UNS S32760 Super Duplex Stainless Steel for Wet FGD Air Pollution Control Systems

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ABSTRACT

Duplex stainless steels have been used extensively for wet flue gas desulfurization systems due to their high strength and good resistance to high chloride environments. Duplex stainless steels have inherently lower nickel content than their austenitic counterparts, and therefore, offer lower and more stable raw material prices. Super duplex stainless steels, such as S32760, are often used in higher chloride environments as an upgrade over 2205. S32760, commercially known as Zeron® 100, is a super duplex stainless steel with excellent corrosion resistance to high chloride environments, superior strength to superaustenitic and nickel based alloys, as well as being very cost effective to high nickel materials of construction. This paper will discuss the applications and uses of S32760 super duplex stainless steel in wet FGD systems. Corrosion comparisons of S32760 to other high nickel bearing alloys in high chloride and bromide environments as well as certain acid environments will be presented.

S32760 alloy has proven to be a cost effective material of construction that fills the gap between the lower alloyed duplex stainless steels, such as 2205, and the 6Mo alloys. As S32760 alloy is an established material of construction, it is readily available in product forms necessary to complete an FGD or WESP system.

KEY WORDS

Super duplex, FGD, WESP, Flue Gas Desulfurization, Corrosion, Pollution Control

INTRODUCTION

Combustion of coal generates NO~~x~~$_x$, SO_2, particulates, and other pollutants that contaminate the environment. Pollution control legislation by governments across the globe has mandated a significant reduction in emissions from these power plants. The most effective way to significantly reduce emissions of SO_2, and in some cases mercury, is through the use of flue gas desulfurization (FGD). There are several FGD methods available, examples include various dry scrubbing methods, sea water scrubbing, and wet scrubbing with lime or limestone. The majority of the scrubbers currently being installed use the wet limestone technology. This method is the best suited to scrubbing the high volume of flue gas emitted by large power plants. A schematic of an FGD system is shown in Figure 1.

The corrosive conditions within an FGD system are complex, with many factors contributing to the severity of the environment. The selection of an appropriate material will depend on the operating parameters of the system as well as the environment surrounding the specific components. The most important corrosive species generated during the combustion of coal are chlorides and fluorides along with sulfur bearing species. Contributing to the corrosive environment is the temperature, acid dew point, pH, crevice forming deposits, erosion, etc. Typically, several alloys are used in a system, which will be matched to the conditions under which a component is operating. Fortunately, extensive operating experience has been generated which can be used as guide to selecting appropriate materials of construction.

The purpose of this presentation is to review the properties and corrosion resistance of the super duplex alloy, Z100 (UNS S32760), in relation to pollution control systems. In addition, typical current applications of the S32760 alloy in the FGD and other systems are described.

BACKGROUND - SUPER DUPLEX STAINLESS STEELS

The first duplex stainless steels, developed in the 1920's, lacked toughness and ductility, and thus, were of little utility. Development of modern duplex stainless steels began in the late 1970's with the expanded commercial use of the AOD (Argon Oxygen Decarburization) process, which among other things, permitted the controlled addition of nitrogen. Duplex stainless products first gained success in the European markets, which later translated to international acceptance. The wide spread usage of duplex alloys was further driven by the sharp escalation in raw material prices during the mid 2000's, resulting in their wide spread use as a cost effective upgrade over traditional austenitic alloys.

Duplex stainless steels are Cr-Ni-Fe alloys which may also contain Mo, N, Cu, W, Mn and other alloying elements, as shown in Table 1. It is noted that a range of duplex alloys now exists with corrosion resistance covering a broad spectrum of environments. The so called "Lean Duplex" alloys are intended to be used where high strength and moderate corrosion resistance is needed. These alloys are typically seen as suitable replacements for 304L or 316L in most environments. The "Standard Duplex" alloy, namely 2205, has been the workhorse alloy for FGD in Europe, and more recently in the United States. The combination of strength, corrosion resistance, and low alloy surcharge has resulted in a near complete displacement of 317LMN and 904L in scrubber environments containing up to approximately 12,000 ppm chlorides. The 25Cr alloy, known commercially as 255, saw its first extensive FGD application in the United States at Gibson Station in the mid 1980's. The good performance of this alloy in this application has lead to more widespread use elsewhere. The Super Duplex alloys S32750 and S32760, commercially know as 2507 and Z100, respectively, have been widely and successfully applied in Oil and Gas and Desalination applications for many years. More recently, these alloys have gained acceptance in the FGD community and are being applied in environments where excellent corrosion resistance is needed.

The duplex name comes from the fact that the alloys develop a microstructure containing approximately equal amounts of austenite and ferrite phases. The duplex microstructure results in properties that are a combination of those of ferritic and austenitic alloys, as demonstrated in Table 2. Duplex alloys are generally tougher and more ductile than ferritic alloys while having better SCC resistance and higher strength than austenitic alloys.

Table 1
Nominal compositions of commercially available duplex alloys.
$PRE_{W} = Cr + 3.3Mo + 1.65W + 16N$

Family	Alloy	PRE_W	Cr	Ni	Mo	N	W	Other
Lean Duplex	UNS S32001	25	21	1.5	0.3	0.16	-	5 Mn
	UNS S32101	26	21.5	1.5	0.3	0.22	-	5 Mn
	ATI 2102™	26	21.5	1.5	0.3	0.22	-	2.8 Mn
	UNS S32304	26	23	4.5	0.3	0.10	-	
	UNS S32003	30	21.8	3.5	1.7	0.17	-	
Standard Duplex	UNS S31803	35	22	5	3	0.16	-	
	UNS S32205	36	22.5	5.8	3.2	0.17	-	
25 Cr Duplex	UNS S32550	40	25.5	6	3.3	0.21	-	
Super Duplex	UNS S32760	42	25	7	3.5	0.25	0.7	0.7 Cu
	UNS S32750	42	25	7	4	0.27	-	

Table 2
Qualitative comparison of the properties of austenitic, ferritic, and duplex alloys.

	Austenitic S.S.	**Ferritic S.S.**	**Duplex S.S.**
Nickel Content	High	Very Low	Lower
Tensile Strength	Moderate	Low	High
Elongation	High	Low	Moderate
Formability	Excellent	Low	Good
SCC Resistance	Poor	Excellent	Good
Low T. Toughness	Excellent	Poor	Good
Magnetism	Non-Mag.	Magnetic	Magnetic

HISTORY OF Z100 (S32760)

The first widely available super duplex stainless steel was developed by Gradwell and co-workers in the mid 1980's. This alloy was called Zeron 100 and was developed as a casting alloy (J93380) for pump applications in the oil and gas industry. The performance of the steel in this application generated a demand for the alloy in wrought product forms also. This demand was serviced by Weir who, together with the European manufacturers, developed the manufacturing procedures required to obtain the desired quality of the product.

As demand for the steel grew, clients called for ASTM, NACE, British Standards and other codes to include and cover the Zeron range of products. Moreover, with the introduction of the EC Procurement Directive in 1993, it became an exception for clients to specify any trade name in requests for quotation and a generic description for the alloy was required for the business to continue. In 1993-94, ASTM considered the properties of several heats of Z100 in a range of product forms and on the basis of this designated the code UNS S32760 to the alloy and introduced this number into several standards.

In 1994, UNS S32760 was included in NACE MR0175, again based upon the performance and properties of the proprietary alloy. Finally, in 1997, UNS S32760 was listed in ASME complete with applicable design stresses. These listings were again based upon the properties of the proprietary alloy.

Z100 (S32760) SUPER DUPLEX ALLOY PROPERTIES

Z100 was the first of the super duplex stainless steels, characterized by its high molybdenum and nitrogen content compared to earlier duplex alloys. The alloy was first developed for resistance to seawater, but has found applications in many environments where resistance to halides and acids is needed. The addition of copper and tungsten give the alloy resistance to mineral acids such as sulfuric and hydrochloric. Being a highly alloyed duplex stainless steel, the alloy has very high strength, good resistance to SCC, and excellent pitting resistance.

The minimum mechanical properties per ASTM A240 of S32760 and some other alloys are listed in Table 3. The very high strength of S32760 allows for the opportunity to reduce the wall thickness of some FGD components, thereby reducing project costs. This savings could be significant for the sump area at the bottom of the absorber tower where the thickest plate is typically used. Wall reduction for slurry piping is also a possible area for savings.

Table 3
Minimum mechanical properties per ASTM A240.

Alloy	Y.S. Ksi(MPa)	UTS Ksi(MPa)	Elong. %
S31603	25 (172)	70 (483)	40
S31703	30 (207)	75 (517)	40
S31726	35 (241)	80 (552)	40
S32003	65 (448)	90 (621)	25
S32205	65 (448)	95 (655)	25
S32250	80 (552)	110 (759)	15
S32760	80 (552)	110 (759)	25
N08367	45 (310)	100 (690)	30

Because of its high design stress in ASME B31.3 there are opportunities for wall thickness savings at high pressures, as shown in Table 4. This also leads to consequential savings in fabrication costs and time. For example, at 100 bar, Z100 can be used as NPS 4 schedule 10S pipe, compared with schedule 40S for S31254 (6%Mo austenitic). In larger diameter pipes, it is possible to offer intermediate schedules, such as 20 or 30, because these are seam welded pipe and the plate is stocked at thicknesses to make these schedules subject to reasonable quantities. The savings are most significant in the larger diameter pipes.

Table 4
Thickness Comparisons between S31254 and S32760 per ASME B31.3

PIPE WALL THICKNESS CALCULATED PER ASME B31.3 INTERNAL PRESSURE 100 Bars (1450 psi), at 100°F (40°C)									
	S31254				ZERON 100				
NPS	Nom. Wall (mm)	Sch	(mm)	Nom. Weight	Nom. Wall (mm)	Sch	(mm)	Nom. Weight	Saving lb/ft
1.5	1.308	10S	2.77	2.09	1.085	10S	2.77	2.09	0
4	**3.098**	**40S**	**6.02**	**10.79**	**2.569**	**10S**	**3.05**	**5.61**	**5.18**
6	4.561	40S	7.11	18.97	3.782	40S	7.11	18.97	0
8	5.938	20	6.35	22.36	4.923	20	6.35	22.36	0
14	**9.638**	**40**	**11.13**	**63.44**	**7.991**	**30**	**9.53**	**54.57**	**8.87**
16	**11.014**	**40**	**12.70**	**82.77**	**9.133**	**30**	**9.53**	**62.58**	**20.19**
18	**12.391**	**40**	**14.27**	**104.67**	**10.274**	**30**	**11.13**	**82.15**	**22.52**
20	**13.768**	**40**	**15.09**	**123.11**	**11.416**	**30**	**12.70**	**104.13**	**18.98**
22	**15.145**	**60**	**22.23**	**197.41**	**12.558**	**30**	**12.70**	**114.81**	**82.60**
24	**16.522**	**40**	**17.48**	**171.29**	**13.699**	**30**	**14.27**	**140.68**	**30.61**

CORROSION RESISTANCE

With regard to corrosion resistance, the materials of construction for components of a traditional FGD system are largely dependent on the chloride content of the slurry. This is determined by the chloride concentration of the coal being burned, and the rate at which fresh water is added to the slurry (blow down). In cases where a high blow down rate is not possible, e.g. where water supply and/or treatment is inadequate, the slurry chloride content may become very concentrated.

A useful way of ranking the resistance of a material to chlorides is through the Pitting Resistance Equivalent number, PRE. Although many formulas can be used, Equation 1 gives a common formula for calculating the PRE for stainless steels. The elements Cr, Mo, W, and N provide resistance, especially when present together [1-3]. Nitrogen is particularly effective in the alloys with high Mo content [4-6].

$$PRE_W = Cr + 3.3Mo + 1.65W + 16N \quad (1)$$

The higher the PRE_W, the more resistant the alloy is to pitting and crevice corrosion in the presence of chlorides. Z100 (S32760) has a guaranteed minimum PRE_W of 41.

Typical PRE_W values for various alloys are shown in Table 5 along with the values for the critical crevice corrosion temperature (CCCT) and the critical pitting temperature (CPT) as determined by standard ASTM tests. It is noted that the CCCT and CPT of S32760 are far superior to standard duplex 2205 and approach that of the 6Mo alloy N08637. A plot of CPT vs. PRE_W may be seen in Figure 2.

Table 5
Critical Crevice Corrosion Temperature and Critical Pitting Temperature in standard ASTM solutions.
$PRE_W = Cr + 3.3Mo + 1.65W + 16N$

UNS Number	CCCT[1] °F (°C)	CPT[2] °F (°C)	PRE_W
S31603	27 (-3)	63(17)	23
S31703	35 (2)	93(34)	29
S31726	68 (20)	134(56)	34
S32205	68 (20)	122(50)	36
N08904	75 (24)	104(60)	35
S32550	72 (22)	169(76)	41
S32760	104 (40)	170(77)	42
N08367	113 (45)	194(90)	47

1. per ASTM G 48 Practice B
2. per ASTM G150

The absorber outlet ducting will be exposed to some slurry carry over from the absorber as well as residual SO_3 from the flue gas. Since the temperature in the absorber outlet is typically well below the sulfuric acid dew point, low pH condensates containing chlorides are often present. Thus, Ni-Cr-Mo alloys, such as N10276 or N06022, are often employed. However, the increased efficiency and improved design of modern scrubbers somewhat alleviates this issue, allowing for the application of stainless steels in some cases. Z100 (S32760) has been found to have excellent resistance to dilute sulfuric acid, as well as sulfuric acid containing chlorides, as shown in the plots of Figures 3 and 4. The improved resistance of Z100 (S32760) over similar alloys can be attributed to the addition of copper and tungsten. Thus, Z100 (S32760) should be considered for outlet ducting when the application of stainless steels is appropriate.

A general guide for alloy selection for FGD absorber towers is presented in Figure 5. This table applies to a temperature range of 50°C – 60°C (120°F – 150°F) and a fluoride content of less than 50 ppm. This table is based on the open literature on the subject and is intended to be used as a guide only. Factors such as deposit formation, fabrication procedures, contaminants, additives, etc., must also be taken into consideration when selecting the appropriate material.

SIMULATED SLURRY TESTING

There is obvious concern that alloys for use in FGD scrubber systems may suffer from crevice corrosion, as crevices abound in all commercial designs. Early laboratory tests [7] were conducted in simple sulphate/ chloride solutions and the results suggested that pH had little effect on the critical crevice corrosion temperature (CCCT). However, more recent work by Weir Materials & Foundries [8] in more realistic slurries has shown that pH has a strong effect and the CCCT can decrease over 20°C as the pH decreases from pH 5 to pH 3.

During normal operation pH levels are generally from 4.5 to 6, but under adverse conditions pH values as low as 4 are possible. Hence, WM&F has carried out a series of electrochemical tests in simulated

FGD slurries at this pH. Table 6 shows the results of CCCT tests in a simulated anthracite slurry at pH 4. In this environment normal operating temperatures are about 50°C. The results show that wrought Z100 is superior to the 6Mo wrought alloy, while the older cast 25Cr duplex is unsuitable for this environment. Welded and cast Z100 are also suitable in this application.

Table 7 shows the CCCT data for a simulated lignite slurry, where operating temperatures are typically 60° – 65°C. Once again wrought Z100 is clearly superior to the 6Mo austenitic alloy. Cast and welded Z100 are also suitable, but the older 25Cr duplex alloy is not. These results show the excellent resistance of Z100 to crevice corrosion, particularly the wrought product.

Table 6
Critical crevice temperature for some stainless steels in simulated anthracite FGD slurry at pH = 4.

Slurry composition:

CaSO4	10 wt%
Chloride	40 g/l
Fluoride	50 mg/l
"Dithionate"	200 mg/l
Fe3+	10 mg/l
A13+	30 mg/

Form	Alloy	CCCT (°C)
Wrought	S32760	>80
	S31254	64.7
Welded*	S32760	58.5
Cast	J93380	57.8
	25Cr Duplex	42

*CPT

Table 7
Critical crevice temperature for some stainless steels in simulated lignite FGD slurry at pH = 4.

Slurry composition:

CaSO4	10 wt%
Chloride	15 g/l
Fluoride	200 mg/l
"Dithionate"	200 mg/l
Fe3+	10 mg/l
A13+	30 mg/

Form	Alloy	CCCT (°C)
Wrought	S32760	>83
	S31254	66.7
Welded*	S32760	63.4
Cast	J93380	62.6
	S32550 (Zeron 25)	39.6

*CPT

EROSION CORROSION TESTING

Erosion corrosion can be a significant problem in FGD systems, especially in areas in direct contact with the slurry. These areas include the absorber sump, slurry piping, pumps, valves, and agitators. The calcium sulphate and limestone in FGD slurries are not particularly erosive. It has been found that fly ash causes most of the erosion.

Tests have been conducted in simulated FGD brines including fly ash in a recirculating erosion test rig [9]. Results from pin erosion tests showed that Z100 offered superior erosion resistance to austenitic alloys such as 316L as well as more highly alloyed materials. Figure 6 shows the erosion resistance of several alloys including Z100 as a function of pH. It can be seen that Z100 has the best erosion resistance, which is not affected by pH i.e. the alloy does not corrode significantly at low pH.

Following these promising results a test loop was constructed utilizing a Z100 pump and pipework and handling the same slurry [9]. After 3000 hours running the pump and pipework were in excellent condition, with some etching of the material at the vane tips (i.e. the region of greatest velocity). Polishing of the impeller vanes by the slurry actually increased the pump efficiency with increasing running time.

EFFECT OF BROMIDE ON CORROSION OF Z100 (S32760)

Some FGD projects are considering bromide additions to remove mercury compounds from the limestone slurry. Bromide concentrations up to 10g/l are contemplated. To determine the effect of bromide on the corrosion of Z100, electrochemical crevice corrosion tests were conducted using the method described previously [10]. Two test solutions were used; the first identical to that described previously with 40g/l chloride adjusted to pH4. The second solution had 10g/l less chloride, which was replaced with 10g/l bromide, as sodium bromide, also adjusted to pH4. The tests started at room temperature and, after one hour to stabilize, the temperature was increased at 5°C/hour until the maximum temperature was reached (84.5°C). The Critical Crevice Temperature (CCT) results, shown in Table 8, clearly demonstrate that Z100 maintains a high resistance to crevice corrosion in FGD solutions in the presence of 10g/l bromide. No significant effect on the CCT at pH4 was observed.

Table 8
Critical crevice temperature for some stainless steels in simulated FGD slurry at pH = 4.

Bromide (g/l)	Chloride (g/l)	CCT (°C)
0.5	40	>84.5
0.5	40	>84.5
10	30	>84.5
10	30	83

FABRICATION OF Z100 (UNS32760)

Z100 is readily welded by all the common arc welding processes i.e. TIG (GTAW), MMA (SMAW), SAW etc. For as-welded use it is fabricated with overalloyed Zeron® 100X consumables, which have a higher nickel content to ensure the correct phase balance in the weld metal. Material thicknesses from

1.6mm to 63mm have been welded successfully and it is estimated that over one million welds are now in service around the world. In common with other high alloy materials, successful welds in Zeron® 100 require qualified welders working to approved procedures.

ZERON® 100 (S32760) POLLUTION CONTROL APPLICATIONS AND EXPERIENCE

The excellent corrosion resistance of Z100 combined with its high strength make it suitable for a wide range of applications in FGD plants. Some FGD applications of Z100 are given in Table 9.

Table 9
Some Z100 [S32760] FGD experience.

Client	Project	Contractor	Component
Powergen	Ra~~d~~tcliffe Station	John Brown	Flow Distributor Plates
C.E.G.B.	Drax	Babcocks	Slurry Pumps
Broadbents	Drax	Babcocks	Sep~~e~~arator Baskets
C.E.G.B.	Drax	Babcock Contractors	Absorber Tower
Envirotech ~~Pumps~~	Various	Various	Pumps
Broadbent Mixers	Various	Various	Agitators
Lightning Mixers			
Plenty Mixers			
Munters	Tampa Electric	Munters	Mist Eliminator

Cast Z100 can be used for pumps, valves, and agitators, while the wrought product can be used for ducting, where acid condensation may occur, up to 300°C. Other applications include gas distribution plates, sprinkler heads, fasteners, centrifuges, and absorber towers. With absorber towers, the high strength of super duplex stainless steel means it is more economic to make absorber vessels from solid alloy rather than clad steel. One power station in the USA has changed from clad to solid super duplex for absorber vessels because of the economics.

Z100 has been used successfully for the slurry pumps, agitator stools and gas distribution plates at the Drax FGD plant in the UK since 1994. A picture of the FGD slurry recirluation pumps at Drax can be seen in Figure 7. The pumps are lasting 30,000 to 40,000 hours between major overhauls. Z100 has also had the advantage that minor damage can be weld repaired, while white cast irons, also used for FGD pumps, cannot.

The slurry centrifuges at Ratcliffe FGD plant were supplied in Z100 in 1996. After thirteen years operation, they are in excellent condition. After a short time of operation, the GRP slurry return lines at Ratcliffe FGD plant were suffering severe erosion. These have now been replaced with spools of Z100 and have given no further problems. A picture of the Z100 centrifuges at Ratcliffe can be seen in Figure 8.

SUMMARY

The combination of high strength, excellent corrosion resistance, and good erosion resistance make Z100 (S32760) a good choice for many pollution control applications. The higher strength of the alloy presents the opportunity for reduced wall thickness over austenitic alloys, which could result in significant project cost savings. In addition, super duplex alloys contain inherently less nickel and molybdenum, leading to lower and less volatile raw material costs. The alloy has extensive experience in many industries and is widely available in most product forms.

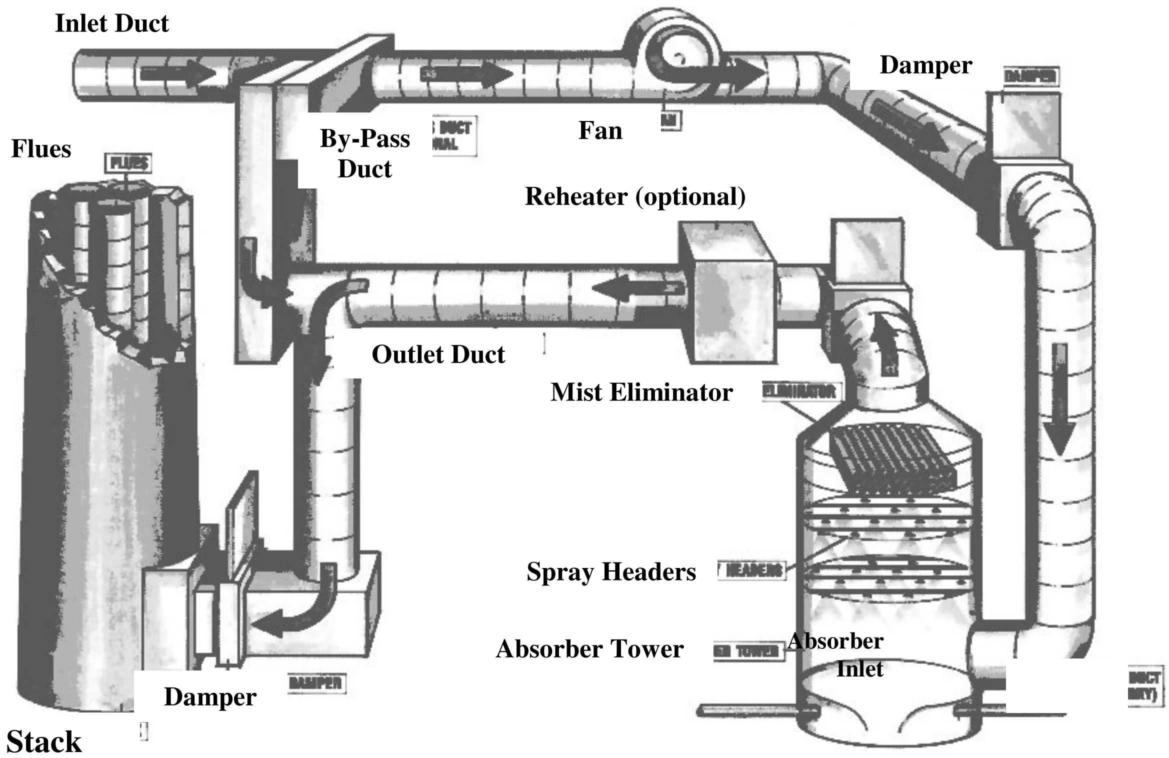

Figure 1: Schematic of an FGD system.

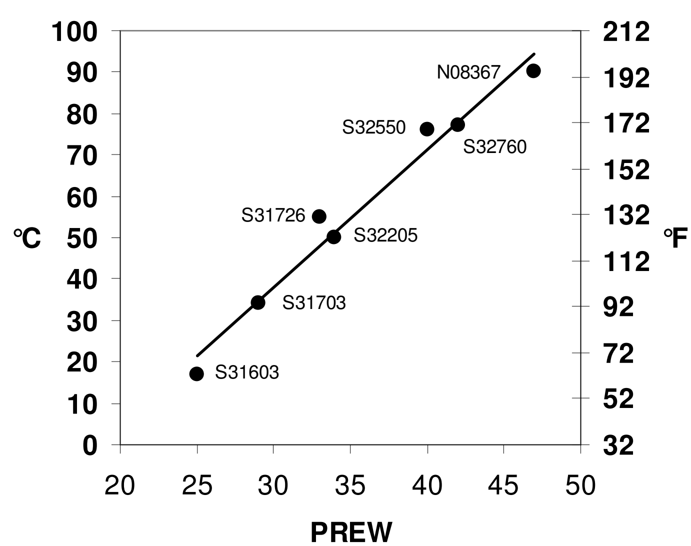

Figure 2: Plot of PRE_W vs. CPT for various alloys.

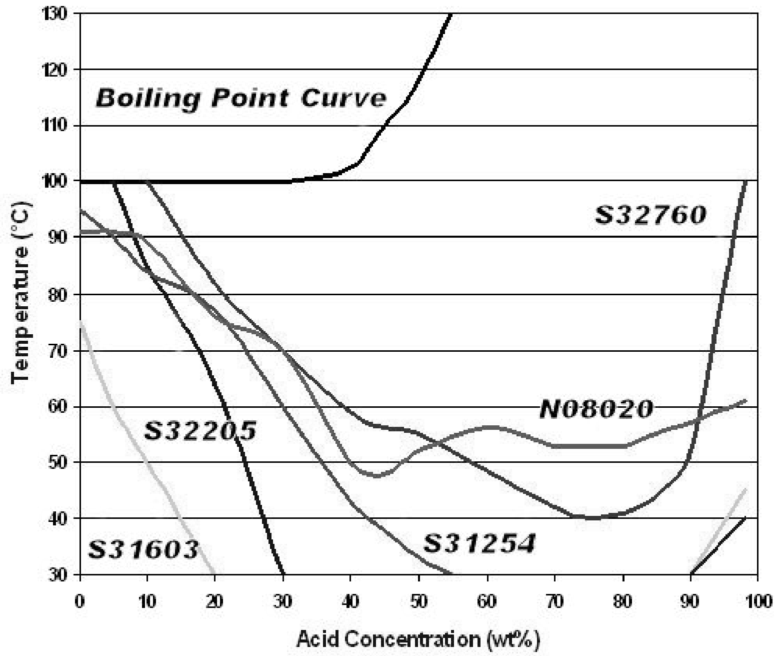

Figure 3: Iso-corrosion rates for various alloys in sulfuric acid. Lines indicate a corrosion rate of 0.1mm/yr (0.004 in/yr).

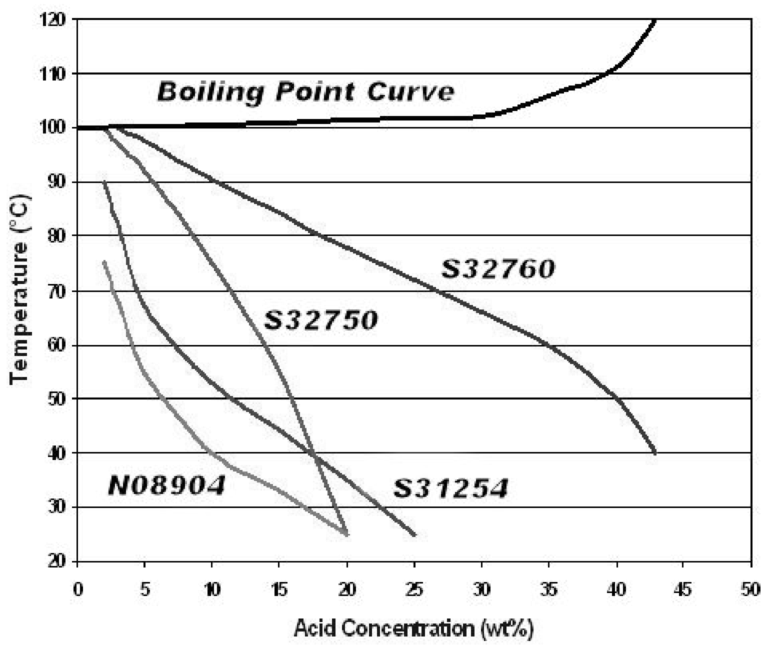

Figure 4: Iso-corrosion rates for various alloys in sulfuric acid plus 2g/L chlorides. Lines indicate a corrosion rate of 0.1mm/yr (0.004 in/yr).

		Mild	Moderate		Severe		Very Severe		
	Cl - ppm	500	1,000	5,000	10,000	30,000	50,000	100,000	200,000
Mild	pH 6.5	S31603		S31726 N08904		S32760 S32550	N08367	N10276	
Moderate	pH 4.5								
Severe	pH 2.0	S31726	S32205						
Very Severe	pH 1.0	S31726 N08904	N08367						

Figure 5: Alloy selection chart for FGD absorber towers.

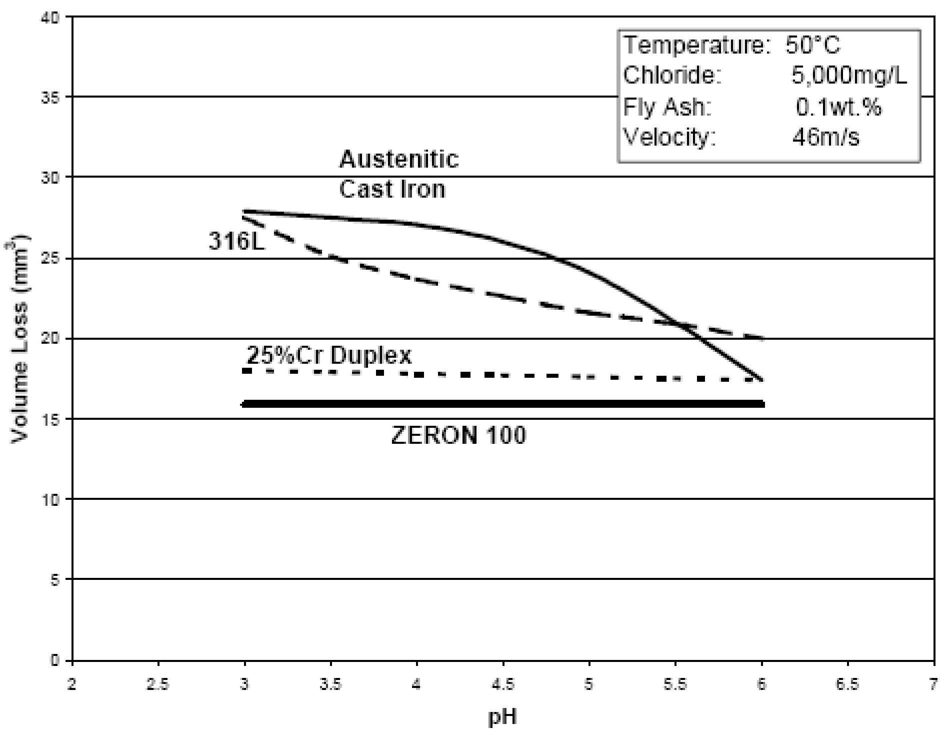

Figure 6: Pin erosion rig test results in a simulated FGD slurry.

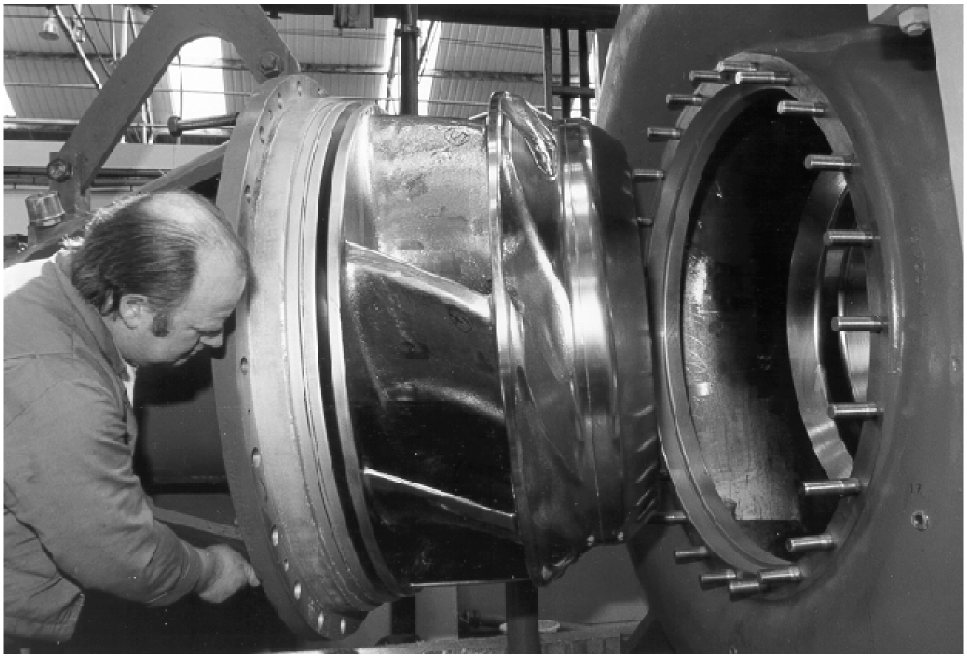

Figure 7: Z100 slurry recirculation pump fitted at Drax FGD Plant in the UK.

Figure 8: Z100 centrifuge at Ratcliffe Power Station in the UK.

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