REPORT

The Use of ZERON 100 In Flue Gas Desulphurisation Plant

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SUMMARY

The report highlights the corrosion data generated in simulated flue gas desulphurisation (FGD) environments for ZERON 100, the potential applications, and some of the uses in the UK.

1.0 INTRODUCTION

Flue Gas Desulphurisation (FGD) is used to remove sulphur containing gases (mostly sulphur dioxide) from the flue gas discharges of coal fired power stations. The most common method for doing this is the wet limestone process, where a slurry of crushed limestone and water is passed down an absorber tower as the flue gases rise up. The limestone is converted to gypsum (calcium sulphate) which is periodically removed and fresh limestone is added. Because of the recirculation method and the wish to minimise water additions, the dissolved solids content of the slurry is often high, depending on the nature of the coal being burnt and the composition of the make up water. Chlorides, in particular, can be very high; 40,000mg/l is not uncommon, but the sulphate content is also high. During operation the temperature can be in the range 45^0 to 70^0C and the pH is generally from 4 to 6, depending on the type of coal being burnt.

Figure 1 shows a schematic diagram of a typical FGD absorber tower. This shows some of the areas where either corrosion resistant alloy components or rubber lined steel are used e.g. absorber tower walls, slurry recirculation pumps.

There are two principal types of coal burned in power stations and these give rise to somewhat different slurry compositions.

Anthracite or hard coal is generally low in fluorides, but, at least in the UK, the chloride level is high. This gives rise to a slurry with the following characteristics :

Chloride	-	20 to 40 g/l
Fluoride	-	~ 50 mg/l
Temperature	-	45^0 to 50^0C
pH	-	4.0 - 5.5

Lignite or brown coal is generally higher in fluorides, although most of these will be insoluble CaF_2, and only soluble fluorides will influence corrosion. Chlorides in lignite fuels are lower than with anthracite, while operating temperatures are higher. Typical lignite slurry characteristics are as follows :

Chloride	-	5 to 15 g/l
Fluoride	-	100 to 200 mg/l
Temperature	-	60^0 to 70^0C
pH	-	4.5 to 6

When sulphur dioxide is oxidised to gypsum the overall reaction is :

$$2\,SO_2 + O_2 + 2\,Ca\,(HCO_3)_2 \rightarrow CaSO_4 + 4CO_2 + 2H_2O$$

However, the oxidation of sulphur dioxide does not occur in a single step and there are a number of intermediate stages. These result in the formation of partially oxidised sulphur species such as sulphite, (SO_3^{2-}) thiosulphate ($S_2O_3^{2-}$), dithionate ($S_2O_6^{2-}$) and possibly others.

Sulphites react rapidly with oxygen to form sulphate, and are generally thought to have no significant effect on the corrosion of stainless steels in aerated solutions. Thiosulphate has been shown to affect the resistance of 304 and 316 stainless steels to pitting at elevated temperatures in acid brines (1). There is nothing published on the effect of dithionate on the pitting of duplex stainless steels.

In addition to partially oxidised sulphur species, real FGD slurries also contain significant quantities of metal ions such as Fe^{3+}, Al^{3+} and Mn^{2+}. There are also halides present such as the fluorides and chlorides discussed above and bromides as well. All of these species can affect the corrosion behaviour and it is important that they are present in laboratory test slurries.

2.0 ZERON 100

Zeron 100 is a superduplex stainless steel with a composition producing a microstructure which is 50% ferrite and 50% austenite. This combines the properties of strength and ductility. Zeron 100 is available in both cast and wrought product forms, and the nominal compositions are shown in Table 1, along with those of some other common stainless steels.

The high levels of chromium, molybdenum and nitrogen in the alloy give it excellent resistance to localised corrosion in chloride containing fluids. The additions of copper and tungsten give the alloy resistance to acids, particularly mineral acids such as sulphuric and hydrochloric acids.

An indication of the resistance to pitting in chloride solutions is given by the Pitting Resistance Equivalent Number (PREN) which is an empirical relationship linking the chromium, molybdenum and nitrogen contents of corrosion resistant alloys.

$$PREN = \%\,Cr + 3.3\%\,Mo + 16\%\,N$$

Common austenitic alloys such as 316L have a PREN of 24, while 22%Cr duplex has a PREN of 34. Zeron 100 has a guaranteed minimum PREN of 40, and is the only alloy to guarantee a minimum PREN value.

The minimum mechanical properties of Zeron 100 at room temperature are shown in Table 2, with those of austenitic alloys such as 316L and 6%Mo austenitic for comparison. It can be seen that the proof stress of Zeron 100 is more than 2.5 times that of 316L and 1.8 times that of 6%Mo. The high strength means that substantial reductions in wall thickness can be obtained, particularly in high temperature / high pressure applications. In addition to savings in the cost of parent material, this also results in savings in fabrication costs and time.

The useful operating range for Zeron 100 is the same as for other duplex and superduplex alloys i.e. -60^0C to $+300^0C$. At temperatures lower than -60^0C there is a decrease in impact toughness. At temperatures above 300^0C the alloy slowly becomes embrittled due to the precipitation of a third phase (alpha prime).

Zeron 100 is readily welded, by all the common arc 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.

3.0 CORROSION

3.1 General Corrosion

In certain parts of FGD plant hot, strong acids can condense. Zeron 100 has excellent resistance to mineral and organic acids. Figures 2 and 3 shows the iso-corrosion curves (0.1mm/y) in sulphuric and hydrochloric acids respectively. The results clearly show the superior performance of Zeron 100 compared not only with 6%Mo austenitics, but also with other superduplex alloys such as UNS S32750. This is believed to be due to the copper and tungsten content of the alloy, in addition to the chromium and molybdenum. Copper and tungsten are not present in other alloys, such as S32750.

In many acid systems chlorides can also be present, and the unique composition of Zeron 100 gives it excellent resistance to such fluids. Figure 4 shows the iso-corrosion curves (0.1mm/y) for Zeron 100 and some competitor alloys. The superior performance of Zeron 100 is clearly demonstrated.

The ASTM G28 test is often used to rank materials for service in aggressive oxidising acidic environments. Method A (boiling 50% H_2SO_4 + 42g/l ferric sulphate) is used for welded samples and Figure 5 shows the corrosion rates for welded Zeron 100 against three commonly specified nickel alloys. It can be seen that Zeron 100 has a much lower corrosion rate than all the nickel alloys commonly considered for these aggressive environments.

3.2 Crevice Corrosion

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 (2) were conducted in simple sulphate/ chloride solutions and the results suggested that pH had little effect on the critical crevice corrosion temperature (CCT). However, more recent work by Weir Materials & Foundries (3) in more realistic slurries has shown that pH has a strong effect and the CCT can decrease over 20^0C 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 3 shows the results of CCT tests in a simulated anthracite slurry at pH 4. In this environment normal operating temperatures are about 50^0C. The results show that wrought Zeron 100 is superior to the 6%Mo wrought alloy, while the older cast 25%Cr duplex is unsuitable for this environment. Welded and cast Zeron 100 are also suitable in this application.

Table 4 shows the CCT data for a simulated lignite slurry, where operating temperatures are typically 60^0 - 65^0C. Once again wrought Zeron 100 is clearly superior to the 6%Mo austenitic alloy. Cast and welded Zeron 100 are also suitable, but the older 25%Cr duplex alloy is not.

These results show the excellent resistance of Zeron 100 to crevice corrosion, particularly the wrought product.

3.3 Erosion Corrosion

The calcium sulphate and limestone in FGD slurries are not particularly erosive, and it is the fly ash which causes most of the erosion.

Tests have been conducted in simulated FGD brines including fly ash in a recirculating erosion test rig (4). Results from pin erosion tests showed that Zeron 100 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 Zeron 100 as a function of pH. It can be seen that Zeron 100 has the best erosion resistance, which is not affected by pH ie the alloy does not corrode significantly at low pH.

Following these promising results a test loop was constructed utilising a Zeron 100 pump and pipework and handling the same slurry (4). After 3000 hours running the pump and pipework were in excellent condition, with some etching of the material at the vane tips (ie the region of greatest velocity). Polishing of the impeller vanes by the slurry actually increased the pump efficiency with increasing running time.

4.0 APPLICATIONS AND EXPERIENCES

The excellent corrosion resistance of Zeron 100 combined with its high strength make it suitable for a wide range of applications in FGD plant.

Cast Zeron 100 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^{0}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 (5). One power station in the USA has changed from clad to solid super duplex for absorber vessels because of the economics (5). A recent paper (6) has described the successful operation of the absorbers for up to 20 years.

Zeron 100 has been used successfully for the slurry pumps, agitator stools and gas distribution plates at the Drax FGD plant in the UK since 1994. The pumps are lasting 30,000 to 40,000 hours between major overhauls. Zeron 100 also had the advantage that minor damage can be weld repaired, while white cast irons, as used for FGD pumps, cannot.

The slurry centrifuges at Ratcliffe FGD plant were supplied in Zeron 100 in 1996. After twelve 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 in Zeron 100 and have given no further problems.

5.0 CONCLUSIONS

The combinations of high strength and good corrosion resistance make Zeron 100 eminently suitable for a wide range of applications in FGD plant. The excellent test results have lead to the use of Zeron 100 for several components in the FGD plants at Drax Power Station, UK and Ratcliffe Power Station, UK.

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TABLE 1. The nominal composition of some common stainless steels.

ALLOY	NOMINAL COMPOSITION (WT%)							PREN*
	Fe	Cr	Ni	Mo	N	Cu	W	
316L	Bal	17	10	2	-	-	-	24
6%Mo Aust.	Bal	20	18	6	0.2	0.7	-	43
Zeron 100 (wrought)	Bal	25	7	3.5	0.25	0.7	0.7	>40
Zeron 100 (cast)	Bal	25	8	3.5	0.25	0.7	0.7	>40

Bal = Balance
*PREN = %Cr + 3.3 x % Mo + 16 x % N

TABLE 2. Minimum mechanical properties of some stainless steels.

FORM	ALLOY	0.2% Proof Stress (MPa)	UTS (MPa)	Elongn. (%)
WROUGHT	316L	213	500	45
	6%Mo Aust.	300	650	35
	Zeron 100	550	750	25
CAST	Zeron 100	450	700	25

TABLE 3. Critical crevice temperature for some stainless steels in a simulated anthracite FGD slurry at pH4.

Slurry composition:

$CaSO_4$	10 wt%
Chloride	40 g/l
Fluoride	50 mg/l
"Dithionate"	200 mg/l
Fe^{3+}	10 mg/l
Al^{3+}	30 mg/l

FORM	ALLOY	CCT (°C)
Wrought	Zeron 100	>80
	6%Mo Aust.	64.7
Welded	Zeron 100	58.5
Cast	Zeron 100	57.8
	Zeron 25	42.0

TABLE 4. Critical crevice temperature for some stainless steels in a simulated lignite FGD slurry at pH4.

Slurry composition:

$CaSO_4$	10 wt%
Chloride	15 g/l
Fluoride	200 mg/l
"Dithionate"	200 mg/l
Fe^{3+}	10 mg/l
Al^{3+}	30 mg/l

FORM	ALLOY	CCT (°C)
Wrought	Zeron 100	>83
	6Mo aust	66.7
Welded	Zeron 100	63.4
Cast	Zeron 100	62.6
	Zeron 25	39.6

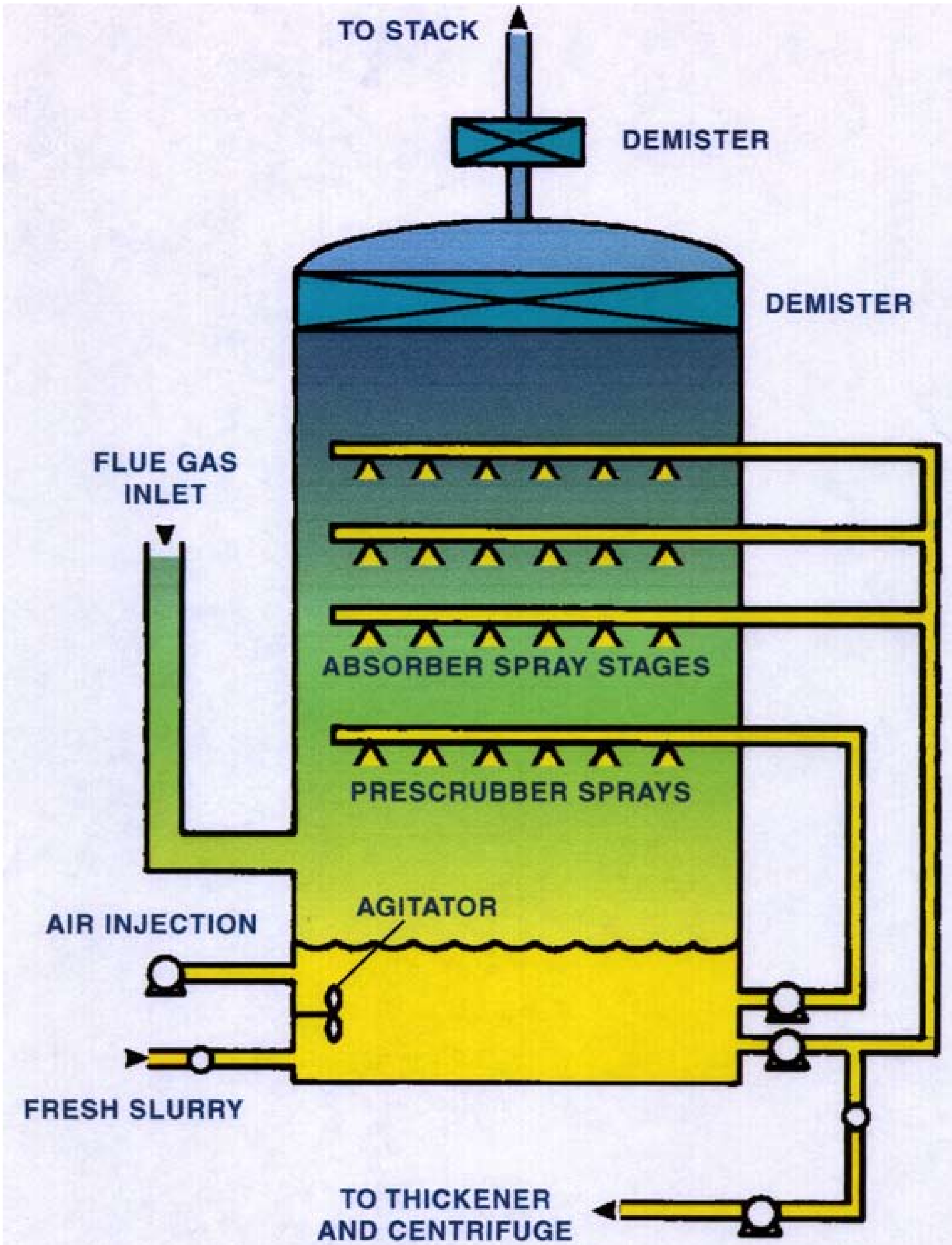

FIGURE 1 Schematic diagram of a typical FGD absorber tower (Babcock design).

FIGURE 2 Iso-corrosion curves (0.1mm/y) for some stainless steels in sulphuric acid

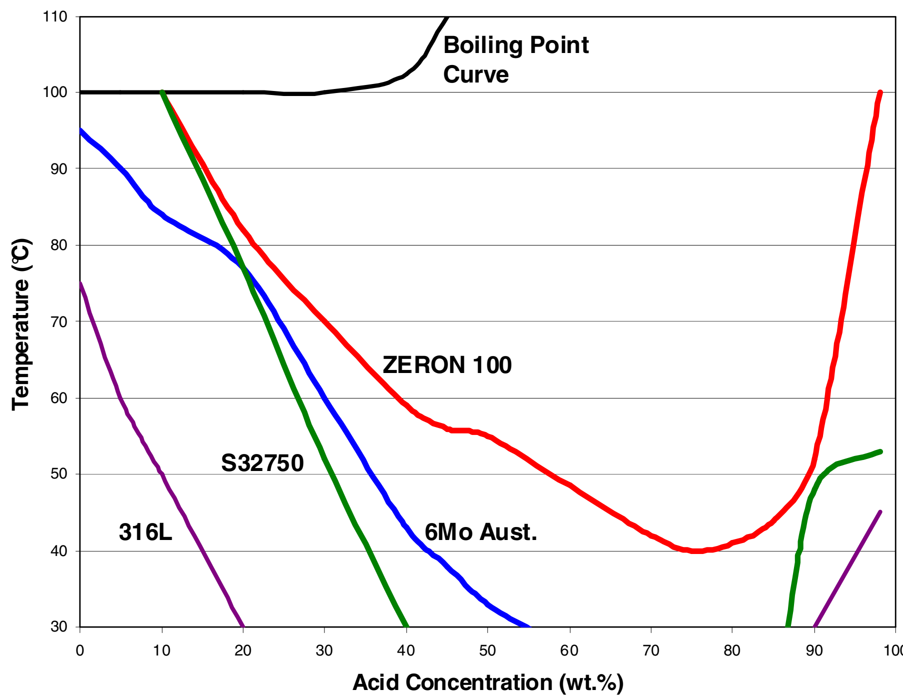

FIGURE 3 Iso-corrosion curves (0.1mm/y) for some stainless steels in hydrochloric acid

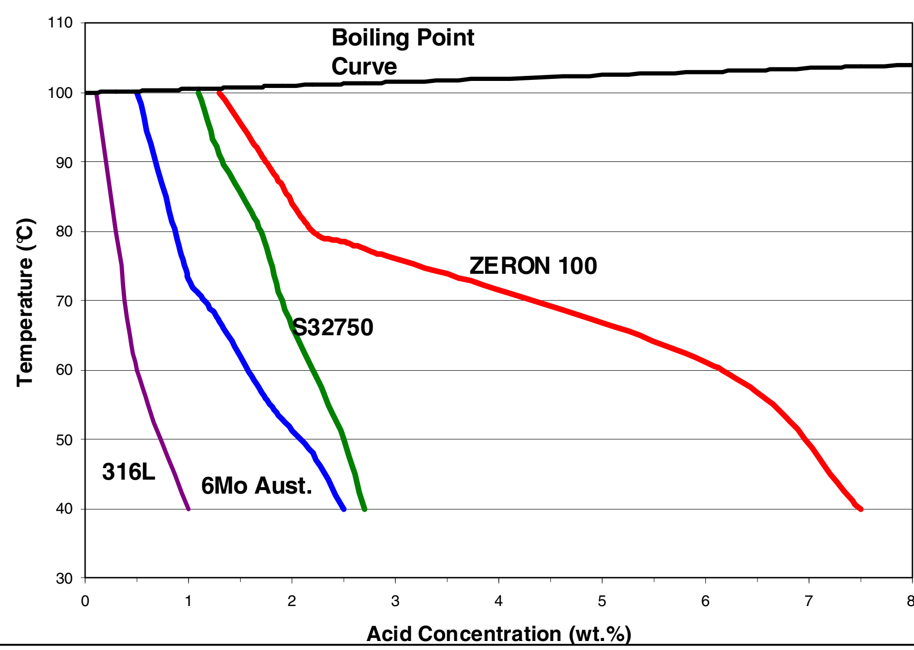

FIGURE 4 Iso-corrosion curves (0.1mm/y) for some stainless steels in sulphuric acid plus 2g/L chloride

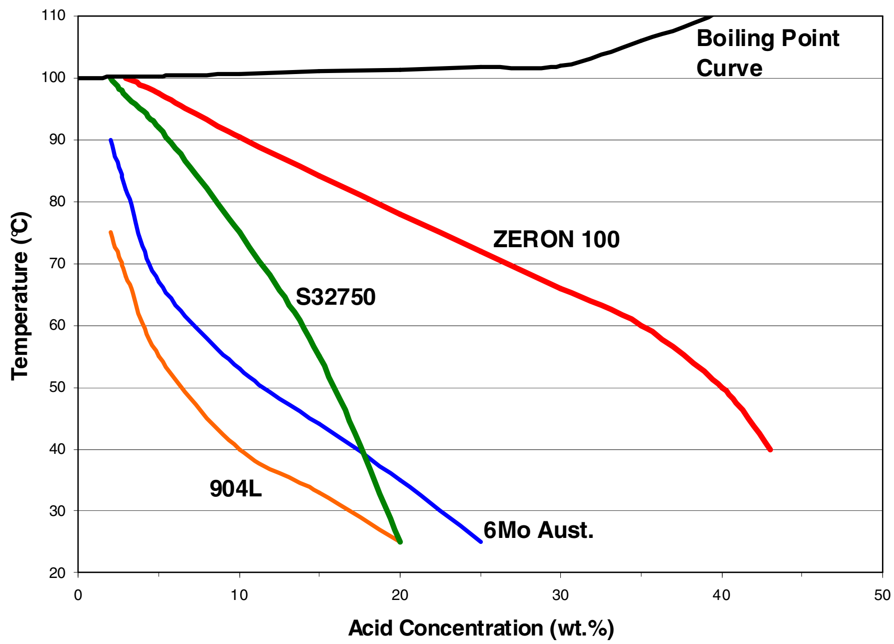

FIGURE 5 Corrosion of some nickel alloys and Zeron 100 in ASTM G28A test

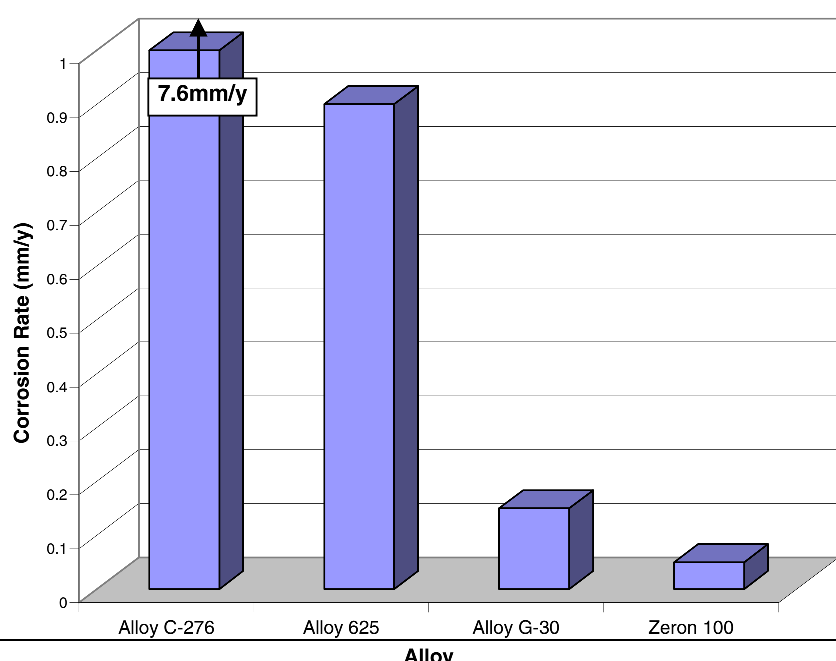

FIGURE 6 Pin erosion rig test results in a simulated FGD slurry