Influence of tube metallurgy on corrosion resistance of liquor heaters

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Liquor heater tubes of duplex stainless steels and Alloy 600 demonstrate improved resistance to stress corrosion cracking, but care in chemical cleaning is still required.

Digester liquor heaters maintain the temperature of the circulation cooking liquor in the pulp digestion process. Typical operating conditions for a unit in kraft pulping are 200°C (392°F) steam on the shell side and 150-170°C (302-338°F) cooking liquor in the tubes.

Carbon steel was originally used in this service but exhibited a very short life. Ferritic chromium stainless steels, such as American Iron and Steel Institute (AISI) Type 410 developed during the 1920s, provided an increase in service life and remained in use well into the 1950s. As the rate of production increased and the sulfidity rose, the rate of general corrosion also increased substantially for the ferritic chromium steels, resulting in reduced life. Furthermore, these tubes were sensitive to fatigue cracking in areas close to the tube sheets. The need for a steel with better resistance to general corrosion and fatigue was clearly indicated. Commercially available steels that met these requirements were the austenitic stainless steels of the 18Cr/8Ni variety, such as AISI Types 304 and 316.

Beginning in the late 1950s, there was a general switch to austenitic stainless steel for digester liquor heater tubes. Unfortunately, many mills found that these tubes also developed leaks in most cases, sometimes after very short service times. Subsequent analyses determined that the failures were due to a stress corrosion mechanism. Another common failure cause is acid cleaning for deposit removal.

Commonly used tube metallurgies

A number of different materials are used for the liquor heater tubes but the most common ones are listed in **Table I**. The table shows the common trade names and the corresponding UNS numbers.

The presently used materials fulfill to varying degrees the requirements for service as liquor heater tubes. In this discussion, properties of the materials are related to the different types of failure modes.

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Mechanical and physical properties

Material for liquor heater tubes should have low thermal expansion, high thermal conductivity, and high strength to stand up best in an environment where stress corrosion cracking could occur.

Table II shows that both Alloy 600 and the duplex steels have lower thermal expansion than AISI 304 and 316. The thermal conductivity is equal to AISI 304 and 316.

The duplex stainless steels have twice the yield strength of AISI 304 and 316 (**Table III**). For convenience, values are given in both newtons per square millimeter (N/mm^2) and kilopounds per square inch (ksi). The high tensile strength of the duplex steels also ensures high fatigue strength (**Fig. 1**). The liquor heater tubes might be subject to fatigue conditions close to the upper tube sheet where the hot steam meets the white liquor on the inside of the tubes.

Stress corrosion cracking

The main life-limiting factor at present for liquor heater tubes of AISI 304 and 316 stainless steel is stress corrosion cracking (SCC). Stress, high temperature, and chlorides are usually the cause of such cracking.

Stresses and high temperature always prevail in liquor heaters, but steam usually contains very small amounts of chloride. In the upper part of the inlet half, however, the conditions are conducive to concentration of the chlorides by evaporation. It has been found that cracking occurs in this area for the most part. The time necessary for a sufficient amount of chloride to accumulate varies from case to case. Time to cracking has ranged from a few months to, more generally, between two and five years.

If a leak occurs in a joint between tube and tube sheet, considerable amounts of chloride can reach the tubes. A minor liquor leak, if undetected, will be concentrated by evaporation.

To prevent SCC in liquor heaters, stainless steels with low nickel content (ferritic or duplex stainless steel) or high nickel alloys should be used.

Figure 2 shows the much better SCC resistance of a duplex stainless steel S 31803 (SAF 2205) than AISI 304L

I. Chemical composition of tube metallurgies, percentage by weight

Grade	UNS	Type	C_{max}	Si	Mn	Cr	Ni	Mo	N
AISI 304	S 30304	Austenitic	0.08	0.6	1.5	19	9	...	...
AISI 316	S 30316	Austenitic	0.08	0.6	1.5	17	12	2.5	...
Alloy 600	N 06600	Nickel base	0.05	0.3	0.5	16	75	...	...
3RE60	S 31500	Duplex	0.03	1.7	1.5	18.5	4.9	2.7	0.07
SAF 2205	S 31803	Duplex	0.03	0.8	1.5	22	5.5	3.0	0.14
SAF 2304	S 32304	Duplex	0.03	0.5	1.2	23	4	...	0.1

II. Thermal expansion per degree, mean values × 10^6

	Temperature, °C (°F)							
Grade	20-100	(68-200)	20-200	(68-400)	20-300	(68-600)	20-400	(68-800)
AISI 304 and 316	16.5	(9.0)	17.0	(9.5)	17.5	(9.8)	18.0	(10.0)
Alloy 600	12.5	(6.9)	13.0	(7.2)	13.5	(7.5)	14.0	(7.8)
S 31500	13.0	(7.0)	13.5	(7.5)	14.0	(7.8)	14.5	(8.0)
S 31803	13.0	(7.0)	13.5	(7.5)	14.0	(7.8)	14.5	(8.0)
S 32304	13.0	(7.0)	13.5	(7.5)	14.0	(7.8)	14.5	(8.0)

III. Mechanical properties at 20°C (68°F)

	Yield strength				Tensile strength			
	0.2% offset		1.0% offset					
Grade	N/mm² min	ksi min	N/mm² min	ksi min	N/mm²	ksi	Elongation in 2 in. or 50mm, min	Typical Vickers hardness value
AISI 304	210	30	240	34	500-700	73-100	45	155
AISI 316	220	32	250	36	500-700	73-100	45	160
Alloy 600	245	35	270	37.5	550-750	80-100	30	160
S 31500	450	65	500	73	700-900	101-131	30	260
S 31803	450	65	500	73	680-880	99-128	25	260
S 32304	400	58	450	65	600-820	87-119	25	230

and 316L.

Nickel-base alloys, such as Alloy 600, are known to have excellent SCC resistance.

Liquor corrosion resistance

In the past, AISI 410 steel had too low a resistance to white liquor corrosion, which caused short tube service life. All tube metallurgies used today have very good resistance to white liquor. Apart from the practical experience, there are laboratory data that clearly show the low corrosion rates. **Table IV** shows results of one test performed by INCO (*1*) for 68 days in the head of a liquor heater at a flow rate of 2400 gal/min.

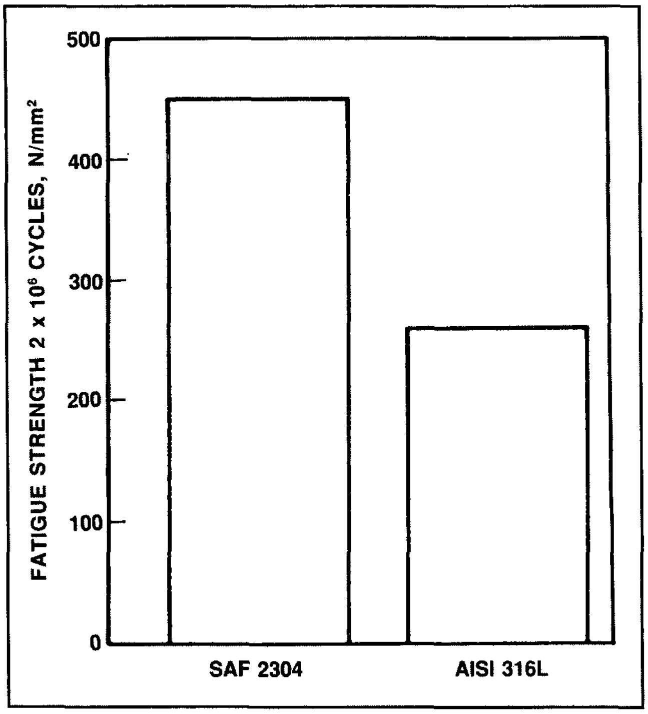
Another test was carried out by Sandvik (*2*) in a kraft white liquor with different duplex steels and AISI 316L at 225°C (437°F) for 336 h. The composition of the white liquor was: total alkali ($NaOH + Na_2CO_3 + Na_2S$), 176 g/L; active alkali ($NaOH + Na_2S$), 154.8 g/L; sulfidity ($Na_2S/NaOH + Na_2S$), 36.7.

Results are shown in **Table V**. In spite of the high test temperature, all steels showed low corrosion rates. However, S 32304 indicated the lowest corrosion rate. The reason for this is probably the high chromium content, the highest of all the tested steels. Molybdenum has little influence on corrosion resistance in white liquor.

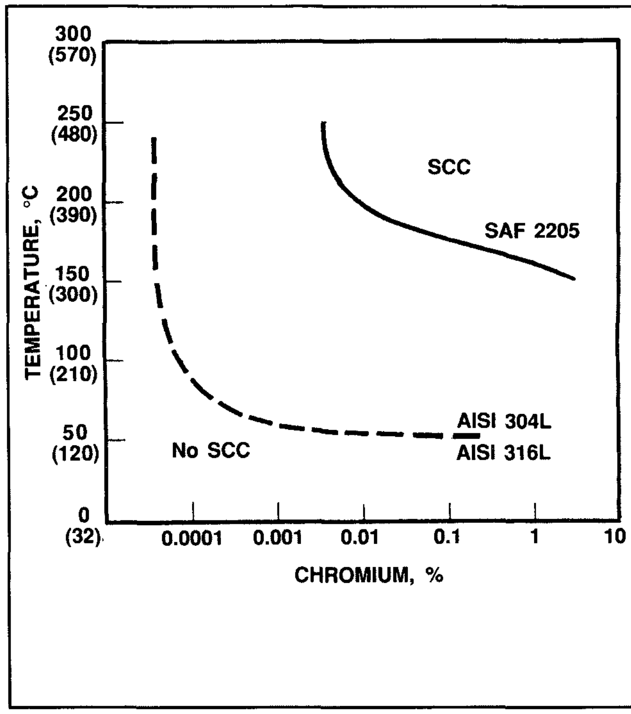
Cleaning of liquor heater tubes

Unfortunately, liquor heater tubes frequently have to be cleaned from deposits of salts. These salts of calcium carbonate or calcium sulfate are extremely difficult to dissolve. Without considering the background for the formation of the deposits, the deposits must be removed to reestablish proper heat transfer from steam to liquor. Mechanical cleaning (drilling of the tubes through one tube sheet), high-pressure waterjetting (350 bar), or chemical cleaning are means for deposit removal. Chemical cleaning, i.e., acid cleaning, is the most common because it is easiest to apply. Hydrochloric acid (muriatic

1. Results of fatigue strength tests of SAF 2304 and AISI 316L with reversed bending stress at room temperature



2. Laboratory results for resistance to stress corrosion cracking of a duplex stainless steel, AISI 304L, and AISI 316L



IV. White liquor corrosion test at 173°C (344°F)

Grade	*Corrosion rate, mils/year*
AISI 304	0.5
AISI 316	0.8
Alloy 600	0.9

V. Corrosion rates in white liquor at 225°C

	Composition, %			*Corrosion rate,*
Grade	*Cr*	*Ni*	*Mo*	*mm/year*
AISI 316L	17	13.0	2.2	0.044
S 31803	22	5.5	3.0	0.017
S 31500	18	4.9	2.7	0.045
S 32304	23	4.0	...	0.010

acid) is the favored acid.

If stress corrosion cracking is the most common cause of failure for AISI 304 and 316 liquor heater tubes, acid cleaning with hydrochloride acid probably is the second most common cause. The reason is most likely the lack of knowledge of the corrosivity of the acids and how to apply these acids properly for deposit removal without corrosion damage of the liquor heater tubes.

Hydrochloric acid may rapidly corrode through the liquor heater tube wall if the temperature is high and the acid is not inhibited.

INCO tests (*3*) show that Alloy 600 corrodes substantially at elevated temperature in hydrochloric acid saturated with air (**Table VI**).

Stainless steels can be used only at low concentration of hydrochloric acid solutions (**Fig. 3 and Table VII**).

In spite of the high corrosion rates of common metallurgies for liquor heater tubes, hydrochloric acid cleaning can be used if the acid is properly inhibited and strict temperature control is maintained.

The effect of inhibitors on the hydrochloric acid corrosivity was investigated by the Swedish Corrosion Institute (*4*), and roughly a tenfold decrease was found (**Table VIII**).

Thus, hydrochloric acid cleaning can be performed if proper inhibitors are used and the temperature is maintained below the upper temperature limit of the inhibitor.

Phosphoric acid concentrations of 5-10% at temperatures of 60-70°C (140-158°F) and sulphamic acid (NH_2SO_3H) concentrations of 2-6% at temperatures of 60-80°C (140-170°F) can also be utilized for chemical cleaning without any addition of inhibitors. If these two acids are used, there is little, if any, risk for corrosion attack of the liquor heater tubes.

Service experience

Ever since the first stress corrosion cracking failure of AISI 304 liquor heater tubes was noted, new materials have been considered. Today hundreds of liquor heaters are equipped

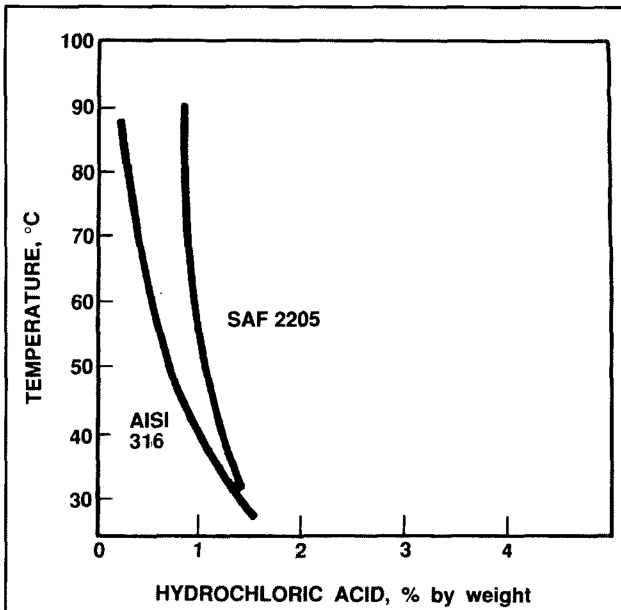
VI. Corrosion test of Alloy 600 in hydrochloric acid

Conc., %	Temperature °C	Temperature °F	Duration	Velocity, ft/min	Corrosion rate mils/year	Corrosion rate mm/year
5	30	86	20 hours	16.5	97	2.5
5.9	30	86	5 days	Quiet	45	1.1
5	85	185	20 hours	16.5	1950	49.5
5.9	80	176	5 days	Quiet	710	18.0

VII. Corrosion rates in hydrochloric acid, tested at 40°C (104°F) for 1 + 3 + 3 days on activated specimens, mm/year (mils/year)

Grade	Concentration, % 0.5	Concentration, % 1.0
AISI 316	0	0.7 (27.6)
S 31500	0	0.6 (23.8)
S 31803	0	0
S 32304	0	0.3 (12)

3. Isocorrosion diagram in hydrochloric acid, 0.1 mm/year (4 mils/year).



VIII. Corrosion rates in inhibited hydrochloric acid for test duration of 24 h

HCl concentration, %	Temperature °C	Temperature °F	Inhibitor	Inhibitor concentration, %	Corrosion rate AISI 304 mm/year	Corrosion rate AISI 304 mils/year	Corrosion rate AISI 316 mm/year	Corrosion rate AISI 316 mils/year
5	75	167			11.4	499	2.3	90
5	75	167	Rodine 213	0.2	1.1	45	1.1	45
10	50	122			11.4	449	2.3	90
10	50	122	Rodine 213	0.2	1.1	45	1.1	45

with duplex stainless steels and Alloy 600 tubes.

Since the mid-1960s, the duplex stainless steel S 31500 has been installed in 200 plants all over the world.

The later developments, S 31803 and S 32304, have been installed in a number of units in Canada and the United States, as well as in Scandinavian countries. The following examples are typical cases from U.S. pulp mills.

In one plant, S 32304 is being used constantly to replace AISI 316 tubes in old liquor heaters. The AISI 316 tubes fail from stress corrosion cracking at the hot steam end of the liquor heater.

In another plant, welded AISI 304 liquor heater tubes repeatedly showed stress corrosion cracks in the welds. Seamless S 31803 tubes were recently installed.

In at least one case where S 32304 is used for evaporator tubes, regular chemical cleaning with muriatic acid (hydrochloric acid), with inhibitor, is carried out. The tubes have operated for many years without any trouble.

Summary

Duplex stainless steels and Alloy 600 tubes can solve corrosion problems that occur when liquor heater tubes are made of AISI 304 or 316. These newer materials have:

- High resistance to stress corrosion cracking
- Better mechanical and physical properties (mainly the duplex stainless steels)
- Somewhat better general resistance to corrosion.

Chemical cleaning of liquor heater tubes should be carried out with caution. If hydrochloric acid is used, inhibition must be done.□

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