materials of construction are not limited by any possible corrosive considerations. Typical calender environments are as follows:
1. Temperature 75 to 150°F (25 to 65°C).
2. Equipment cleaned with water spray = at 150 psi (1035 kPa).
3. Relative humidity = 75%.

Coater

Modern on and off machine coaters are generally constructed of stainless steels as shown in Figure 15-6. The environmental issue is one primarily of coating formulations that contain sodium and ammonium chlorides. Harsh cleaners contribute to the requirement for non-corroding materials. Chromium and nickel plated components have been used successfully. Copper based alloys are not recommended due to possible stress corrosion cracking from ammoniacal compounds. Typical coater environments are as follows:
1. Temperature 75 to 250°F (25 to 120°C).
2. Equipment cleaned with water spray = at 150 psi (1035 kPa) and with caustic boil-out solutions.
3. Relative humidity = 75%.
4. Equipment collects paper coating chemicals between cleaning intervals.

Size Press

Conditions and materials selection are the same as for coaters, above. Typical size press environments (Figure 15-7) are as follows:
1. Temperature 75 to 150°F (25 to 65°C).
2. Equipment cleaned with water spray = at 150 psi (1035 kPa).
3. Relative humidity = 75%.
4. Equipment collects starch solution, made up of salts which are used for static control and are corrosive between cleaning intervals.

Reel

Materials of construction are not limited by corrosive considerations. Galvanized steel and Type 304 are commonly used. Typical reel environments (Figure 15-8) are as follows:
1. Temperature 70 to 100°F (20 to 40°C).
Figure 15-5 Soft Nip Calender

Figure 15-6 Modern Machine Coater

Courtesy Beloit Corporation
NOTES

2. Equipment cleaned with water spray = at 150 psi (1035 kPa).
3. Relative humidity = 75%.
4. Equipment collects paper dust between cleaning intervals.

Hydraulic Systems

Material recommendations should be based on the section of machine where equipment will be placed. Possible ingress of water based fluids such as in the press may require stainless steel alloys to prevent internal corrosion and contamination of the hydraulic system.

Figure 15-7 Typical Size Press

Courtesy Beloit Corporation
15. PAPER MACHINE

15.4 WHITE WATER CORROSION AND CLEANING

Showers and Piping

Piping and showers on modern papermaking machines are typically Type 316L stainless steel in the wet end (from the stock approach piping to end of former) and press sections. Type 316L stainless steel has the proven corrosion resistance and necessary strength to meet the needs of this application.

White Water Return

The white water return system on modern paper machines is constructed of cold rolled stainless steel Type 316L sheet. Thickness depends upon the required strength of the white water collection device. Most white water is then collected in a ceramic tile lined wire pit (seen beneath the Fourdrinier section in Figure 15-2). Piping in the white water return sections of the machine are commonly constructed of Type 316L stainless steel. The pumps are CF-8M (J92900), the cast equivalent of Type 316.
15. Paper Machine

NOTES

Auxiliary Equipment

Auxiliary equipment such as electrical boxes, electrical conduit, cable trays and fire protection equipment operate in the high humidity and corrosive atmospheric environment near the paper machine. Type 304 stainless steel is usually adequate, although many contemporary machines specify Type 316 stainless steel. Paper machine fasteners, a special problem, are discussed in the section on “Fasteners.”

Dewatering Pumps

The large vacuum pumps used for dewatering the sheet downstream of the paper machine are either cast iron or cast iron case with CB-6 [16Cr 5Ni 1Mo (J91804)] internals. Figure 15-9 is a cutaway of a vacuum pump. The cast iron cases are frequently lined with stainless steel.

Common Chemical Solutions to Which Papermaking Machines Are Exposed

The following is an outline of some common chemicals used in the paper industry. These include chemicals used in the process of making paper and in the cleaning of the equipment.

White Water/Tray Water Environments

The following chemical concentrations represent some of the worst case sampling of the paper industry’s “White Water/Tray Water” conditions. (In other words, what the components are exposed to at the headbox, formers and press sections of the papermaking machines).

White Water Corrosivity

Slightly acidic white water is not corrosive to Type 304 stainless steel. Before recycling of mill process waters became common and before the change from zinc hydrosulphite to sodium hydrosulphite as a brightening agent, Type 304 stainless steel gave reasonably good service in white water in many mills. Bennett,1 Wensley2 and Garner3 all studied the effects of pH and concluded that pH levels below 4.5 became increasingly corrosive to Types 304/304L and 316/316L stainless steels. Wensley and others have reported the beneficial effects of sulphates, in the absence of sulphate reducing bacteria, noting that white water became increasingly corrosive to stainless steel when the chloride ion concentration exceeded the sulphate ion concentration, and less corrosive when sulphate ion...
Figure 15-9 Vacuum Pump - Stainless Steel Body

- Centre Shroud
- 45° Angled Inlets
- Lifting Lugs
- Double Extended Shaft
- Side Discharges
- Cartridge Bearing Housings
- Stainless Steel Body
- Inspection Parts
- Bottom Discharges
- Easy Access Stuffing Boxes
- Conical Porting

Courtesy Nash Engineering Company
concentration exceeded chloride ion concentration. Wensley also found that corrosion resistance increased with the percent molybdenum within the 2.0 to 3.0% range for Type 316 stainless steel.

Garner studied the effect of thiosulphate and concluded that Type 304 was especially sensitive to even low concentrations, whereas Types 316, 317 and the duplex grades were more resistant. These studies and field experience indicate that Type 316/316L is the minimum alloy that has useful resistance in current white water environments. The 2.5% minimum molybdenum version of the standard Type 316 is more corrosion resistant than the standard grade currently produced at 2.1 to 2.2% molybdenum. The trend is toward even higher molybdenum content alloys such as Type 317L, 904L (N08904) and duplex Alloy 2205 (S32205).

The white water environment is also conducive to microbiological influenced corrosion (MIC). The rich organic nature of the white water leads to MIC, particularly in stagnant and low flow areas of the paper machine. All the alloys mentioned in this section are subject to MIC. Prevention of MIC requires regularly scheduled cleaning along with biocide application. Only the 6% molybdenum and nickel base alloys containing chromium are resistant to MIC in the as-welded condition.

### Machine Cleaning Solutions

Acid based or caustic based foam cleaners can be used to clean pulp stock etc. from the machine. Generally, caustic based cleaners are used with a pH range of 10 to 13. Acid cleaners are generally phosphoric acid based with a pH range of 1 to 6. Both are used at room temperature.

### Passivation

During fabrication stainless steel is subject to fabricating defects, heat tint alongside and on the side opposite of welds, iron embedded from contact with steel layout tables and steel tools, weld spatter, scratches, etc. The surface at these local defects is no longer passive and is subject to localized corrosion. These defects are usually removed during post fabrication cleanup, mechanically with flapper wheels or aluminum oxide grinding discs, chemically by pickling or by application of pickle paste, or by hand-held electropolishing tools. Passivity is restored as the defects are removed. Once the surface is clean, further passivation by the nitric acid treatments (described in ASTM A380) will enhance the passivity and corrosion resistance of the cleaned surface. The nitric acid treatments alone, however, are seldom adequate for the heavy cleaning required after fabrication. Unless defects are thoroughly removed after fabrication, it may be necessary
to clean in place with pickle paste or citric-EDTA (ethylenediamine tetra-acetic acid) chelants to remove all embedded iron.

**Caustic Boil-Out**

Many mills regularly schedule caustic boil-out of the headbox and forming section. A solution of sodium hydroxide at a pH of approximately 13 is used. Temperature is about 120°F (50°C). Chelants such as the sodium or disodium salt of EDTA are often used to enhance the cleaning properties of the boil-out solution. Frequency can be less than once a month and duration is 2 to 5 hours per operation. Caustic boil-out solutions are used to dissolve and remove accumulated organic compounds. Certain polymeric materials such as polycarbonate are susceptible to severe attack. High strength steels are susceptible to stress corrosion cracking (SCC), and copper based alloys are susceptible to corrosion and dealloying during caustic boil-outs.

**REFERENCES**

16. Suction Rolls

by Max D. Moskal, Mechanical and Materials Engineering

16.1 Alloys Old and New

Suction rolls are part of the paper machine but deserve their own section and discussion. Usually drilled to about 20% open area, suction rolls are used to remove water from paper at the wet end of the paper machine. Prior to 1950, suction shells were cast from copper Alloy C83600, 85Cu 5Sn 5Pb 5Zn. As paper machine width, speed, and nip pressure increased, stronger alloys were introduced: nickel aluminum bronze, forged Type 410 (S41000), and centrifugally cast stainless steels Type CA-15 (J91150), Type CF-3M (J92800) and CF-8M (J92900). As roll speeds and nip pressure continued to increase, premature failures of these roll materials led to the introduction of special grades of cast and wrought duplex stainless steels. The composition of roll materials is shown in Tables 16-1 to 16-3. Tables 16-1 and 16-2 show currently available suction roll alloys. Table 16-3 shows alloys, many of which are still in use but have been discontinued by producers in favour of the alloys shown in Table 16-2. In the selection and performance of suction roll materials, corrosion resistance and fatigue strength in paper machine white water, nip pressure, roll width and residual stress level all play important roles, as will be discussed below.

<table>
<thead>
<tr>
<th>Table 16-1 Nominal Composition of Copper-Base Suction Shell Alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Designation(s)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>C83600 1N bronze[^2] GC-CuSn5ZnPb</td>
</tr>
<tr>
<td>C95810 (mod.) GC-CuAl9.5Ni[^3]</td>
</tr>
<tr>
<td>C90500 GC-CuSn10Zn[^4]</td>
</tr>
</tbody>
</table>

[^1]: Composition range, wt%; additional elements may be added or present in minor amounts.
[^2]: Trade name Sandusky International.
[^3]: Trade name Kabelmetre Alloys.
[^4]: Size currently limited to 3,500 mm max. length.
[^5]: Discontinued.
### Table 16-2 Nominal Composition of Stainless Steel Suction Shell Alloys Currently Available

Materials are categorized according to structure.

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition, %&lt;sup&gt;(a)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td><strong>Austenitic</strong></td>
<td></td>
</tr>
<tr>
<td>CF3M</td>
<td>0.02</td>
</tr>
<tr>
<td>CA-15, C-169</td>
<td>0.07</td>
</tr>
<tr>
<td>PM-4-1300M</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Martensitic</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Duplex-Centrifugally Cast</strong></td>
<td></td>
</tr>
<tr>
<td>Alloy 86, Alloy EPV</td>
<td>0.02</td>
</tr>
<tr>
<td>ACK-100&lt;sup&gt;(b)&lt;/sup&gt;</td>
<td>0.02</td>
</tr>
<tr>
<td>ACL-105, KRC-A894</td>
<td>0.02</td>
</tr>
<tr>
<td>KCR-110</td>
<td>0.02</td>
</tr>
<tr>
<td><strong>Duplex-Rolled and Welded</strong></td>
<td></td>
</tr>
<tr>
<td>3RE60 SRG&lt;sup&gt;(c)&lt;/sup&gt;</td>
<td>0.02</td>
</tr>
<tr>
<td>2205 SRG Plus&lt;sup&gt;(c)&lt;/sup&gt;</td>
<td>0.02</td>
</tr>
<tr>
<td>2304 AVS&lt;sup&gt;(d)&lt;/sup&gt;</td>
<td>0.02</td>
</tr>
<tr>
<td><strong>Duplex-Powder Metallurgy</strong></td>
<td></td>
</tr>
<tr>
<td>Duplok 27&lt;sup&gt;(c)&lt;/sup&gt;</td>
<td>0.02</td>
</tr>
<tr>
<td><strong>Duplex-Forged</strong></td>
<td></td>
</tr>
<tr>
<td>PM-2-2106MC</td>
<td>0.06</td>
</tr>
</tbody>
</table>

(a) Typical composition, wt%; balance of composition is iron; other elements may be added or present in minor amounts.

(b) Contains nitrogen and cobalt.

(c) Contains nitrogen.

(d) Hot isostatic pressed; contains 0.3% nitrogen.

### Table 16-3 Nominal Composition of Stainless Steel Suction Shell Alloys Discontinued by the Manufacturer

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition, %&lt;sup&gt;(a)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td><strong>Austenitic</strong></td>
<td></td>
</tr>
<tr>
<td>CF8M</td>
<td>0.05</td>
</tr>
<tr>
<td>PM-3-1811-MN</td>
<td>0.015</td>
</tr>
<tr>
<td><strong>Martensitic</strong></td>
<td></td>
</tr>
<tr>
<td>DSS-69</td>
<td>0.04</td>
</tr>
<tr>
<td>A-70</td>
<td>0.03</td>
</tr>
<tr>
<td><strong>Duplex-Centrifugally Cast</strong></td>
<td></td>
</tr>
<tr>
<td>A-63</td>
<td>0.05</td>
</tr>
<tr>
<td>A-75</td>
<td>0.02</td>
</tr>
<tr>
<td>VK-A170</td>
<td>0.07</td>
</tr>
<tr>
<td>VK-A171</td>
<td>0.07</td>
</tr>
<tr>
<td>VK-A271</td>
<td>0.06</td>
</tr>
<tr>
<td>VK-A378&lt;sup&gt;(b)&lt;/sup&gt;</td>
<td>0.05</td>
</tr>
<tr>
<td>KCR-A682&lt;sup&gt;(c)&lt;/sup&gt;</td>
<td>0.06</td>
</tr>
<tr>
<td><strong>Duplex-Forged</strong></td>
<td></td>
</tr>
<tr>
<td>PM-3-1804M</td>
<td>0.06</td>
</tr>
<tr>
<td>PM-3-1808N</td>
<td>0.08</td>
</tr>
<tr>
<td>PM-2-2205S</td>
<td>0.07</td>
</tr>
</tbody>
</table>

(a) Typical composition, wt%; balance of composition is iron; other elements may be added or present in minor amounts.

(b) Contains nitrogen and tungsten.

(c) Contains niobium (columbium).
16. SUCTION ROLLS

16.2 CORROSION

Although corrosivity of the white water environment is largely predetermined, the papermaker can still exert some control. The sulphate ion contamination and residual hydrosulphite, which can be especially damaging, can be reduced by following the practices outlined in Reference 2.

Freshwater showers will provide more effective cleaning and reduce corrosive effects. Good maintenance of the roll is also an important factor in minimizing corrosion. Drilled holes must be kept clean of deposits by the use of needle showers and periodic off-machine cleaning. A careful program of biological control should be maintained. The papermaker should also avoid the use of cleaning chemicals (such as muratic acid) that are known to be damaging to shell alloys and roll covers.

16.3 OPERATING STRESSES

Both the applied stress and internal residual stresses inherent in the shell material contribute to the stress in operation of the suction roll. The responsibility for the level of applied stress rests chiefly with the roll designer who selects the limit of design stress for the material chosen. Each shell material will have a limit of stress that will give long life in a particular environment. The magnitude of applied stress is a function of roll configuration and applied loads.

Drilled hole patterns must also be favourably designed to reduce the effects of applied stress. The most important factor influencing the applied stress in the roll is shell thickness. Applied stress decreases as the shell thickness increases. A stress calculation procedure has been developed by TAPPI that can be used as a guide for determining stresses in suction rolls. There is as yet little agreement amongst roll manufacturers as to how to calculate the stresses in suction rolls. The TAPPI procedure has recently been modified so that stress calculations can be made on a personal computer. While the TAPPI procedure still needs to be refined, it does provide mill personnel with a uniform method of determining minimum thickness requirements, drill patterns, and evaluating roll failures irrespective of the roll manufacturer.

Gun-drilled or reamed holes for improved surface finish will reduce
16. SUCTION ROLLS

corrosion and improve the cleanliness of drilled holes in service. Gun-drilling or reaming is usually not performed on bronze shells.

The residual stress that is inherent in the alloy and the heat treatment are also important factors contributing to roll life. Shells made from materials with known high residual stresses should be designed more conservatively or, preferably, not used at all. This is discussed in more detail below under “Material Selection.”

16.4 MANUFACTURING QUALITY

There is little published information relating to suction shell manufacturing quality. Shells should be inspected using liquid penetrant prior to drilling to detect such flaws as porosity, slag, and cracks. Skillful control of melting and casting procedures can minimize these defects. Weld repairs should be used with discretion and only before shell heat treatment. Type IN bronze should not be weld-repaired because of hot shortness which develops in the alloy. Careful attention should be given to drilling and machining quality and dimensional control. Industry-wide standards giving acceptance criteria for casting flaws and drilling quality have not yet been developed.

16.5 MATERIAL SELECTION

When a new or replacement roll is contemplated, the question of material selection is of primary importance. Selection of a new alloy should involve an evaluation of the condition of the existing roll and the factors contributing to its deterioration. The changes in the corrosion environment that have occurred on the paper machine should also be evaluated. One is tempted to select an identical alloy if the previous material served for 15 or 20 years. However, it is likely that changes in the machine environment have occurred at a recent time and that the life of the new roll of the same alloy could be substantially reduced. Also, the roll material in use may have been superseded by an improved version and no longer be in production. Table 16-3 lists suction roll alloys that have been discontinued by the manufacturer.

Most suction roll vacuum boxes on older paper machines have been manufactured from epoxy painted cast iron. More recently, manufacturers have used weld fabricated Type 316L (S31603) stainless steel suction boxes to better resist corrosion and deterioration.

16.6 IN-SERVICE INSPECTION

Periodic inspection of the suction roll is a critical step that will help extend its life and minimize unexpected shutdowns. Rolls should be removed from the machine, disassembled, and thoroughly cleaned, then inspected. The inspection interval is determined by local experience and is normally about once a year. Inspection should include an evaluation of drilled hole cleanliness, fatigue cracking of the shell, and rubber cover deterioration or detachment. Water-washable liquid penetrant has been successfully used to detect cracks on the inside and outside surfaces. A careful visual examination is made for corrosion and cracks.

When cracking is observed during an annual inspection, immediate consideration must be given to replacement because of the long lead time required for shell manufacture. Consideration should also be given to inspecting the roll more often than once per year to observe the rate of crack growth. A careful record must be made whenever cracks are observed. TAPPI TIP 0402-19, Reference 5, provides guidelines for suction roll inspection. TAPPI TIP 0402-01, Reference 6, provides a standard form for documenting inspection results and roll failures.
NOTES

SUMMARY

Good judgment in roll design, material selection, and control of the paper machine environment all contribute to the long life of suction rolls. Good quality control during the manufacture of the shell and timely in-service cleaning and roll inspection also contribute to a favourable service life.

REFERENCES

3. TAPPI TIP 0402-10 “Guide for evaluation of paper machine suction roll shells.”
4. TAPPI TIP 0402-11 “Liquid penetrant testing of new suction roll shells.”
5. TAPPI TIP 0402-19 “Guidelines for nondestructive examination of suction roll shells.”
6. TAPPI TIP 0402-01 “Suction roll shell report.”
The principal low alloy steel, stainless steel and nonferrous alloy fasteners and the ASTM specifications to which they are produced and ordered are shown in Table 17-1. ASTM A193 “Standard Specification for Alloy-Steel and Stainless Steel Bolting Materials for High-Temperature Service” and ASTM A194 “Standard Specification for Carbon and Alloy Steel Nuts for Bolts for High-Pressure and High-Temperature Service” are the most widely used fastener specifications. Nonferrous nuts and bolting materials are covered by ASTM F467 “Standard Specification for Nonferrous Nuts for General Use” and ASTM F468 “Standard Specification for Nonferrous Bolts, Hex Cap Screws and Studs for General Use.” Fasteners are identified by stencilling either the alloy’s common name (304, 316, 410 etc.) or the ASTM grade (B6, B8M etc.) on the bolt, stud and nut to reduce mix-ups in the field. Table 17-2 shows the marking, for the more common austenitic alloy bolting materials.

Since bolted joints are fully designed, strength is a primary selection criterion, as well as corrosion resistance. The tensile and yield strength of the common carbon and low alloy steel, stainless steel and nonferrous fastener materials used in the pulp and paper industry are shown in Table 17-1. Table 17-1 includes the duplex Alloy 2205 (S32205), an important fastener alloy, which is not yet covered by ASTM fastener specifications. The proof strength given in some of the ASTM specifications is the highest load the bolt can sustain without incurring permanent set. Since joints and fasteners are designed, alloy upgrading for better corrosion resistance is limited to alloys that have equal or higher mechanical properties. For example, if the joint is originally designed with Alloy Steel B7 fasteners and it becomes necessary to upgrade for better corrosion resistance, 17-4 (S17400) stainless steel is one of the few materials that has high enough tensile and yield strength to be substituted for Alloy steel B7 fasteners without redesigning the joint.

Fasteners are normally torqued to a minimum of 90% of yield strength. The proof loadings in ASTM specifications approximate the minimum yield strengths. It is much better to over torque than to under torque.

There are two principal applications for fasteners: flange joints and machinery bolting. Flange bolting materials are normally the same as the piping material, most commonly Type 304 (S30400) or Type 316 (S31600). These and other austenitic stainless steels are subject to galling during tightening. Prevention of galling requires care and inspection of threads. Austenitic bolts and studs can and should be ordered with rolled threads.

### Table 17-1 Common Fasteners Used in Pulp and Paper Industry

<table>
<thead>
<tr>
<th>ASTM</th>
<th>Grade</th>
<th>Alloy</th>
<th>HT °F (°C)</th>
<th>TS ksi (MPa)</th>
<th>YS ksi (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon and Low-alloy Steel-Structural</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A354 (bolts)</td>
<td>BC</td>
<td>Low alloy stl</td>
<td>Q &amp; T</td>
<td>124 (860)</td>
<td>109 (753)</td>
</tr>
<tr>
<td>A325 (bolts)</td>
<td>Type 3</td>
<td>Low CrNiCu</td>
<td>Q &amp; T</td>
<td>105 (725)</td>
<td>81 (556)</td>
</tr>
<tr>
<td>A490 (bolts)</td>
<td>Type 3</td>
<td>Low CrNiMoCu</td>
<td>Q &amp; T</td>
<td>150 (1032)</td>
<td>130 (894)</td>
</tr>
<tr>
<td>Alloy and Stainless Steel Bolting</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A193 (bolts)</td>
<td>B7</td>
<td>4140</td>
<td>1100 (593)</td>
<td>125 (860)</td>
<td>100 (720)</td>
</tr>
<tr>
<td>A194 (nuts)</td>
<td>B6</td>
<td>410</td>
<td>1100 (593)</td>
<td>110 (760)</td>
<td>85 (585)</td>
</tr>
<tr>
<td></td>
<td>B8</td>
<td>304</td>
<td>S.A.</td>
<td>75 (515)</td>
<td>30 (205)</td>
</tr>
<tr>
<td></td>
<td>B8M</td>
<td>316</td>
<td>S.A.</td>
<td>75 (515)</td>
<td>30 (205)</td>
</tr>
<tr>
<td></td>
<td>BBR</td>
<td>N50</td>
<td>S.A.</td>
<td>100 (690)</td>
<td>55 (380)</td>
</tr>
<tr>
<td></td>
<td>BBS</td>
<td>N60</td>
<td>S.A.</td>
<td>95 (655)</td>
<td>50 (345)</td>
</tr>
<tr>
<td></td>
<td>BBMLCuN</td>
<td>6% Mo</td>
<td>S.A.</td>
<td>75 (515)</td>
<td>30 (205)</td>
</tr>
<tr>
<td>None</td>
<td>S31803</td>
<td>Duplex 2205</td>
<td>S.A.</td>
<td>90 (620)</td>
<td>65 (450)</td>
</tr>
<tr>
<td>F593 (bolts)</td>
<td>630</td>
<td>17-4</td>
<td>1150 (621)</td>
<td>130-170</td>
<td>105 (756)</td>
</tr>
<tr>
<td>F594 (nuts)</td>
<td>416</td>
<td>416</td>
<td>1050 (565)</td>
<td>110-140</td>
<td>90 (619)</td>
</tr>
<tr>
<td>Nonferrous Bolting</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F467 (nuts)</td>
<td>C65100</td>
<td>SiBrz</td>
<td>-</td>
<td>100-130</td>
<td>50 (345)</td>
</tr>
<tr>
<td>F468 (bolts)</td>
<td>C63000</td>
<td>AlBrz</td>
<td>-</td>
<td>100-130</td>
<td>50 (345)</td>
</tr>
<tr>
<td></td>
<td>C65100</td>
<td>SiBrz</td>
<td>-</td>
<td>100-130</td>
<td>50 (345)</td>
</tr>
<tr>
<td></td>
<td>N04400</td>
<td>NiCu</td>
<td>-</td>
<td>80-130</td>
<td>40 (276)</td>
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<tr>
<td></td>
<td>N05500</td>
<td>NiCuAL</td>
<td>-</td>
<td>130-180</td>
<td>90 (619)</td>
</tr>
<tr>
<td></td>
<td>R05400</td>
<td>TiGr2</td>
<td>-</td>
<td>55-85</td>
<td>45 (311)</td>
</tr>
<tr>
<td></td>
<td>N10276</td>
<td>C276</td>
<td>S.A.</td>
<td>101 (695)</td>
<td>42 (290)</td>
</tr>
</tbody>
</table>

Q & T - Quench and Tempered
S.A. - Solution Anneal

### Table 17-2 Identification Markings on Common Alloy Steel and Stainless Steel Bolting

<table>
<thead>
<tr>
<th>Common Alloy Name</th>
<th>ASTM A193 Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>4140</td>
<td>B7</td>
</tr>
<tr>
<td>410</td>
<td>B6</td>
</tr>
<tr>
<td>304</td>
<td>B8</td>
</tr>
<tr>
<td>305</td>
<td>B8P</td>
</tr>
<tr>
<td>316</td>
<td>B8M</td>
</tr>
<tr>
<td>347</td>
<td>B8C</td>
</tr>
<tr>
<td>321</td>
<td>B8T</td>
</tr>
<tr>
<td>N50</td>
<td>B8A, B8RA</td>
</tr>
<tr>
<td>N60</td>
<td>B8S, B8SA</td>
</tr>
<tr>
<td>BBMLCuN</td>
<td>B9j</td>
</tr>
</tbody>
</table>
NOTES

rather than machined threads. Threads can be deburred with rotating brushes or by electropolishing. Electropolishing does a very good job of removing burrs and smoothing the thread surfaces. Electropolishing is especially beneficial for cut threads which have more burrs and are rougher than rolled threads. Using a zinc-free anti-seize lubricant and careful assembly with a torque wrench provide further insurance against galling during assembly.

N 60 (B8S) (S21800) nuts, made of a special stainless steel with high silicon designed to reduce galling, can be substituted for Types 304 or 316 nuts to guard against galling. Aluminum bronze nuts are another alternative that can be used in mild non-acidic environments to reduce galling. In tropical environments, Types 304 and 316 fasteners, subject to direct sun, may reach metal temperatures high enough for chloride stress corrosion cracking (SCC) to occur. When chloride SCC occurs, ASTM A193 Grade B6, Type 410 (S41000) fasteners are an alternative, although not quite as resistant to general corrosion as Types 304 and 316. Duplex Alloy 2205 is a more corrosion resistant alternative, although not yet listed in the ASTM fastener specifications.

The second principal application for fasteners is in machinery where vibration, in addition to strength and corrosion resistance, is a primary consideration. Paper machine fastener problems have been discussed in considerable detail in Reference 1. It is suggested that Reference 1 be kept handy for maintenance personnel. Some key points are summarized below.

Paper machine fasteners are dynamically loaded and subject to vibration, overload, fatigue, stress corrosion cracking, hydrogen embrittlement, pitting, crevice corrosion and galvanic corrosion. Loosening is a common failure mode for dynamically loaded bolting and must be guarded against.

The paper machine operates in a moist, slightly acidic environment with chlorides, residual oxidants such as chlorine, and other chemical species frequently present. Carbon and low alloy steel bolting are subject to significant corrosion in the paper machine environment, which usually makes unbolting difficult or impossible. Galvanized bolting is little better. The zinc galvanizing does initially provide protection for the steel beneath, but lasts only a few years in the humid paper machine environment. Hydrogen, released at the cathodic surface by galvanic action of the zinc corroding to protect the underlying steel, can embrittle the higher strength steels and result in hydrogen induced cracking (HIC).

Types 304 and 316 fasteners, as well as other austenitic alloys, which have good general corrosion resistance in most paper machine environments, are sometimes subject to chloride SCC in the hot moist atmosphere.
When chloride SCC does occur, Type 410 stainless steel can be used or other more resistant alloys, such as Alloy 400 (N04400), duplex Alloy 2205, and 17-4 PH (S17400) heat treated to 1100°F (595°C). Corrosion fatigue is a common mode of paper machine fastener failures. 17-4 PH is often the best option for upgrading when fatigue failures occur. The 17-4 PH alloy should be age hardened above 1025°F (550°C) to improve resistance to chloride SCC. A few paper machine environments are so corrosive that it has been necessary to upgrade to Alloy 400 and Alloy C276 fasteners.

When corrosion indicates that upgrading is required, care must be taken that the more corrosion resistant alloys under consideration for upgrading have mechanical properties equal to or better than the fasteners that have failed. When Types 304 or 316 are to be replaced, strength seldom limits the alloy for upgrading, as most alternatives have higher strength. However, when corrosion of alloy steel B7 fasteners requires a more corrosion resistant alloy, very few alloys other than 17-4 PH, have adequate strength to be good candidates for replacement without completely redesigning the joint.

REFERENCES

This reference provides a great deal of useful information on fastener assembly, fastener materials, modes of failure and corrosion behaviour.
The stainless steels most widely used in pulp and paper mills are the austenitic nickel-containing stainless steels, while the austenitic-ferritic duplex stainless steels are finding increased use. Both types are easily welded using the same arc welding processes, i.e., shielded metal arc (SMAW or stick), gas tungsten arc (GTAW or TIG) or gas metal arc (GMAW or MIG) welding used for joining carbon and low alloy steels. The welding procedures for stainless steels will vary in some respects from the ordinary steels. These differences should be recognized to obtain high quality welds for optimum corrosion performance. This section highlights proven stainless steel welding practices.

### 18.1 Preparation for Welding

Quality welds for optimum corrosion performance start with proper preparation before the arc is struck. The first consideration is proper design for corrosion services. Two cardinal rules are:

- design for complete and free drainage, and
- eliminate or seal weld crevices.

Butt welds should have complete joint penetration unless specifically exempt by the design engineer. Examples of poor and good design are illustrated in Reference 1.

An essential, but often overlooked, preparation step is to communicate welding details to the welder and verify that the welder has the proper training and qualifications for the particular job. Even though the welds in question may not legally require detailed specifications and qualifications, the mill should provide the welder with documents describing the welding details. Also it is essential that the welder has the proper training and ability to perform the type of welding required.

The weld joints should be tack welded to maintain a uniform root opening and alignment along the entire length. Tack welds in stainless steel must be spaced closer than would be needed for ordinary steel to minimize distortion. A common guide is to use about half the spacing between stainless tacks as for carbon steel when distortion is a factor. When tack welds are to be incorporated into the final weld, they should be free of surface oxides and cracks. They should be of a size and shape suitable to become a part of the final weld.

The weld area requiring cleaning before welding includes the joint edges and two or three inches of the adjacent surfaces. Grinding or other mechanical means should be used to remove all paint, scale, oxides and...
A suitable solvent should be used to remove any oil or grease in the weld area. In addition to removing oil and grease, the solvent should not leave a residue or be harmful to the welder or to the component being welded. In weldments containing crevices, non-chlorinated solvents should be used to safeguard against crevice corrosion or stress corrosion cracking in service.

An essential pre-welding step in pipe and tube welding is establishing an internal inert gas purge. Purging will be discussed in the pipe welding subsection.

18.2 WELDING PROCESSES

Engineering and maintenance personnel in pulp and paper mills who are associated with welding are familiar with the commonly used arc welding processes of SMAW, GTAW and GMAW for welding ordinary steels – so descriptions of each process will not be given. The following remarks are limited to areas significant to stainless steel welding with each process.

**Shielded Metal Arc Welding (SMAW)**

The commonly used specification for stainless steel covered electrodes in North America is ANSI/AWS A5.4. The operability, including the applicable welding position, is determined by the particular coating formula. A5.4 recognizes five different classifications. The two classifications most applicable to paper mills are the –15 (lime) and –16 (basic-titania) types where all-position operability is often needed.

Stainless steel electrodes operate rather like the carbon and low alloy steel electrodes of the –15 and –16. Welders can use similar arc starting and stopping techniques to prevent porosity, crater cracks and similar defects. The electrodes must be properly stored in heated cabinets after opening the original package as a safeguard against weld metal porosity. After over-exposure to moisture, the electrodes should receive a recondition bake. Lacking specific manufacturers' recommendations, commonly used baking temperatures are:
- storage of opened electrodes: 225°F (110°C)
- recondition bake: 500°F (260°C)

Maintaining a low moisture level is particularly critical for the duplex stainless steel electrodes to avoid underbead cracking.

After the weld is complete, it is essential that all welding slag be removed. Normally the slag is easily detached from the weld bead, but in some instances it may be necessary to use a stainless steel wire brush or light grinding. Any remaining slag particles are a potential spot for crevice corrosion.

**Gas Tungsten Arc Welding (GTAW)**

Essentially all the root pass pipe or tubing welds in paper mills should be made by GTAW to produce a root pass with optimum corrosion and service performance. In addition, the process can be used to weld in all positions and is a good process to use for welding thin material. For stainless steels, the shielding gas is pure argon, helium, or mixtures of the two. Helpful equipment features include: high frequency starting or lift starting, a provision for current decay and a gas lens torch feature to provide better gas shielding protection to the weld.

**Gas Metal Arc Welding (GMAW)**

The type of GMAW metal transfer has a profound influence on the process characteristics to the extent that it is often misleading to make general statements about GMAW without indicating the arc transfer mode. The three modes most used in welding stainless steel are spray, short circuiting, and pulsed arc. Even here with some of the new power sources, the distinction between short circuiting and pulsed arc has become less clear. However, all three have the advantage of higher deposition rates than manual GTAW and no slag to remove as with SMAW.

Briefly, some features of each of the arc transfer modes are:
Spray Arc
- usually used to weld 1/4 in. (6.4 mm) and thicker material
- limited to flat or horizontal welding
- highest deposition rate of three transfer modes
- shielding gas: argon with 1% O₂ or argon with 2% O₂

Short Circuiting Arc
- usually for thickness of 1/16 in. (1.6 mm) up to about 1/4 in. (6.4 mm), but best for single pass welding
- used in all-position welding
- lowest deposition rate of three
- shielding gas: 90% Ar, 7.5% He, 2.5% CO₂ or 90% He, 7.5% Ar, 2.5% CO₂

Pulsed Arc
- for thickness of 1/16 in. (1.6 mm) or thicker
- excellent for all-position welding
- intermediate in deposition rate
- shielding gas: same as for short circuiting, or argon with 1% O₂

There are shielding gases used other than indicated above for short circuiting and pulsed arc; however, the accepted practice is that the mixture contain at least 97.5% inert gas, i.e., argon, helium or a mixture of the two. Additionally, plastic liners in the wire feed conduit are helpful in reducing drag with stainless steel wire.

Other Welding Processes

Stainless steels can be welded by most of the other commercial welding process in addition to the above mentioned three. An arc welding process finding increased use in pulp and paper mills for stainless steels is the flux cored arc welding (FCAW) process. The deposition rate of FCAW is normally higher than that of SMAW. Also it is easier to produce cored wires of special compositions or ferrite levels than it is to melt large heats for solid wire. The submerged arc welding (SMAW) process is also used to weld stainless steel principally by equipment manufacturers rather than by the mills.

18.3 Stainless Steel Weld Filler Metals

It is often said that the stainless steel base metals are welded with a “matching composition” filler metal. Actually, filler metal compositions are slightly different from the base metal to insure comparable mechanical properties, desired welding characteristics, and about 4 – 10% ferrite in the welds of the standard austenitic grades. Table 18-1 identifies the filler metals used for the principal alloys used in paper mills.
### Table 18-1 Suggested Filler Metals for Welding Stainless Steels and High Alloys

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Casting</th>
<th>Shielded Metal Arc Welding Electrode</th>
<th>Bare Welding Electrodes &amp; Rods</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI (UNS)</td>
<td>ACI Type (UNS)</td>
<td>ANSI/AWS A5.4 (UNS)</td>
<td>ANSI/AWS A5.9 (UNS)</td>
</tr>
</tbody>
</table>

#### Austenitic

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Casting</th>
<th>Shielded Metal Arc Welding Electrode</th>
<th>Bare Welding Electrodes &amp; Rods</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L(1) (S30403)</td>
<td>CF-3(1) (92500)</td>
<td>E308L (W30813)</td>
<td>ER308L (S30882)</td>
</tr>
<tr>
<td>316L(1) (S31603)</td>
<td>CF-3M(1) (92800)</td>
<td>E316L (W31613)</td>
<td>ER316L (W31683)</td>
</tr>
<tr>
<td>317L (S31703)</td>
<td>CG-3M (92999)</td>
<td>E317L (W31713)</td>
<td>ER317L (S31783)</td>
</tr>
<tr>
<td>317LMN (S31726)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>904L (N08904)</td>
<td>—</td>
<td>E385 (W88904) or (2)</td>
<td>ER385 (N08904) or (2)</td>
</tr>
<tr>
<td>6% Mo Grades</td>
<td>CN-3MN (94651) CK-3MCuN (93254)</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

#### DMW & Overlay

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Casting</th>
<th>Shielded Metal Arc Welding Electrode</th>
<th>Bare Welding Electrodes &amp; Rods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenitic Stainless Steel to Carbon or Low Alloy Steels</td>
<td>*</td>
<td>E309 (W30910)</td>
<td>ER309 (S30980)</td>
</tr>
<tr>
<td>Overlays on Steel</td>
<td>E312 (W31310)</td>
<td>ER312 (S31380)</td>
<td></td>
</tr>
</tbody>
</table>

#### Martensitic

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Casting</th>
<th>Shielded Metal Arc Welding Electrode</th>
<th>Bare Welding Electrodes &amp; Rods</th>
</tr>
</thead>
<tbody>
<tr>
<td>410 (S41000)</td>
<td>CA-15 (91150)</td>
<td>E410 (W41010)</td>
<td>ER410 (S41080)</td>
</tr>
<tr>
<td>—</td>
<td>CA-6MN (91540)</td>
<td>E410 NiMo (W41016)</td>
<td>ER410 NiMo (S41086)</td>
</tr>
</tbody>
</table>

#### Precipitation Hardening

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Casting</th>
<th>Shielded Metal Arc Welding Electrode</th>
<th>Bare Welding Electrodes &amp; Rods</th>
</tr>
</thead>
<tbody>
<tr>
<td>17-4 PH (S17400)</td>
<td>CB7Cu-1 (91280)</td>
<td>E630 (W37410)</td>
<td>ER630 (S17400)</td>
</tr>
</tbody>
</table>

#### Duplex (3)

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Casting</th>
<th>Shielded Metal Arc Welding Electrode</th>
<th>Bare Welding Electrodes &amp; Rods</th>
</tr>
</thead>
<tbody>
<tr>
<td>2205 (S31803)</td>
<td>ASTM A890-4A (92205)</td>
<td>E2209 (W39209)</td>
<td>ER2209 (S39209)</td>
</tr>
<tr>
<td>2507 (S32750)</td>
<td>ASTM A890-5A (93404)</td>
<td>E2553 (W39553)</td>
<td>ER2553 (S39553)</td>
</tr>
<tr>
<td>329 (S32900)</td>
<td>—</td>
<td>E2553 (W39553)</td>
<td>ER2553 (S39553)</td>
</tr>
</tbody>
</table>

#### High Alloys

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Casting</th>
<th>ANSI/AWS A5.11</th>
<th>ANSI/WS A5.14</th>
</tr>
</thead>
<tbody>
<tr>
<td>625 (N06625)</td>
<td>CW-6MC (N26625)</td>
<td>ENiCrMo-3 (W86112)</td>
<td>ERNiCrMo-3 (N06625)</td>
</tr>
<tr>
<td>C-22/622 (N06022)</td>
<td>CW2M (N26022)</td>
<td>ENiCrMo-10 (W86022)</td>
<td>ERNiCrMo-10 (N06022)</td>
</tr>
<tr>
<td>C-276 (N10276)</td>
<td>CW-2M (N26455)</td>
<td>ENiCrMo-4 (W80276)</td>
<td>ERNiCrMo-4 (N10276)</td>
</tr>
</tbody>
</table>

---

(1) The low carbon (L) grades are preferred when welding is involved. The standard grades, i.e., 304/CF-8 (S30400/J92600) and 316/CF-8M (S31600/J92900) with a maximum of 0.08% carbon can be welded with the low carbon grade of filler metals. The E316L (W31613) or ER316L (W31683) filler metals have been used also and are acceptable to join 304L/CF-3 (S30403/J92500) stainless steel for pulp and paper mill environments.

Notes for Table 18-1 continue on next page
Ferrite in Stainless Steel Welds

Types 308/308L (S30800/S30803), 316/316L (S31600/S31603) and 317/317L (S31700/S31703) welds contain small amounts of ferrite in the austenitic matrix. This small amount of ferrite is very beneficial in reducing the strong tendency for cracking or for fissures in fully austenitic welds. Ferrite is also helpful when the welds are restrained or of heavy sections. Ferrite is magnetic; so stainless steel welds are slightly magnetic, which can be detected with a small magnet. Some more highly alloyed stainless steels and the Ni-Cr-Mo compositions do not contain ferrite; so it can not be concluded that ferrite is essential for sound welds in all grades of stainless steels, simply that 4–10% ferrite makes it easier to obtain sound welds in the basic austenitic grades.

In duplex stainless steels, which are nominally 50% ferrite and 50% austenite, welds made with exactly matching composition filler metals may contain as much as 80% or more ferrite, with resultant low ductility and poor corrosion resistance in some environments. Therefore, most duplex filler metals have an increased amount of nickel, even though they are referred to as “matching composition”, in order to obtain the desired austenite-ferrite phase balance and properties in the as-welded condition. Reference 11 is an excellent source of information on the fabrication and welding of duplex stainless steels.

The ferrite in the weld metal is readily corroded during inhibited hydrochloric acid cleaning, which has led to corrosion of heat exchanger tubing and partially lined or partially weld overlaid digesters. Remedial measures and alternative acids are discussed in the section 20 on “Corrosion.”
Stainless Steel Weld Filler Metals For 6% Mo

Due to molybdenum segregation in the as-deposited weld metal, it became necessary to fabricate 6% molybdenum stainless steels with higher molybdenum content filler metals containing 9% and 16% molybdenum. In the bleach plant ENiCrMo-4 and ERNiCrMo-4 became standard for bleach plant applications. Welds made with these higher molybdenum content had equal or superior corrosion resistance to the 6% Mo base metal with one notable exception.

In mills that used caustic to neutralize chlorine dioxide stage to 6-7 pH, the nickel base filler metals were subject to transpassive corrosion as reported in the Bleach Plant section (Section 13) of this bulletin. It was found that higher chromium, lower molybdenum filler metals, ENiCrMo-11 and ERNiCrMo-11, nickel base alloy G30 in Table 18-1, would resist this transpassive corrosion and approximate base metal resistance in this near neutral chlorine dioxide environment. It has become standard practice to use the NiCrMo-11 filler metals to fabricate washers for mills that use caustic to neutralize their chlorine dioxide stage environment. For mills that do not neutralize chlorine dioxide stage with caustic, the standard higher molybdenum content filler metals are used.

18.4 PIPE AND TUBE WELDING

Pulp and paper mills often have thousands of feet of stainless steel pipe or tubing, most of which is joined by welding rather than by mechanical means. Mill personnel often become involved in piping system changes or in piping maintenance work.

A detailed discussion on stainless steel pipe welding techniques and procedures is beyond the scope of this document, but some of the essential points are cited, along with a list of references for more detailed information. The most widely used weld joint for stainless steel and high alloy piping is a butt weld made with a GTAW root pass and an open root or consumable insert. Socket welds and backing ring welds have inherent crevices, which in some services may result in crevice corrosion. Most often piping in paper mills is manually welded; however, for large projects, automatic orbital welding is finding increased use and produces welds with more consistent internal root surface than is obtainable by manual welding.

Additional pipe welding guidelines follow:

- In manual welding, both the open root with hand-fed filler metal and the use of consumable inserts can provide good root pass welds in the hands of capable welders. The choice is often made based on past experience.
- The same previously mentioned weld preparations, such as cleaning described earlier, also apply to pipe welding. Accurate joint fit-up is particularly important to obtain a consistent root contour.
- All stainless steel and high alloy pipe welds should be made with internal inert gas backing. The one exception could be pipes of large diameter that allow welding from both sides. Argon is the preferred backing gas, with nitrogen sometimes used for cost savings. The backing gas protects the molten weld metal from oxidation and prevents heat tint oxides from forming next to the weld in the heat affected zone, provided oxygen is kept below 0.1% in the backing gas. The effect of heat tint oxides on corrosion is discussed under “Post-Fabrication Cleaning” below. In multiple pass welds, the inert backing gas should be maintained for two or three passes after the root weld. Details of gas purging procedures are discussed in the references.
- There are flux cored rods available for GTAW pipe root pass welding that are designed to omit the inert gas backing. The flux in the core melts and covers both the face and back side of the root, and the slag formed must be removed after the weld cools. It should be recognized that the heat affected zone next to the weld is exposed to air and a heavy heat tint oxide scale will be developed on the base metal. There are many mill service applications where the heat tint oxide could cause product contamination or environments where the reduced corrosion resistance as a result of the heat tint could be detrimental.
Pipe Welding References

There are a number of excellent articles and documents on stainless steel pipe welding, including publications by the American Welding Society, TAPPI, and the Nickel Development Institute (NiDI). Brief comments on specific references follow.

1. References 1 and 3 cover the basic elements of manual GTAW pipe welding stainless steel and nickel alloys. The publications may be obtained free of charge from: Nickel Development Institute, 214 King Street West, Suite 510, Toronto, Ontario, Canada M5H 3S.

2. References 4 and 5 are a good source of pipe welding information for mills engaged in the manual welding of stainless steel pipe. They may be obtained from: American Welding Society, 550 N.W. LeJeune Rd., Miami, FL 33126.

3. Reference 6 specifically addresses welding 6% molybdenum stainless steel pipe with an open root joint. However, it also provides detailed welding procedures applicable to welding all austenitic stainless steel pipe and was written specifically for the pulp and paper mills. The document can be obtained from: TAPPI, 15 Technology Parkway, P.O. Box 105113, Atlanta, GA 30348-5113.

4. Reference 7 explains the automatic orbital tube welding process and cites stainless steel welding applications. It is a good source for those interested in learning the basics of the automatic process and may be obtained from NiDI, at the address given above.

5. Reference 8 outlines considerations for fit-up, welding and inspection of circumferential butt welds made during shop spooling and field installation of austenitic and duplex stainless steels and nickel base alloys.

18.5 DISSIMILAR METAL WELDING (DMW)

There are many instances where dissimilar metals need to be joined together. Fortunately, stainless steels and nickel alloys are compatible with each other and with a wide range of ferrous alloys. Some of the basic DMW guides follow.
Preheat and Postweld Heat Treatments (PW HT)

A preheat or PW HT is not required for austenitic stainless steels or nickel alloys, but may be necessary in a DMW when the other metal to be joined requires preheat and/or PW HT. An example of alloys often requiring a preheat and/or PW HT are low alloy steels, such as the chromium-molybdenum alloys, and martensitic stainless steels. The rule is to use the preheat and/or PW HT prescribed for the alloy requiring the control.

Filler Metal Selection

A cardinal rule in DMW is to “use a higher alloy filler metal.” For example in a weld between carbon steel and stainless steel, a stainless steel or a nickel alloy filler metal should be used. NEVER use an ordinary steel filler metal to join stainless steel or a nickel alloy to a carbon or low alloy steel. Such a weld would be hard, brittle and prone to cracking.

In welds made to carbon or low alloy steels, the corrosion resistance of the filler metal is seldom a concern. In most applications, the steel side would have much lower corrosion resistance than any of the higher alloy filler metals that might be used.

Austenitic Stainless Steels to Ferritic Steels

The standard filler metals for DMW with a service temperature not over 800°F (425°C) are Type 309 (S30900) or Type 312 (S31200) for temperature not over 600°F (315°C). For temperatures over 800°F (425°C), a nickel alloy filler metal such as NiCrFe-2 (W 86133) should be used. The coefficient of thermal expansion of the nickel alloy weld is a closer match to that of the carbon steel, which minimizes the thermal stress on the weaker side of the joint.

Nickel Alloy Dissimilar Metal Welds

The NiCrFe and NiCrMo nickel alloys may be welded to each other, to stainless steels, and to carbon or low alloy steels, using the nickel alloy filler metal used to weld to themselves. Filler metal selection is not as straightforward for some of the other nickel alloy combinations; more detailed sources, such as Reference 3, should be consulted.

Welding Processes

SMAW is often the preferred process for DMW, since the dilution is more predictable (about 25 to 30%). In GMAW, the dilution may vary from 10 to 50%; in GTAW, it may vary from 20 to 100%. It is difficult to predict weld serviceability when dilution varies widely.

18.6 Post-Fabrication Cleaning

Post-fabrication cleaning may be as important as any of the fabrication steps discussed. The surface condition of stainless steels is critical when the stainless must resist aggressive environments, such as exist in paper mills. The corrosion of the chromium containing nickel alloys are not affected to the same degree, but it is still good practice to observe the cleaning rules for stainless steels. Surface conditions that can reduce corrosion resistance may include surface contamination, embedded iron, heat tint oxides, and mechanical damage. Figure 18-1 illustrates some of the common conditions. Reference 12 discusses post-fabrication cleaning of stainless steels for bleach plant service.

Surface Contaminants

In aggressive environments, organic contaminants on stainless steel surfaces can foster crevice corrosion. Such contaminants include grease, oil, crayon marks, paint, adhesive tape and other sticky deposits.

Surfaces to be pickled or acid-treated must be free of...
organic contaminants if the acid is to be effective in removing free iron, surface oxides, or similar conditions. Because little can be done during fabrication to reduce organic contamination, it must be removed during the final cleanup.

Visual inspection is usually effective in spotting organic contamination. Wiping with a cloth or paper is effective in finding oil or grease contamination. Degreasing with a nonchlorinated solvent is effective for removing contamination. A chlorinated solvent is not recommended because residual chlorides may remain in crevices and cause crevice corrosion or chloride stress corrosion cracking later when the unit is placed in service.

**Embedded Iron**

Sometimes, new alloy tanks, vessels, and piping rust shortly after fabrication. This is often due to iron embedded in the surface during fabrication. The iron particles corrode in moist air or when wetted, leaving

Figure 18-1 Types of Surface Defects Arising During Fabrication

- Heat Tint
- Embedded Iron or Rust
- Heat Tint
- Weld Spatter
- Scratch
- Arc Strike
- Undercut
- Rough Grinding Burr
- Paint
telltale rust streaks. In addition to being unsightly as they corrode, the larger particles of embedded iron may initiate crevice corrosion in the underlying stainless steel, which would otherwise not occur.

A simple test for embedded free iron is the “Wet and Drying” test described in Reference 10. Upon completion of the test, there should be no evidence of rust stain or corrosion products on the surface.

Pickling, which is carried out after degreasing, is the most effective method for removing embedded iron. A commonly used pickling treatment is a 10% nitric – 2% hydrofluoric acid bath at 120°F (50°C). Pickling not only removes embedded iron and other metallic contamination, but also leaves the surface bright, clean, and in its most corrosion-resistant condition. Because pickling is aggressive, it will destroy a polished or high-lustre surface. (Use with extreme care!)

Small objects are best pickled by immersion in pickling baths. For larger sized components, there are commercially available nitric-hydrofluoric acid pickling pastes that are easy to apply and are very effective in cleaning and removing free iron. With either method, it is essential to completely remove the acid by thorough rinsing in clean water.

Embedded iron can also be removed by citric acid plus EDTA or other proprietary chelating agents, which are very effective in removing embedded iron. These chelating agents will not remove heat tint oxide scale, which must be removed by other means.

When pickling is not practical, blasting can be used, but not all abrasives yield good results. Glass bead blasting produces good results, but before blasting, a test should be made to determine that it will remove the surface contamination. Also, periodic tests should be made to see how much reuse of beads can be tolerated before they begin to recontaminate the surface. Walnut shells have also performed well as an abrasive.

Abrasive blasting with steel shot or grit leaves a rough smeared surface layer prone to corrosion, but is sometimes the only practical method of removing oxide scale from stress relief treatments or severely abused surfaces of unprotected, field-erected tank bottoms. Even clean sand will leave a rough smeared surface with some iron embedded in the surface. Pickling and electropolishing after sandblasting will restore base metal corrosion resistance. Citric acid with chelating agents will remove embedded iron residues.

Heat Tint

When stainless steels are heated to moderately high temperatures in air, a dark, thicker-than-normal oxide develops on the surface. Heat tint normally occurs on the face and often on the root side of welds unless special precautions are taken to effectively exclude oxygen while the metal is at elevated temperatures. The heat tint colour varies from black to blue, violet, and straw colour. The thicker oxide reduces the passivity of the surface. The chromium content of the metal just below the oxide is reduced, resulting in an area of lower corrosion resistance. In some rather corrosive aqueous environments, areas not cleaned of heat tint often develop pits, while the adjacent clean stainless steel surface is free of attack. The obvious action is to prevent heat tint oxides from developing by exclusion of oxygen from the areas heated by welding. If heat tint does develop, it should be removed by pickling or mechanical means.

Mechanical Damage

When the surface has been damaged and reconditioning is needed, the repair is usually made by grinding or by welding and grinding. Shallow defects are first removed by grinding, preferably with a clean, fine-grit abrasive disc, a flapper wheel, or a pencil-type grinder. The maximum grinding depth to remove defects is often specified by the fabrication specification and may vary from 10 to 25% of the total thickness. When weld repair is needed, it can be made by any of the arc processes, but GTAW is often used because of the greater ease in making small repair welds. Filler metal should always be added. Wash passes or cosmetic welds should not be allowed because of the risk of weld cracking and reduced corrosion resistance.
NOTES

6. TAPPI TIP 0402-20 “GTAW root pass welding of 6% molybdenum austenitic stainless steel pipe – open root joint with hand-fed filler.”
19.1 GENERAL CONSIDERATIONS

Abrasion is the most common type of wear; its destructive effects are widespread throughout most industries, including the pulp and paper industry. Abrasion is due to hard particles or protrusions being forced against, and moving along, a solid surface. It becomes more severe the harder the particles are, compared to the surface they are moving against. This section gives an overview of abrasion processes, and briefly reviews guidelines for materials selection, with a focus on stainless steels compared to other ferrous alloys. References 1 and 2 give a more thorough treatment of abrasion mechanisms. References 3 and 4 give useful information on the various options available for controlling abrasion and other forms of wear.

As abrasion can occur in many ways, various criteria have been developed to classify the type of contact environment that is present. The situation where an abrading particle slides freely along a surface is described as two-body wear. In cases where the abrading particle is trapped between two surfaces, the situation is called three-body wear. Two-body wear is usually significantly greater than three-body wear, due to the greater amount of metal cutting that occurs in the two-body system. By contrast, abrasive particles in three-body wear may spend a large proportion of their residence time between the two surfaces in rolling, rather than cutting.

Abrasion is also classified as being low-stress, high-stress, or gouging abrasion. These are qualitative descriptors, but they can be useful for a first characterization of an abrasive situation. In low-stress abrasion, the amount of plastic deformation and work hardening of the abraded surface would be expected to be relatively low; damage occurs mainly by cutting and the abrading particles generally remain intact. In high-stress abrasion, imposed loads are greater, so that a higher proportion of surface plastic deformation and work hardening may be expected. At the same time, the amount of surface cutting also increases due to the creation of fresh abradant by fracture of existing abrading particles. Plastic deformation and work hardening predominate in gouging abrasion, where imposed loads are highest of all.

Examples of low-stress abrasion may be found on many pieces of mill equipment, such as pumps, chutes, screens, and hoppers. Instances of high-stress abrasion may be found in feed screws and valves, and in wood-handling operations. Gouging abrasion is most common in mining and mineral processing, where imposed working loads are typically higher than in the pulp and paper industry.

19.2 MATERIALS SELECTION

Abrasion rates depend on many metallurgical and environmental factors. Therefore, it is important to realize that materials do not have an intrinsic level of abrasion resistance. Metallurgical factors that influence abrasion include hardness, microstructure (i.e., the presence of ferrite, austenite, pearlite or martensite), alloy content, and the presence of second phase particles. Environmental factors include the nature of the abrasive, the presence of a corrosive liquid or gas, temperature, load, sliding speed and humidity. For more details about the relative importance of these factors, see Reference 1.

Because of the complexity of abrasion processes, materials selection is not an exact science and, for every example of a successful application, there often seems to be a counter example. Having said this, it is possible to provide some general guidelines.

For situations where corrosion is not a factor, the abrasion resistance of steels and cast irons will be largely dependent on their hardness, carbon content and microstructure. Generally, increased hardness and carbon content give increased levels of abrasion resistance, through the formation of martensite and carbides in the microstructure. At the high end of the carbon range (e.g., with alloys such as the white cast irons), factors such as toughness and impact resistance become increasingly important. While hardness is readily available to guide abrasion resistance, it must be remembered that there are many exceptions to the rule. This is because the true measure of abrasive wear resistance is the maximum hardness of the work hardened, abraded surface, and not the initial bulk hardness. Alloys that rapidly work harden as a result of abrasion can thus also give good performance.
This helps explain why austenitic stainless steels, which readily work harden but do not contain either martensite or carbides, can give acceptable performance in some abrasive wear conditions. Increasing alloy content in austenitic stainless steels decreases their work hardening rate. Type 304L (S30403) and the proprietary alloy Nitronic 30 (S20400) have been shown to resist some abrasive conditions better than Type 316L (S31603), on account of their higher work hardening. For the mill engineer, the practical problem is how to predict if a given abrasion situation will cause a sufficient amount of work hardening. In this respect, prior field experience is probably the best guide. In the pulp and paper industry, most abrasion problems will involve at least some amount of corrosion, and it is important to remember that the presence of a corrosive environment can significantly change the overall abrasion performance of many ferrous materials. This is especially true for alloy steels and white cast irons, which are often the first choice for combating “pure” abrasion. Examples of mill equipment where a combination of abrasion and corrosion can occur include beaters, deflakers, stock refiners, chip refiners, pumps, storage bins, and chutes. In beaters, deflakers, and stock refiners, abrasive-resistant cast irons [25% Cr and Ni-HiCr Type D (ASTM A532)] and precipitation hardening alloys [such as 17-4 (S17400)] are used in situations where abrasion resistance is the overriding consideration. The 17-4 alloy would normally only be used for light abrasion duty; 25% Cr and Ni-HiCr Type D would be selected for more intense service. When corrosion is also significant, the 25% Cr white cast irons or high carbon cast stainless steels are used, e.g., for refiner plates. In pumps, abrasion from sand and grit has led to widespread replacement of the standard CF-3 (J92500) and CF-3M (J92800) grades with the cast duplex grades, CD-6MN (J93371) and CD-4MCuN (J93372). These two cast duplex grades have much improved resistance to sand and grit erosion as well as better corrosion resistance. For storage bins and chutes, where a smooth surface must be maintained to allow easy flow of bulk solids, Types 409 (S40900) and 304 (S30400) have replaced abrasion resistant (“AR”) carbon steels, which rapidly corrode in mill process waters. Duplex stainless steels would also be candidates for these applications.

In each case, it is necessary to balance the amount of abrasive wear resistance needed with the appropriate level of corrosion resistance. This tends to make local site experience with good record keeping the most reliable materials selection guide.
REFERENCES


20. Corrosion

20.1 Alloy Usage – Materials of Reference

Material of reference, as used in this section, means the most common and most widely used material in this section of the mill. Mills upgrade to more highly alloyed materials when the materials of reference are not resistant to the conditions that exist in their particular mill. Stainless steels Types 304L (S30403), 316L (S31603), 317L (S31703), 904L (N08904), the 6% Mo austenitic stainless steels, and the duplex Alloy 2205 (S31803/S32205) are the principal wrought stainless steel alloys used by the pulp and paper industry. Each of these wrought grades has a cast counterpart. Composition and properties of the wrought alloys are shown in Tables 2-1 and 2-2 in Section 2 of this bulletin. Table 2-3 shows the family of 6% Mo and 7% Mo alloys, the ASTM specifications and the producers of these alloys. There is no single designation for these highly corrosion resistant alloys as there is for the others in Tables 2-1, 2-2. Table 2-4 shows the composition and properties of the principal cast alloys.

Types 304L and duplex Alloy 2205 are the materials of reference for the alkaline digester and chemical recovery section of sulphate mills. Corrosion resistance in the alkaline environment increases almost directly as chromium content increases. Molybdenum makes no significant contribution to corrosion resistance in this highly alkaline environment; hence Type 304L is normally preferred to Type 316L in the alkaline section of kraft mills.

Type 316L is the material of reference for the same sections of sulphite mills and for the headbox and white water sections of both sulphate kraft and sulphite mills. In the headbox and approach piping the material of reference is Type 316L electropolished with smooth flush welds that will pass a cotton ball test.

Types 316L, 317L, 904L, the 6% Mo grades, and more recently the duplex grades, are used in bleach plant and sulphite mills. Type 317L is the first upgrade from Type 316L for bleach plants in North America. Type 904L and Alloy 2205 are the first upgrades from Type 316L in Europe and elsewhere. The 6% Mo alloys can be considered the materials of reference for the C and D stages although there are a number of applications where nickel base alloys and titanium are preferred. Refer to Table 13-4, “Materials for Bleaching Plant Equipment” in this bulletin. Type 316L is the material of reference for the newer, oxygen, hydrogen peroxide and ozone stages as well as the older caustic and hypochlorite stages.

The cast duplex grades have long been the preferred alloys for pumps.
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and more recently for suction press rolls. In wrought form the duplex alloys are the preferred grades for batch digesters and are finding an increasing number of applications throughout the mill wherever Type 316L falls short of expectations. Duplex is also used in lieu of Type 316L in large vessels where the duplex alloy’s higher strength permits a thinner wall thickness that offsets much of the higher cost of the duplex material. Usage of duplex is expected to continue to increase as more fabricators become familiar with welded fabrication of the duplex alloys.

20.2 INTERGRANULAR ATTACK (IGA)

Prior to the development of the argon oxygen decarburization (AOD) process for refining stainless steel, Types 347 (S34700) and 321 (S32100), both stabilized grades, were used for welded construction in order to prevent intergranular attack (IGA) at the grain boundaries in the heat affected zone (HAZ) of welds. Today the low carbon “L” grades – 316L, 317L, 904L, etc. – are standard for welded construction. At the low carbon content of the “L” grades, there is insufficient carbon for enough chromium carbide precipitation at the grain boundaries to sensitize the low carbon grades within the time the heat affected zone normally remains in the sensitization range. Figure 20-1 shows the time and temperatures required to sensitize stainless steels of different carbon contents to intergranular attack (IGA), also often referred to as intergranular corrosion or “sugaring.” Engineers should be aware that the low carbon grades have been sensitized in certain mixed carbon steel - stainless steel structures where codes require the carbon steel to be stress relieved for long enough times to sensitize the low carbon grades of stainless steel.

The L grades have 5,000 psi (35 kPa) lower tensile and yield strength than the older 0.08% carbon grades, such as Types 304 (S30400), 316 (S31600), and 317 (S31700).

Many warehouses stock “dual certified grades.” Dual certified grades have 0.030% max. carbon and the tensile and yield strength of the older 0.08% max. carbon grades. Stainless steel mills achieve the higher strength for the low carbon grades by adding a small amount of nitrogen, about 0.05%. Dual certified grades are fully suitable for welded fabrication.

20.3 PASSIVATION

Passivation, a widely and often misused term, refers to the formation of the protective film that retards or prevents further corrosion. Stainless steels are auto-passivating in air. Passivation of stainless steels occurs spontaneously in air as stainless steel is removed from the pickling vat at the steel mill. The oxide film that forms almost instantly in air that makes stainless steel passive and gives stainless steel its outstanding corrosion resistance is a thin, adherent, chromium-iron-nickel oxide film. Chromium is the element providing the primary corrosion resistance. Molybdenum, when present, greatly improves resistance to pitting. Nitrogen, when present, also greatly improves resistance to pitting. The Cr-Fe-Ni oxide film that forms so readily in air makes stainless steel passive, i.e., resistant to corrosion in many media. Even when damaged during fabrication, the undamaged portion of the surface remains passive. As fabrication defects are removed, the film reforms beneath the defect as it is removed, restoring passivity at the defect site.

The words passive and passivation have several meanings. To metallurgists and corrosion engineers passive means “not actively corroding”. To other engineers concerned with fabrication and cleaning of stainless steels, passivation means cleaning in one or more of the nitric acids treatments described in ASTM A380 Table A2.1 Part II “Cleaning-passivation with Nitric Acid Solution”. Cleaning and removal of surface defects which many engineers think of as “passivation” is discussed in the Welding section of this bulletin and in the following subsection.
20.4 POST FABRICATION CLEANING

Most of the commonly encountered corrosion problems, in environments where that grade of stainless steel normally performs well, can be traced to incomplete or inadequate cleaning of the surface following fabrication. For best performance, it is essential to prevent or remove all fabrication related defects, such as arc strikes, weld spatter, scratches, gouges, heat tint scale, and embedded iron from all wetted surfaces after fabrication. The heavy cleaning required after fabrication may be done by blasting with various abrasives, by power brushing with aluminum oxide discs or flapper wheels, by pickling or by electropolishing.


Figure 20-1 Effect of Carbon on Carbide Precipitation

Time required for formation of carbide precipitation in stainless steels with various carbon contents. Carbide precipitation forms in the areas to the right of the various carbon-content curves. Within time-periods applicable to welding, chromium-nickel stainless steels with 0.05% carbon would be quite free from grain boundary precipitation.
Citric acid – EDTA chelating treatments for removal of embedded iron are covered in Table A2.1 Part III. Electropolishing is covered in ASTM A967, “Standard Specification for Chemical Passivation Treatments for Stainless Steel Parts”, but is not mentioned in ASTM A380. Both specifications state clearly that the nitric acid passivation treatments, while useful, are not suitable for the heavy cleaning required after fabrication. The nitric acid passivation treatments will enhance the corrosion resistance of stainless steel, provided the surface has already been properly cleaned. These nitric acid treatments are particularly effective for machined parts. The citric acid and EDTA chelating treatments are very effective in removing embedded iron, although they are not effective in removing the dark heat tint scale formed during welding.

Sandblasting has become the preferred method of post fabrication cleaning as pickling has been increasingly restricted by environmental regulations. Sandblasting is very effective in removing oxide scale left from annealing or stress relief treatments and heat tint oxide scale left from welding. However, sandblasting even using clean sand, once through leaves a residue of embedded iron in the sandblasted surface. The embedded iron left by sandblasting is easily detected by a water wetting test or by the ferroxyl test both described in ASTM A380. The residue of embedded iron will show up as dark spots and streaks on the surface. This residue of embedded iron may be unsightly cosmetically but is not necessarily harmful in services where the liquid being handled corrodes away the residual iron and cleans the surface. The residue of embedded iron can be very harmful in services where the residual iron will discolor the pulp, for example, the headbox of paper machines, or where the residual iron will cause problems with the liquid being handled. For example, residual iron cannot be tolerated on the surface of hydrogen peroxide towers as it accelerates decomposition of hydrogen peroxide.

There are other blasting media that leave little or no iron embedded in the surface; glass beads, walnut shells and similar materials. These media, especially glass beads, are widely used as alternatives to sand. Water wetting, as mentioned above, is a simple test to determine if embedded iron has been removed by these less aggressive blasting media.

To summarize then:
1. Sandblasting will remove oxide scale from heat treatment and stress relieving treatments and the heat tint from welding but leaves a residue of embedded iron.
2. The residue of embedded iron is unsightly cosmetically but not always harmful depending upon the service and prior experience.
3. Pickling and electropolishing are very effective in cleaning the surface and removing embedded iron.
4. Citric acid – EDTA chelating treatments are very effective in removing embedded iron but will not remove heat tint scale.
5. Nitric acid cleaning treatments are useful in removing free iron, that is lightly attached iron, and other foreign matter, but will not remove all embedded iron.
6. Nitric acid treatments are useful in enhancing the normal protective film on stainless steel surfaces that have been thoroughly cleaned.
7. Blasting with other media, such as glass beads and walnut shells, may remove heat tint scale and embedded iron without the need for pickling. The water test will show whether embedded iron has been completely removed by these milder blasting media.

20.5 CREVICE CORROSION, PITTING AND PREN

The oxide film, which gives stainless steel its outstanding corrosion resistance and renders it passive, can be penetrated locally in tight stationary crevices in environments that are not aggressive enough to corrode boldly exposed base plate. This type of corrosion is termed crevice corrosion.

Crevice corrosion occurs in tight stationary crevices when there are sufficient chlorides in the water. Crevices occur under gaskets at flanged joints, under washers at bolted joints, under stationary O rings, paint, crayon markings, adhesive tape and under sticky deposits. Generally accepted guidelines for waters at ambient temperature and pH 6.5–8.0 follow.
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- Up to 200 mg/l chlorides, crevice corrosion of Types 304/304L is rare.
- Up to 1000 mg/l chlorides, crevice corrosion of Types 316/316L is rare.
- Above 1000 mg/l chlorides, higher Mo content stainless steels may be required, if there is little tolerance for crevice corrosion. In many instances, some crevice corrosion can be tolerated and treated as routine maintenance.

Note that the chloride concentrations cited above are modified by the word “rare,” as crevice corrosion appears to be statistical in occurrence. For example, in the test program from which the guidelines cited were established, initiation of crevice corrosion occurred at one of 160 identical crevice sites on Type 316 in the test at 600 mg/l chlorides, but at no other of over 1000 identical sites in the test program. Further, Type 304 was resistant at 87.5 to 97.0% of over 500 identical test sites in the tests at 1000 mg/l chlorides. The guidelines are believed reasonable, but they are guidelines, not absolutes. At lower pHs, higher temperatures and in the presence of strong oxidizers such as residual chlorine, the tolerance for chlorides is lower. In the alkaline chemical recovery environment of kraft mills, the tolerance for chlorides may be somewhat higher. Sulphates are beneficial, especially when the sulphate/chloride ratio is greater than 1. Other chemical species present may also affect the tolerance for chlorides, although there is little useful data.

Pitting of boldly exposed base plate occurs in environments that are more aggressive than those where crevice corrosion occurs. While some crevice corrosion can often be tolerated and treated as maintenance, upgrading to more resistant materials is normally necessary when base plate pitting becomes a problem.

Relative pitting resistance in acidic chloride environments can be estimated from an alloy's composition using the formula: Cr + (3.3 x % Mo) + (16 x % N) = PREN, the pitting resistance equivalent number. PREN for 316L is 26.6 for the minimum Cr and Mo required by specifications. When pitting of clean base plate material occurs in acidic chloride environments, upgrading to alloys with a higher PREN is usually necessary. PREN for the minimum composition for stainless and nickel chromium alloys is given in the front of this bulletin in Table 2-2 for the wrought alloys and in Table 2-4 for the cast alloys.

While PREN is useful for estimating relative corrosion resistance in the acidic chloride environments of the bleach plant, it is not applicable, and may give misleading results, if applied to the alkaline environments of the digester and chemical recovery section of sulphate mills. In these alkaline environments, chromium content alone provides a rough, but useful, estimate of relative corrosion resistance.
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ASTM G48, “Standard Test Methods for Pitting and Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution,” also provides a common method of estimating relative resistance in acidic chloride environments. The rankings are generally reported as corrosion pitting temperature (CPT), the maximum temperature at which there was no pitting of boldly exposed base plate, and crevice corrosion pitting temperature (CCPT), the maximum temperature at which there was no crevice corrosion, in 6% ferric chloride solution. CCPT is nearly always lower than CPT, since crevice corrosion normally occurs in environments that are not aggressive enough to cause pitting of boldly exposed base plate. The rankings are similar to PREN ratings.

20.6 CORROSION DATA

Corrosion of carbon steel and copper base alloys is measured by determining the weight loss after exposure for a number of days. The weight loss is assumed to have occurred uniformly over the whole specimen and is reported as millimeters (mm) per year, or mils per year (mpy). For stainless steel, corrosion is so localized and weight loss so low in most exposures that assuming the weight loss occurred uniformly over the whole surface gives minuscule rates that are meaningless. Corrosion data for stainless steel is therefore customarily reported as the maximum depth of crevice corrosion, if corrosion occurred in a creviced area, and as the average and maximum depth of pitting, if the corrosion occurred on boldly exposed base plate. This characteristic corrosion behavior of stainless steel, which is also true of nickel base alloys, titanium and zirconium, makes comparative behavior more difficult to assess from field tests and has led to greater use of electrochemical methods. Electrochemical methods of evaluating corrosion resistance are covered in a number of texts. For further information see Reference 5, Chapter 3, pp. 66-121.

20.7 STRESS CORROSION CRACKING

In mills where the logs are floated in salt water, in chip steaming vessels, and externally under insulation, chloride stress corrosion cracking (chloride SCC) is a common problem for Types 304L, 316L, and even 317L. Chloride SCC is most likely to occur at temperatures above 65-70˚C (150-160˚F) and in areas of high residual stress, i.e., welds. The chloride concentration in the bulk solution is of little significance, as most chloride SCC occurs in locations where conditions favor concentration of whatever chlorides are present in the bulk environment. Type 904L, Alloy 20 (N08020), duplex alloys, 6% Mo austenitic stainless steels, and nickel base alloys have good resistance to chloride SCC and are preferred where chloride SCC is a problem. Resistance to chloride SCC increases in alloys with higher nickel content than Types 304L and 316L and in duplex and ferritic alloys with lower nickel content.

Type 304L tanks are replacing carbon steel and coated carbon steel tanks in the chemical recovery section of the mill. Type 316L towers are replacing acid brick lined towers in the bleach plants for the newer, less aggressive, bleaching processes being used as alternatives to chlorine bleaching. The outside of insulated stainless steel vessels, tanks, and piping out-of-doors may be subject to chloride SCC under insulation if the insulation becomes wet. Sealing the insulation so that rain and moisture are excluded will minimize the possibility of external chloride SCC under insulation. In difficult cases, painting the exterior of the stainless steel tank with an appropriate coating under the insulation can be quite effective.

Preventive measures are set forth in detail in NACE Standard RP0198-98 Item 21084, “Standard Recommended Practice – The Control of Corrosion Under Thermal Insulation and Fireproofing Materials,” available from NACE, P.O. Box 218340, Houston, Texas. Indoor insulated stainless steel tanks, vessels and piping are seldom subject to chloride SCC under insulation unless there is leakage from overhead lines or other equipment that drips on and wets the insulation.
20.8 INHIBITED HCL CLEANING

It is common practice to clean digester heat exchanger tubing, piping and digesters to remove carbonate and other deposited scales using acids. Inhibited hydrochloric acid is most frequently recommended and used by chemical cleaning contractors, as hydrochloric acid readily dissolves most carbonate and other common scales. Even when inhibited, hydrochloric acid is quite corrosive to stainless steels. There are two problems arising from inhibited hydrochloric acid cleaning. One problem is with the standard Type 304 welded heat exchanger tubing. Inhibited hydrochloric acid corrodes the ferrite phase normally present in small amounts in the longitudinal welds of welded heat exchanger tubing, unless the user had the foresight to specify that the tubing must be cold worked and annealed to convert the ferrite to austenite after the longitudinal weld is made. Cold working the weld to prevent corrosion of the weld is not a requirement of the most specifications for which tubing is normally purchased and sold. It can be included as an additional requirement by the purchaser, but seldom is. Weld corrosion from inhibited hydrochloric acid corrosion is a common mode of heat exchanger tubing failure and often results in tube replacement. With piping, especially in the larger sizes, conversion of the ferrite in the welds by cold work is more difficult and seldom done. However, scale buildup in piping is much less of a problem than scale buildup in heat exchanger tubing. HCl cleaning of piping is less frequently needed and seldom done.

Although Type 304 stainless steel tubing is the normal choice for new construction, upgrading to Alloy 20 (N08020), Alloy 825 (N08825), Alloy 600 (N06600), 6% Mo alloys, duplex and other more highly alloyed tubing materials is better practice despite the slightly higher cost. These grades are resistant to weld corrosion during hydrochloric acid cleaning and to stress corrosion cracking.

There is a second problem with inhibited hydrochloric acid cleaning. Unless washing after cleaning is thorough and removes “ALL” of the hydrochloric acid remaining in crevices, such as tube-to-tube sheet crevices, stress corrosion cracking may occur when the exchanger is returned to service and brought up to temperature.

Digesters are also cleaned to remove scale. Again inhibited hydrochloric acid is the agent preferred by the cleaning contractors. The inhibitor is usually effective in minimizing corrosion of carbon steel. However, many digesters are partially lined or fully lined with stainless steel. Crowe reports, “Hydrochloric acid is not recommended, even if inhibited, for cleaning stainless steel clad or weld overlaid digesters because it may
cause pitting and stress corrosion cracking.\textsuperscript{4} Formic acid provides a good alternative for acid cleaning of digesters. Sulphamic and nitric are other alternatives to formic for acid cleaning to remove scale.\textsuperscript{4}

20.9 MICROBIOLOGICALLY INFLUENCED CORROSION (MIC)

Paper machine white waters are an ideal environment for growth of bacteria and for microbiologically influenced corrosion (MIC). There are two approaches to controlling MIC.

1. Design and Post Fabrication Treatment: Electropolishing of the headboxes and approach piping reduces slime and hang-up of pulp fibres and attachment of pulp pads. Reducing recesses and requiring welds to be smooth enough to pass the cotton ball test in all parts of the white water circuit is very helpful. Frequent cleaning to remove pulp pads from dead areas is also helpful.

2. Biocide Addition: The addition of biocides to limit bacterial activity is useful in controlling bacterial activity in the bulk environment. However, scheduled cleaning is still necessary to remove pulp pads from dead areas, as bacterial activity may continue beneath adherent pulp pads even though the bulk environment is benign.

MIC can also occur during new construction when water used for hydrotesting tanks and piping is not drained promptly and is allowed to stand for extended periods of time. Draining promptly after hydrotesting is the obvious remedial measure.

20.10 CORROSION TESTING

When the current material of construction is experiencing greater corrosion than normal, or greater than expected, it is good practice to expose coupons of the current material of construction and candidate replacement alloys on a test rack. Exposure periods of at least 30 days, preferably 90 or 180 days, in the plant environment where unusual corrosion is occurring will normally provide reliable information on corrosion behaviour. The environment should be monitored during the test period as it is often upset conditions that lead to greater than usual corrosion. Alloys and test racks may be obtained from most metal suppliers; however, it is usually more convenient to obtain both alloy specimens and test rack hardware from test specimen suppliers. It is standard practice to include Type 316 on all test rack exposure as it provides a good benchmark in most mill services. It is also standard practice to include duplicate specimens of each alloy exposed. Alloys normally considered for upgrading in 5 major environments are listed in Table 20-1.

20.11 CAST ALLOYS

Cast alloys are expected to, and normally do, have corrosion resistance roughly equivalent to that of their wrought counterparts. There are, however, some exceptions that users should be aware of.

\textsuperscript{(1)} ASTM A743, which is the specification normally used for procurement of most cast stainless steels, does not require heat treatment after foundry weld
repairs. This leaves areas where routine foundry weld repairs have been made more susceptible to corrosion than elsewhere. When the application is in an aggressive environment that has caused localized corrosion near foundry weld repairs, ASTM A744, which requires heat treatment after all foundry weld repairs, can be used for procurement.

(2) ASTM A743 allows the common molybdenum-containing austenitic grades to be heat treated at 1900°F (1040°C), which is not high enough to homogenize molybdenum and obtain the added corrosion resistance expected. When unexpected corrosion occurs with the common grades containing molybdenum, or when the corrosion resistance of the cast grade must be equal to that of the wrought grades, procurement can include a requirement that CF-3M (J92800), CF-8M (J92900), CG-3M (J92999), and CG-8M (J93000) grades be heat treated at 2050°F (1120°C) minimum, as ASTM A743 requires for CN-7M (J94650) which has a similar molybdenum content.

(3) The standard ASTM specifications for cast alloys do not specify where the specimen used to measure carbon content is to be taken. In some environments, where it is known that higher carbon at the surface will lead to unnecessary corrosion, Supplementary Specification S23 in A744 can be used for procurement. S23 requires that the specimen for carbon be taken within 0.01 in. (0.25 mm) of the surface after scale removal.

(4) Although many foundries routinely remove scale formed during heat treatment, some do not. The scale formed during heat treatment is less corrosion resistant than base metal and has led to unnecessary corrosion. Scale removal can be required in procurement.

More detailed information on corrosion behaviour is provided by Jonsson, Reference 3, and by Aromaa and Klarin, Reference 5.
REFERENCES


   This paper deals with post fabrication cleanup, which is very important to the successful use of stainless steel.


   The chapter provides excellent and detailed information on the alloys and corrosion behaviour in nearly all paper mill environments.


# 21. Abbreviations

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Stainless Steels and Specialty Alloys for Pulp and Paper 144
# 21. Abbreviations

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