

LONG TERM EXPERIENCES OF THE USE OF DUPLEX STAINLESS STEEL TO COMBAT CORROSION IN THE PULP AND PAPER INDUSTRY

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ABSTRACT

Duplex (austenitic/ferritic) stainless steels offer properties of interest and a cost effective material selection solution for plant and equipment in the pulp and paper industry. The characteristics of duplex steels leading to successful long term applications of 22 Cr duplex and a copper containing 25 Cr super duplex stainless steel are reviewed. It is concluded that, applied correctly, two-phase stainless steels can provide long term reliable maintenance-free service in many pulp and paper plant environments.

Keywords: Duplex stainless steel, super duplex steel, duplex steel-copper containing, high strength stainless steel, acid corrosion, pitting corrosion, abrasion/erosion, stress corrosion, fatigue, pulp and paper.

INTRODUCTION

A wide range of materials, both metallic and non-metallic, are employed to contain the corrosive/abrasive chemical environments in the pulp and paper industry. Metallic materials in use include carbon steel, 300 series austenitic stainless steel, high nickel super austenitic steels, duplex stainless steels, nickel base alloys and titanium. Corrosion is potentially a severe problem in the pulp and paper industry, due to the large quantities of corrosive chemicals employed in processing and the presence of chlorides from seawater, resulting from log transportation and storage, and many other

sources. In addition to general corrosion resistance, an alloy to be used for equipment construction must, depending upon the specific duty involved, be capable of resisting localised corrosion (pitting and crevice corrosion), stress corrosion cracking, corrosion fatigue and metal loss due to wear/abrasion/cavitation erosion. Mechanical strength/ductility must be sufficiently high and fabricability/weldability good to enable reliable, low maintenance equipment to be produced. Underlying the foregoing requirements, is the need for cost effective materials with attractive life cycle costings.

It is of great benefit if a designer/materials engineer can select a material type which will provide a material selection solution for a wide range of operating conditions and with good cost/life in the plant for which they have responsibility. Duplex (austenitic/ ferritic) steels provide such a material type. The 22 Cr duplex materials possess an attractive combination of properties for the pulp and paper industry; however, at slightly greater cost a 25 Cr super duplex material, such as FERRALIUM⁽¹⁾ alloy (UNS S32550), the performance of which is discussed in this paper, offers still higher mechanical strength and corrosion resistance to acid conditions and pitting/crevice corrosion in chloride environments.

It is important that any alloy type selected is available in a range of forms to enable effective design of complex systems and equipment. Duplex stainless steels are readily available as bar, forgings, pipe, sheet/plate, flanges, fittings, castings and welding consumables.

To an extent duplex stainless steels have been employed in the pulp and paper industry since the 1960's, but it was not until the early 1980's that the features and benefits of duplex, and particularly the copper containing super duplex (UNS S32550), started to be taken advantage of in the industry.

PROPERTIES OF DUPLEX STAINLESS

Duplex stainless steel, like austenitic steel, is not a unique material, but comprises a range of alloys of various compositions, but all containing roughly 50% of austenite dispersed as islands in a ferrite matrix. The ferrite matrix imparts high strength and erosion resistance, the austenite imparts ductility, and the duplex structure is beneficial to weldability compared with fully ferritic or fully austenitic steels. The corrosion resistance in a particular medium depends on the composition and also on the partitioning of the elements between the two phases.

Selection of a duplex structured stainless steel is per se a positive step in providing a material with greater resistance to stress corrosion cracking than the 300 series austenitic materials. This is due to the ferritic matrix of the duplex steel. The duplex structure also results in greater mechanical strength compared with a fully austenitic structure. Relatively low alloy content duplex steels, for example, UNS S32304 (Table 1), provide these benefits over 300 series steels and with general corrosion resistance of a similar order. The higher alloy content of 22 Cr duplex material (UNS S31803) provides better resistance to acid, pitting and crevice corrosion than types 316 and 317 steel by virtue of a more stable passive film. Material of this type offers a good material selection solution for a variety of pulp and paper plant equipment. However, if optimum resistance to corrosion is needed, a 25 Cr high alloy duplex steel may be necessary. Alloys of this type are often referred to as "super duplex steels." Super duplex material possesses corrosion resistance which extends the range

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of conditions in which stainless steels can be successfully employed before there is a need to consider the use of more costly nickel base alloys.

Super duplex materials such as UNS S32550 and S32750 are sometimes characterised as steels with a pitting resistance equivalent (PRE_n)⁽²⁾ >40. PRE_n numbers, which serve as a guide to pitting resistance, for several duplex steels, appear at the end of the section on laboratory and field testing. These PRE_n numbers may be compared with typical PRE_n numbers for type 316 at 29 and super austenitic at 28 to 43 (this number is very dependent upon the molybdenum content, which can range from 3 up to 6% [UNS S31254] and greater, and whether nitrogen is present or not).

It is important to select the correct grade of material, even within the super duplex category, for optimum corrosion resistance, versatility in handling a wide range of corrosive media and for confidence that the alloy will cope with any 'excursions' or transient operating conditions which make the environment more aggressive. Although 25 Cr super duplex steels extend the suite of duplex materials available for the selection, and allow materials engineers within the pulp and paper industry to select stainless steel for arduous duties, they do not represent a total material selection solution. All material types must be chosen with full recognition of not only their strengths, but also their limitations. Duplex and super duplex steels are no exception and have a limit to their acid corrosion resistance (see Figure 1) and safe temperature for use in chloride and acid chloride environments (see reference to ASTM G-48 testing below). Stainless steels are not often used in halogen acids - although UNS S32550 duplex can be used in HCl to the boiling point up to 1% (weight) concentration, at greater acid concentrations the maximum temperature at which an acceptable rate of corrosion (0.1 to 0.5 mm yr^{-1}) still obtains reduces rapidly and soon reaches 40°C and below. The upper limit on temperature for long term use of duplex steels and particularly super duplex alloys is 275°C , to ensure that no microstructural changes occur which could deleteriously affect ductility and, at higher temperatures, corrosion resistance. Account must be taken that the high chromium duplex steels can form deleterious precipitates and sigma phase after shorter periods at temperature, compared with the time at the same temperature for 22 Cr duplex steels. Due care must be taken to weld duplex materials with correct procedures - these procedures are not complex and highly corrosion resistant welds in high and low alloy duplex steels can be produced.

There is general acceptance that chromium, molybdenum and nitrogen increase the resistance to pitting in chloride environments. In more critical conditions, additions of copper provide major improvements to both corrosion and erosion resistance. Thus crevice corrosion tests carried out for the U.S.Navy on a large number of nickel-base alloys and stainless steels indicated that copper was beneficial in reducing the breakdown of oxide films on 25 Cr duplex steel.² Garfias-Mesias, Sykes and Tuck have demonstrated that copper is useful in improving the pitting resistance of 25 Cr duplex steel in 1M HCl and 3.5% NaCl³. These workers conclude that in 1M HCl at 65°C the current density in the active state was 2 to 3 times smaller for a high copper (1.62% Cu) 25 Cr duplex, when compared with a similar alloy containing nil copper (0.075% Cu). In addition, the pitting potential of the nil Cu alloy and a low copper (0.56% Cu) alloy above the CPT (critical pitting temperature) in 1M HCl was significantly lower than the value showed for the high copper alloy.

⁽²⁾ PRE_n numbers, usually based upon $\text{Cr \%} + 3.3 \text{ Mo \%} + 16 \text{ N \%}$, provide a ranking of stainless steels and an indication of relative resistance to pitting in chloride environments,¹ with particular reference to seawater service. A term of + 0.5 Cu % has been proposed by the author's company for inclusion in the PRE_n calculation. Care must be exercised when using PRE_n numbers to rank materials, an alloy microstructure free from deleterious precipitates is required, as well as a high alloy content, to provide high resistance to localised corrosion.

They further conclude that the enhanced performance of the high copper alloy in acid chloride environments can help to explain the pitting behaviour of the alloy; since the pit environment is acidic, the repassivation of incipient pits will be more easily achieved for the high copper alloy, in contrast with the nil copper alloy which would be more susceptible to stable pitting.

Guha and Clark⁴ studied the effect of copper on the corrosion resistance of UNS S32550 in sulphuric acid environments. They found that 1.5% Cu in the 25Cr duplex steel and 1% Cu in a 28 Cr duplex steel is required to confer optimum corrosion resistance. Simpson⁵ demonstrated synergy between copper and nitrogen in promoting corrosion resistance of duplex steels in sulphuric acid. He concluded that in sulphuric acid containing chloride ions the effect of copper or nitrogen alone is insufficient for optimum improvement in corrosion resistance, although copper alone will improve the corrosion resistance of the ferritic phase. Nitrogen is ineffective when added without copper.

The resistance to sulphuric acid of the 25 Cr super duplex material typically containing 1.7% copper (UNS S32550) is shown in Figure 1. A comparison is made with high nickel super austenitic (UNS N08904), 25 Cr super duplex with very low copper (UNS S32750)⁶, 22 Cr duplex (UNS S31803)⁶ and type 316 stainless steel. Material to UNS S32550 exhibits a low rate corrosion over a much wider range of concentrations and temperatures, compared with the other alloys. The chemical compositions of UNS S31803, S32550 and S32750 are given in Table 1.

25 Cr super duplex provides high resistance to pitting and crevice corrosion in seawater environments and other chloride media. The critical pitting potential in the aggressive FeCl₃ (pH 1) conditions of the ASTM G-48 Method A test is 40 to 50°C for UNS S32550, compared with 20°C for 22 Cr duplex (UNS S31803) and 0°C for type 316 steel.

The superior resistance of UNS S32550 (compared with several other duplex stainless steels) to acids and chloride environments is clearly shown in reference 7, which presents a practical guide to using duplex stainless steels.

The abrasion and cavitation-erosion resistance of UNS S32550 is good and superior to standard and high alloy austenitic steels and other duplex stainless steels. Figure 2 compares the cavitation erosion resistance of the 25 Cr super duplex steel with 22 Cr duplex, type 316L and type 317L austenitic steel. This good resistance is valuable when considering a material for the construction of items such as cyclone target plates and digester strainer plates.

Two phase corrosion resistant alloys in general provide good resistance to fatigue in air and corrosive environments. Cast and wrought forms of the 25 Cr duplex possess high fatigue limits; the figures in air and 3% NaCl are shown in Figure 3.

The opportunity to reduce wall/section thickness, save weight and lower cost by purchasing less material resulting from the selection of 25 Cr super duplex is most attractive. Allowable design stresses for UNS S32550 and several other alloys are given in Table 2.

The fabricability and weldability of super duplex stainless steel is good. The availability of a wide range of product forms - bar, forgings, plate, pipe and castings (static and centrifugal) provide the pulp and paper equipment designer with scope to design using forms best economically suited to the equipment shape involved.

LABORATORY AND FIELD TESTING

Numerous laboratory and field tests in environments that relate to the pulp and paper industry have been carried out to investigate the relative resistance of different candidate alloys to general and selective corrosion attack and to abrasion and erosion. This testing has clearly demonstrated the superior performance of super duplex UNS S32550 over standard austenitic steels, and in some cases the high nickel super austenitic steels⁸⁻¹⁵. The ranking obtained in various laboratory tests¹⁶ has generally also been found in field test experience¹⁵. Manning^{16, 17, 18} has clearly shown the advantages of using super duplex UNS S32550 for solving maintenance problems in the pulp and paper industry.

Other testing¹⁶ undertaken to compare UNS S32550 duplex with other alloys commonly used in pulp and paper mills, such as carbon steel and austenitic and high nickel super austenitic steels, has shown a greater resistance to corrosion and abrasion for the duplex material. The laboratory testing conducted in environments that relate to pulp and paper applications and including general corrosion, selective corrosion and abrasion/ corrosion tests are considered to be relevant to service experience with the various alloys in the industry.

A test programme was carried out by a pulp and paper company¹⁹ to assess candidate materials to line a pulp mill hog fuel dryer. Serious corrosion problems had been encountered with carbon steel vessels and the lifting vanes used to dry bark and wood waste (hog fuel) to be burned in power boilers. The corrosion was due to chlorides resulting from the transportation and storage of the pulp logs in seawater. Test lifters in UNS S32550 and austenitic (including super austenitic) alloys were evaluated. The super duplex steel was the only material not to suffer general, pitting, crevice or stress corrosion - even more costly high nickel austenitic steels suffered some corrosion. The super duplex was selected and good service experience has been obtained, as described later.

The same pulp and paper company¹⁹ have carried out a series of corrosion coupon tests over a decade in a chloride dioxide (ClO_2) washer vat environment known to be aggressive to virtually all stainless steels. Sixteen duplex and super duplex steels have been tested, along with austenitic, high nickel austenitic and nickel base alloys^{20,21} 23 Cr, 4 Ni duplexes (UNS S32304) with PREN value around 25 showed the greatest crevice corrosion depth, with 22 Cr, 5Ni duplexes (UNS S31803) with PREN 33.3 to 34.3, exhibiting less corrosion attack, and 25 Cr, 6 Ni super duplex (UNS S32550 and UNS S32750) with PREN 38.6 to over 40, showing least corrosion. In this work the various crevice corrosion resistance alloy types are compared by normalising the multi crevice corrosion data relative to type 317L.

PERFORMANCE HISTORY OF DUPLEX AND SUPER DUPLEX STAINLESS STEELS

22 Cr Duplex Steel

Plate roll clad with UNS S31803 duplex steel has been given over four years of service, with no appreciable corrosion when used to fabricate 2 m diameter by 9m long chip presteaming vessels for Kraft continuous digestors¹⁹. This vessel replaced a carbon steel vessel, in which a type 316L patch had exhibited severe corrosion attack in only one year. This corrosion problem in a coastal mill arose from the use of wood chips from logs transported by sea. Other corrosive media are wood

acids released in the steaming process. The use of clad plate allowed the superior corrosion, abrasion and stress corrosion resistance of the duplex steel to be utilised on the process side and the beneath-insulation stress corrosion cracking resistance of the carbon steel on the outside.

A severely corroded austenitic stainless steel liner in a chip presteaming vessel in a coastal mill was replaced with 22 Cr duplex steel plate. After one year, the duplex plate showed some under-deposit corrosion in areas not swept clean by the moving chip mass. 25 Cr super duplex stainless steel may provide better service in this environment, due to a greater resistance to crevice corrosion attack.

Rotovanes for a fluffer/mixer which rotate at 1800 rpm to mix hydrogen peroxide solution with dewatered groundwood pulp have given good service in 22 Cr duplex steel¹⁹. The environment is pH 9 to 10, 60°C, 200 ppm NaCl. After two months' service, rotovanes in austenitic stainless steel SIS 2343 failed, due to cavitation. Replacement vanes in 22 Cr duplex steel have operated without any problem reported for over six years.

22 Cr duplex steel (UNS S31803) was employed to replace carbon steel, which had been used in the construction of an uninsulated hot stack associated with a precipitator and hog fuel dryer unit²². The original carbon steel hot stack failed after about four years of service. Thinning to failure of the 0.125 inch thick 22 Cr duplex resulting from dew point corrosion occurred within 8 to 9 years, depending upon the position in the stack. Pronounced plate thinning occurred near welds to the duplex steel stiffening angles. This was attributed to the promotion of acid condensation by the action of the stiffening angles as heat sinks. Outside stack surface temperatures as low as 70°C were measured while the hog fuel dryers were being partially bypassed. It appears that condensing acid produces a very corrosive environment in the presence of chlorides in the flue gas from burning of hog fuel and secondary treatment sludge. Preferential corrosion of the ferrite phase occurred. Similar corrosion attack was found in a piece of severely corroded 22 Cr duplex steel removed from the floor underneath the system cold stack after only 14 months of service. Metallographic examination did not show any preferential corrosion of weld HAZ in the duplex steel. In this case, the dew point environment was too aggressive for 22 Cr duplex. The hot stack wall temperature was in practice much lower than was anticipated during original installation.

25 Cr Duplex Steel

Corrosion testing, referred to in the previous section, resulted in the selection of alloy 255 super duplex (UNS S32550) for the lining and lifting vanes in rotary dryers for hog fuel. The bark/hog fuel from sea-borne logs is passed through rotary cylindrical dryers, where tumbling improves contact with the flue gas. The dryers and their extensive internal systems of lifting vanes were originally constructed from carbon steel. Severe metal loss, due to corrosion, occurred immediately from start-up, producing fatigue failures of lifters within six months. The dryers in 25 Cr duplex steel were installed during the mid 1980's (Figure 4) and after nearly ten years there are no reported problems of corrosion or cracking²².

25 Cr duplex steel was selected for use at a sulphite mill as a target plate for a cyclone in which liquor and digested pulp at high pressure and temperature is separated. Severe wear/corrosion had occurred on a type 316L stainless steel target plate, which lasted only six months. The 25 Cr duplex steel target plate provided thirty months' service, thus giving five times the life of 316L stainless steel. At another Kraft mill, in a similar application, the life of a duplex steel plate has

exceeded that of type 316L by over six times. The longer life for the 25 Cr duplex material would be predicted by the abrasion, abrasive slurry, corrosive slurry abrasion and corrosive slurry erosion tests carried out by Manning et al¹⁶. In a mildly corrosive slurry erosion test conducted in a mild acid chloride environment with 150 g of wood chips per litre of solution, 20 g of 400 mesh SiO₂ flour per litre of solution, and a high peripheral velocity (3.99 m/s). UNS S32550 exhibited a metal volume loss approximately one quarter that measured for type 316L steel.

A recovery furnace fan housing scroll fabricated in type 316L and 317L stainless steel used to last six months and twelve to eighteen months respectively, the mode of attack being severe corrosion/erosion. Part of the inner surface of the housing was lined with ¼ inch thick UNS S32550 plate to combat the corrosion attack from moist flue gases containing SO₂ and SO₃, chlorides and organics and abrasion from particulates. After more than five years, the super duplex was still performing well.

Digester strainer plates used to filter out wood fibres from cooking liquor have been produced in the copper-containing 25 Cr duplex alloy. These strainer plates, installed in a sulphite mill, have resisted attack from low pH cooking liquor (containing SO₂ and a high chloride content from log storage in salt water) for over three years. Originally type 316 steel lasted only six months and trials with titanium did not provide any improvement in corrosion/erosion resistance. The high strength and resistance to corrosion/erosion of duplex alloy allowed the re-design of the plates with more holes, which speeds up the filtration process, making it more efficient.

In several mills, the agitator shafts in chlorination towers have been fabricated from 25 Cr duplex steel and perform well. The high fatigue resistance of the alloy is utilised in this type of application. At one sulphite mill UNS S32550 bolts were used to couple together agitator shaft sections in a blow tank for pulp storage. Type 316 steel bolts give only one to two years' life - they loosen, due to vibration, corrosion and erosion and eventually fail, due to galling/seizure as a result of continued tightening during shutdown periods. Replacement bolts in 25 Cr duplex provide over four years' life.

An 8 inch type 317L stainless steel pipe used as a Kraft mill ClO₂ bleach washer line failed within two years, due to pitting corrosion. Replacement pipe in 25 Cr duplex (UNS S32550) performed well for over six years. This good performance would be predicted by the corrosion tests carried out in a chlorine dioxide washer vat environment¹⁹.

PROBLEM SOLVING IN THE PULP AND PAPER INDUSTRY

A guide to material service problem-solving in the pulp and paper industry is presented below.

EQUIPMENT/COMPONENT	TYPICAL SERVICE PROBLEM	MATERIAL SELECTION FOR PROBABLE SOLUTION
Pump/Valve	Pitting of CF-8M or CF-3M (PRE _n 29)	Higher PRE _n material
	General acid corrosion of 300 series steel	Super duplex with Cu
	Erosion damage of 300 series steel	Duplex or super duplex with higher hardness
Digester Strainer Plate	Corrosion/erosion of type 316 steel	Duplex or super duplex with higher hardness/corrosion resistance
Mixer/Agitator	Fatigue of type 316 shaft	Duplex or super duplex with greater fatigue resistance.
	Corrosion/erosion and loosening of bolts in type 316	Duplex or super duplex with higher corrosion resistance and hardness
Cyclone target Plate	Wear/corrosion of type 316L	Duplex or super duplex with higher corrosion resistance and hardness
Fan	Corrosion/erosion of furnace fan housing in type 316L/317L (attack by moist flue gases and particulates)	25Cr duplex steel with adequate corrosion resistance and higher hardness
Rotary Dryer	Corrosion of hog fuel dryer body and corrosion/fatigue of lifters in carbon steel due to chlorides in flue gas	Corrosion resistant steel - duplex stainless steel is a contender
Chlorine dioxide washers	Pitting of 317L	Higher PRE _n material
Presteaming Vessel	Corrosion of carbon steel and type 316L by chloride from seaborne logs and wood acids	Higher PRE _n material

CONCLUSIONS

Duplex (austenitic/ferritic) stainless steels have an important role to play in the fabrication of cost effective equipment for the pulp and paper production.

The properties of 22 Cr duplex (UNS S31803) can be utilised to advantage in providing longer, reliable service than carbon steel and austenitic stainless steel.

25 Cr super duplex (UNS S32550) containing copper can provide long term solutions to material selection as an alternative to austenitic stainless steels.

Laboratory testing in appropriate environments gives a useful ranking of materials for pulp and paper applications which relate to service experience, but results must be interpreted with care.

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TABLE 1

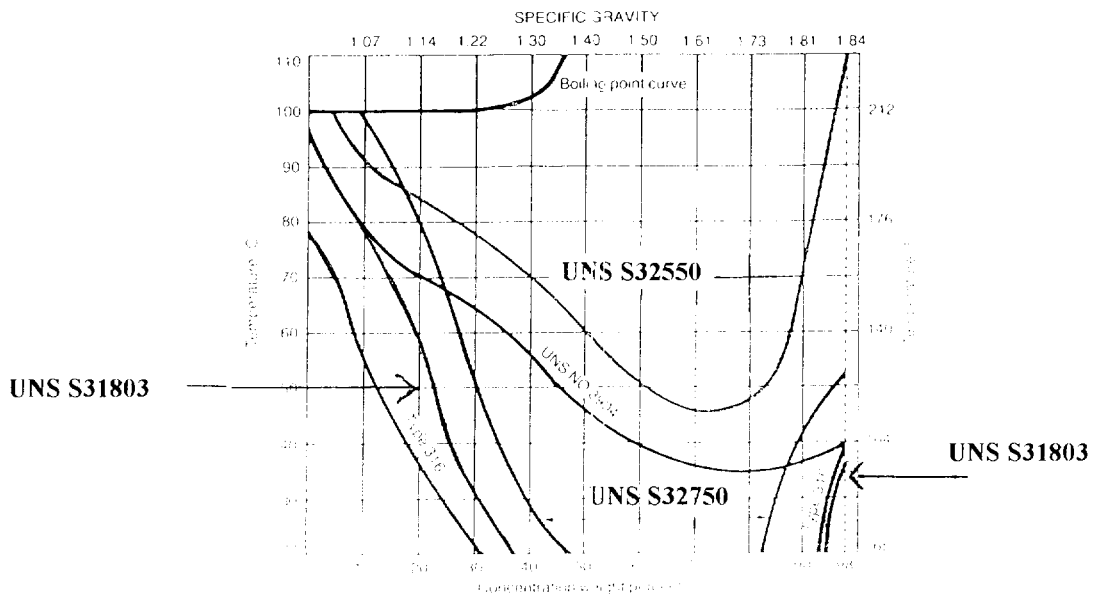
Chemical Compositions of Duplex Stainless Steels (wt.%)

UNS Number	Cr	Mo	Ni	Cu	C (max)	N
S32304	23	-	4	-	0.03	0.12
S31803	22	3	5	-	0.03	0.16
S32550	25	3	6	1.7	0.03	0.26
S32750	25	4	7	-	0.03	0.28

TABLE 2

**Allowable Design Stresses to ASME Section VIII
(up to 38°C - N/mm²)**

UNS NUMBER	ALLOY TYPE	
S32550	Super Duplex	190
N06022	Nickel Base	172
S31803	Duplex	155
N08020	Super Austenitic	137
S31603	Austenitic	115



**FIGURE 1 - Resistance of various alloys to sulphuric acid
(based on 0.1mm yr^{-1} maximum corrosion rate below the curve)**

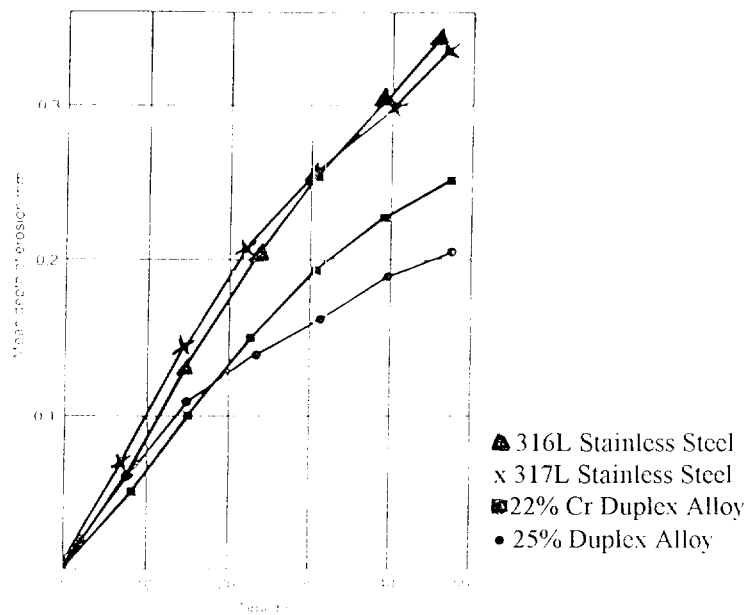


FIGURE 2 - Comparative Resistance to cavitation erosion

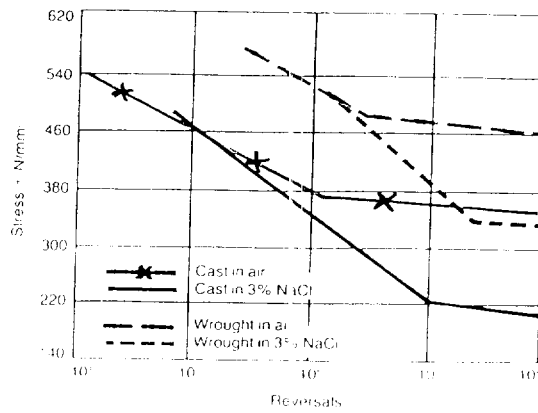


FIGURE 3 - Resistance of wrought super duplex (UNS S32550) and cast super duplex (UNS J94040*) to fatigue and corrosion fatigue
 *Awaiting final ratification

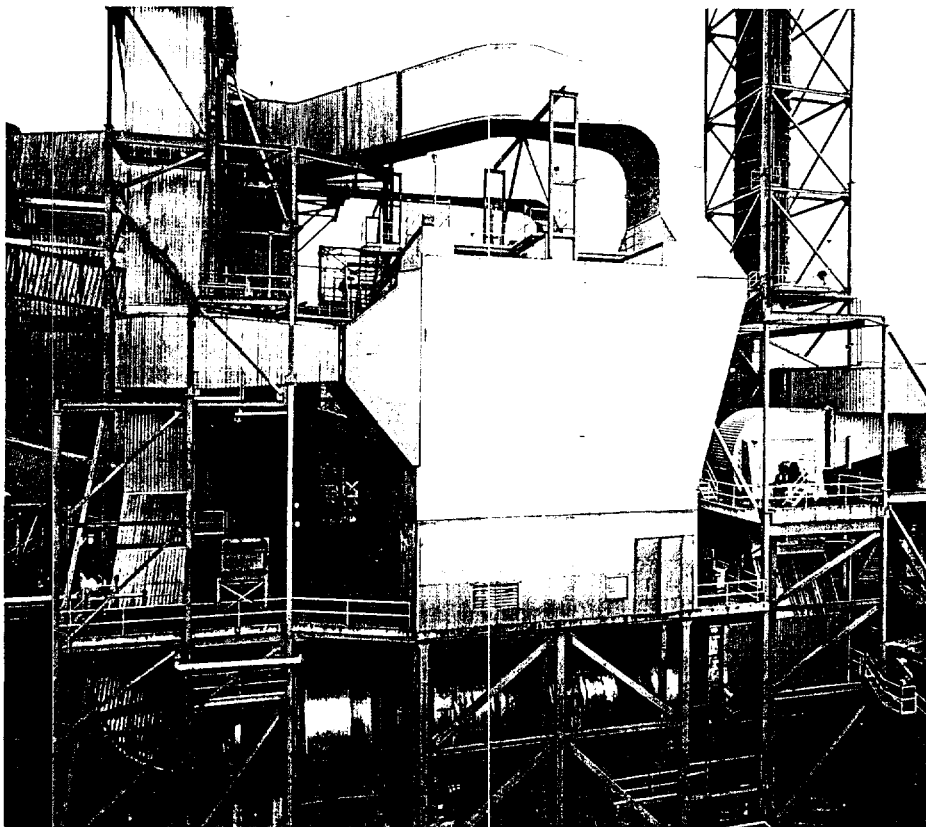


FIGURE 4 - Hog fuel dryer lined with super duplex stainless steel