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REPORT

AN EVALUATION OF SOME ALLOYS FOR FGD SERVICE

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AN EVALUATION OF SOME ALLOYS FOR FGD SERVICE

TABLE OF CONTENTS

<u>SECTION</u>	<u>DESCRIPTION</u>
	EXECUTIVE SUMMARY
1.0	INTRODUCTION
2.0	EXPERIMENTAL
2.1	Materials
2.2	Test Solution
2.3	Test Method
3.0	RESULTS
4.0	DISCUSSION
5.0	CONCLUSIONS
	REFERENCES

TABLES

TABLE 1	Nominal composition of the test alloys.
TABLE 2	Composition of the simulated FGD slurries.
TABLE 3	Critical crevice temperatures in simulated FGD slurries.
TABLE 4	Comparative prices for hot rolled 10mm plate (Spring 2012).

FIGURES

FIGURE 1	Schematic diagram of a typical FGD absorber tower layout.
FIGURE 2	Appearance of sample and mount (not to scale).
FIGURE 3	Typical current density and temperature versus time trace at +300mV SCE in FGD slurry with 40g/L chloride at pH4.



EXECUTIVE SUMMARY

The resistance of some corrosion resistant alloys to crevice corrosion in two simulated FGD slurries at pH4 has been measured. 2205 duplex stainless steel showed a critical crevice temperature (CCT) around the normal operating temperature in both anthracite and lignite slurries, making its use marginal. This is in agreement with the service experience for this alloy. ZERON 100 superduplex, AL-6XN super austenitic and the nickel alloy C-276 all had CCT values in excess of normal operating temperatures for both slurries. This is in agreement with the successful service experience with these alloys in FGD service. ZERON 100 offers the lowest cost as an alternative alloy to 2205, but AL-6XN is easier to apply as cladding.

1.0 INTRODUCTION

Flue gas desulphurisation (FGD) is used to remove sulphur-containing gases (mainly 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. 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.

Because of the recirculation of the slurry and the wish to minimise water additions, the dissolved solids content 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 g/L is not uncommon and the sulphate content is also high. During operation, the temperature can be in the range 45° to 70°C and the pH is generally from 4 to 6, depending on the coal being burnt. If the gypsum is going to be made subsequently into plaster board, it is essential that it be white and so the pH is usually close to 4 so that iron compounds do not precipitate and discolour the gypsum.

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

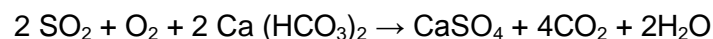
Anthracite or hard coal is generally low in fluorides, but often the chloride level is high. This gives rise to a slurry with the following characteristics:

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

Lignite or brown coal is generally higher in fluorides, although most of these will be insoluble CaF₂, 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 ^o to 70 ^o C
pH	-	4.5 to 6

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



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 (SO₃²⁻), thiosulphate (S₂O₃²⁻), dithionate (S₂O₆²⁻) 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 brines¹. 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.

In Europe it is common to use absorber towers made of carbon steel and coated with neoprene or other polymer. In the USA it is more common to use towers made of solid or clad corrosion resistant alloys. Nickel alloy C-276 is very corrosion resistant and has been used around the flue gas inlet in many towers, where it gives good performance. Duplex stainless steel, 2205, has been used extensively in the USA for the lower regions of the absorber tower, where temperatures are lower. However, there have been numerous reports of corrosion of 2205 in FGD slurries, in some cases requiring replacement with more corrosion resistant alloys². The purpose of the present work was to compare the crevice corrosion resistance in typical FGD slurries of some of the alloys currently used in FGD service.

2.0 EXPERIMENTAL

2.1 Materials

It was decided to compare several corrosion resistant alloys with 2205. The nickel alloy, C-276, was chosen because of its excellent performance in FGD slurries. AL-6XN is a 6%Mo austenitic stainless steel that has given good performance in some FGD plants. ZERON 100 is a superduplex stainless steel that has been used successfully in two UK FGD plants for a variety of components in the absorber towers and associated equipment³.

Table 1 shows the composition of the four alloys that were tested. The pitting resistance equivalent number, or PREN, is an empirical formula, which gives a guide to the resistance of an alloy to localised corrosion by halides. The higher the PREN value, the greater is the resistance to corrosion. It can be seen that both ZERON 100 and AL-6XN are similar in PREN and higher than 2205. The PREN of C-276 is very much higher still, indicating exceptional resistance to chloride attack.

The samples were machined into cylinders of 10mm diameter and 30mm long, with one hemi-spherical end. An M3 hole was drilled and tapped into the flat end to accept an electrical connection. The flat face of the sample was coated with Duramastic lacquer to prevent corrosion there during the test.

2.2 Test Solution

As described above, FGD slurry is a complex mixture of chemicals and simple solutions of calcium chloride and sulphate do not give a true representation of the slurry. FGD slurries are oxidising due to the presence of ferric ions in solution as well as being saturated with dissolved oxygen. Previous research described two synthetic solutions to simulate anthracite and lignite coal slurries³. The composition of these is shown in Table 2.



Although calcium sulphate is largely insoluble, it was added to the slurry because of its ability to settle in areas of low flow and exacerbate crevice corrosion. Chloride was added mostly as calcium chloride, but 2g/L was added as the sodium salt, as this is also present in service. The total chloride content was set at the high end of what is found in service to represent worse case conditions. Both fluoride and bromide were added as the sodium salt at concentrations typical of FGD slurries. The dithionate was made by bubbling sulphur dioxide through 1L of distilled water containing 5g of manganese dioxide. This reacts very quickly and then nitrogen was bubbled through the solution for several hours to remove excess sulphur dioxide. The ferric and aluminium ions were added as their sulphates. The pH was adjusted to 4 with either dilute sulphuric acid or 1M sodium hydroxide, as required, as this is the worst case typically found in service. Adjustments were made throughout the test as required, but a tight control of pH was not required as it drifts to some extent in service.

2.3 Test Method

In previous research it was shown that stainless steels typically adopt a potential of around 300mV SCE in FGD slurries³. It was decided to monitor the potential of each alloy for 24 hours in simulated anthracite slurry at 50°C to confirm these findings. The samples were mounted on a glass rod with a PTFE seal and a brass rod as an electrical connector, as shown in Figure 2. The results showed final potentials closer to 200mV in the single test, but the previous testing, showed quite a scatter in multiple tests, so a value of 300mV SCE was considered acceptable for the present tests for all the alloys.

The same sample holder was used with a silicone rubber washer with a 5mm square cross section and a 7mm central hole around the specimen to form a crevice. The washers were washed in 3% sodium chloride prior to fitting on the sample to remove any soluble surface chemical. The crevice formed by these washers has been found to be similar to many moderately tight crevices found in industrial service.

The samples were inserted into a glass cell with a volume of ~750ml and air was continuously sparged through the cell during the test. The potential was monitored with a saturated calomel electrode connected to the cell via a Luggin capillary. A platinum mesh was used as a counter electrode. The samples were polarised to +300mV SCE over 15 minutes and the current density was then allowed to stabilise for one hour, after which the temperature was increased at a rate of 5°C/hr up to ~85°C, where it was maintained for two hours before the test was terminated.

After the test, the samples were removed, washed and dried and then examined for signs of corrosion.

3.0 RESULTS

Figure 3 shows a typical trace of current density and temperature versus time. When the current density exceeds $10\mu\text{A}/\text{cm}^2$, crevice corrosion is considered to have initiated⁴. The temperature at which this occurs is the critical crevice temperature (CCT). Table 3 shows the critical crevice temperature (CCT) for all the alloys in both test media. Where crevice corrosion occurred, it was found under the washer, close to the outer edge. This is where crevice corrosion would be expected⁴.



4.0 DISCUSSION

The results show that crevice corrosion did not initiate on either AL-6XN or C-276 in either slurry, nor did it initiate on ZERON 100 in the lignite slurry. In the anthracite slurry, crevice corrosion only initiated on ZERON 100 at high temperatures. In both slurries 2205 initiated crevice corrosion at much lower temperatures.

The operating temperature of anthracite slurry is typically 45° to 50°C and clearly 2205 is marginal, at best, for this duty. This explains the high number of corrosion problems with 2205 seen in service.

In lignite type slurries, the operating temperature is typically 65° to 70°C and again 2205 is marginal for this application with CCT values around normal operating temperatures. It is clear that the other three alloys all have superior corrosion resistance in both these environments and this is supported by their many years of successful service experience. Alloys ZERON 100 and AL-6XN are preferred to alloy C-276 because of their lower cost, as shown in Table 4. ZERON 100 offers the lowest price, of the three but it is more difficult to clad to carbon steel than austenitic alloys, such as AL-6XN.

5.0 CONCLUSIONS

1. The critical crevice temperature (CCT) of some corrosion resistant alloys has been measured in two simulated FGD slurries at pH4.
2. Alloy 2205 showed itself to be marginal in both slurries, having a CCT around normal operating temperatures.
3. Alloys ZERON 100, AL-6XN and C-276 all showed CCT values well in excess of normal operating temperatures. This is in agreement with the successful FGD service experience with these alloys.
4. ZERON 100 offered the lowest price of the alternatives to 2205, but AL-6XN is easier to clad to carbon steel for a retrofit.

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3. R Francis, G Byrne, G Warburton and S Hebdon, Paper 479, Corrosion 98, NACE International, Houston, TX, USA, March, 1998.
4. J W Oldfield and W H Sutton, Brit. Corr. J. **13** (1978) 13 and 104



TABLE 1 Nominal composition of the test alloys.

ALLOY	UNS No.	COMPOSITION (wt%)							PREN*
		Fe	Cr	Ni	Mo	N	W	Cu	
2205	S32205	Bal	22.4	4.66	3.1	0.16	-	-	35.2
ZERON 100	S32760	Bal	25.3	6.97	3.58	0.226	0.52	0.57	41.6
AL-6XN	N08367	Bal	20.4	23.7	6.24	0.22	-	-	44.5
C-276	N10276	6.1	15.99	Bal	15.29	-	3.3	-	71.9

Bal = Balance
 PREN %Cr + 3.3(%Mo + 0.5x%W) +16x%N

FIGURE 2 Composition of the simulated FGD slurries.

SPECIES	CONCENTRATION	
	Anthracite	Lignite
CaSO ₄	66.7g/L	66.7
Chloride	40g/L	15g/L
Fluoride	50g/L	200g/L
Bromide	250mg/L	250mg/L
“Dithionate”	200mg/L	200mg/L
Fe ³⁺	10mg/L	10mg/L
Al ³⁺	30mg/L	30mg/L
pH	4	4



TABLE 3 Critical crevice temperatures in simulated FGD slurries.

SLURRY TYPE	CHLORIDE (g/L)	pH	CRITICAL CREVICE TEMPERATURE (°C)			
			2205	Z100	AL-6XN	C-276
Anthracite	40	4	47.8	84.5	>84.5	>84.5
			42.3	80.1	>81.5	>81.5
			56.6	61.3	>84.5	>84.5
			42.4			
Lignite	15	4	68.0	>83	>83	>83
			79.8	>83	>83	>83
			57.1	>84.5	>84.5	>84.5

TABLE 4 Comparative prices for hot rolled 10mm plate (Spring 2012).

ALLOY	PRICE (2205 =1)
2205	1
ZERON 100	1.5
AL-6XN	3.1
C-276	7.0

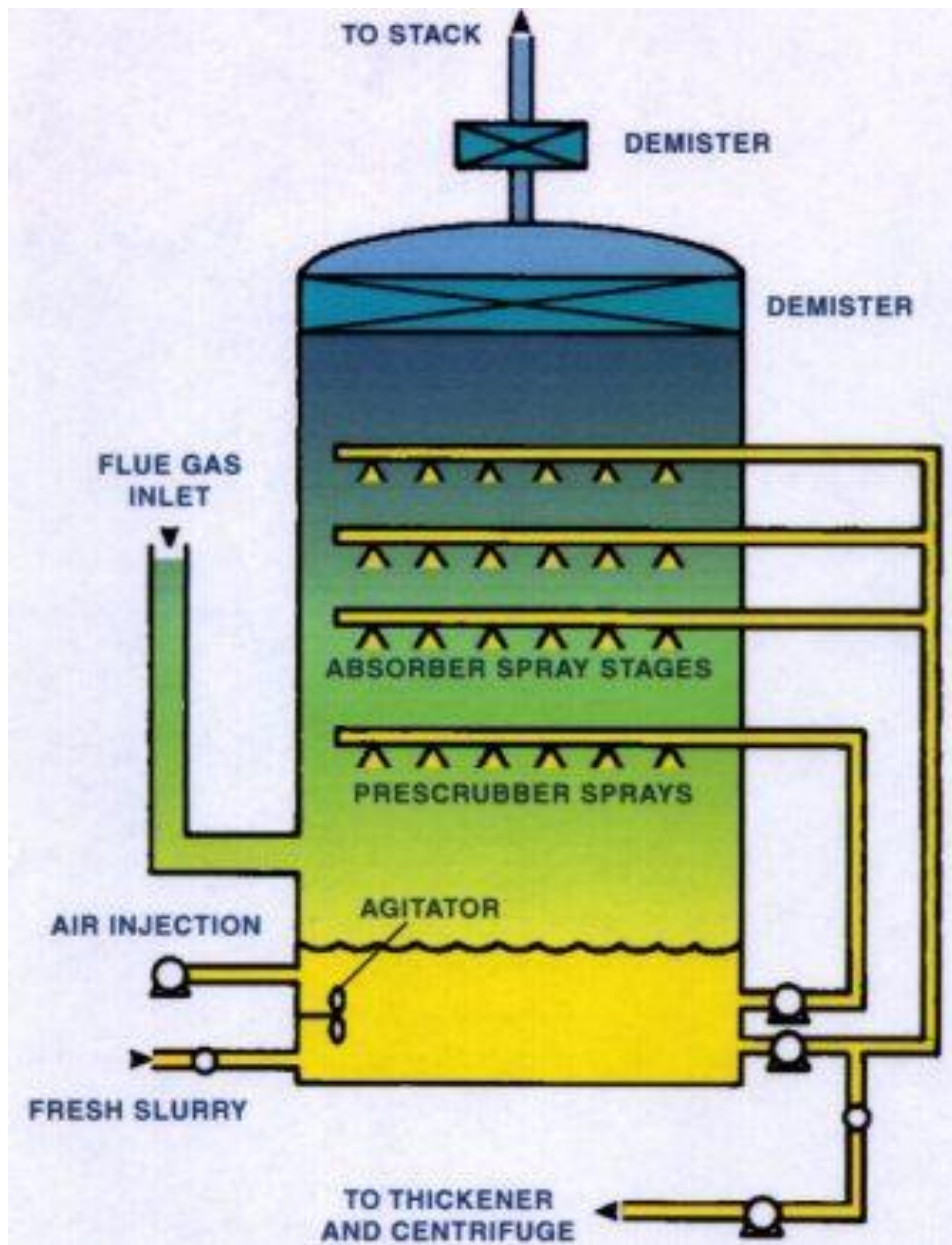


FIGURE 1 Schematic diagram of a typical FGD absorber tower layout.

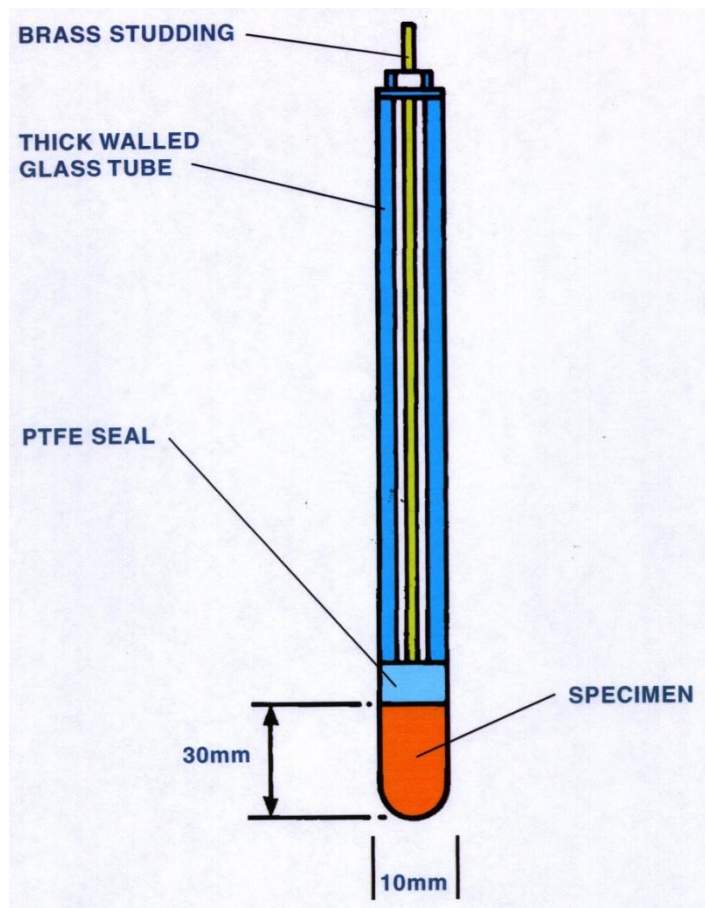


FIGURE 2 Appearance of sample and mount (not to scale).

FIGURE 3 Typical current density and temperature versus time trace at +300mV SCE in FGD slurry with 40g/L chloride at pH4

