FOSSIL

DUCT INJECTION TECHNOLOGY PROTOTYPE DEVELOPMENT

Materials Corrosion Report, Revision 1

By
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DUCT INJECTION TECHNOLOGY PROTOTYPE DEVELOPMENT

MATERIALS CORROSION REPORT
REVISION 1

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NOTICE

Revision 0 of this report, which was issued July 1990, contained an error in the calculated corrosion rates. The values were skewed by a constant factor, although the relative order of the materials corrosion resistances did not change.

This Revision 1 is issued to provide the corrected values. All corrections are marked in the text herein with a vertical line in the left hand margin. Corrections have been made on the following pages:

Page 1 - Abstract
Page 10 - Test Results
Page 11 - Table 5
Page 12 - Figures 4 and 5
Page 13 - Figures 6 and 7
Page 14 - Figures 8 and 9
Page 15 - Discussion
Page 19 - Recommendations

KEYWORDS

Duct Injection	Corten	Dry FGD
Dry Scrubber	Hastelloy C-276	
Carbon Steel	317SS	

ABSTRACT

This report describes a test program conducted to determine the corrosion rate of materials in the dry scrubber or duct injection systems. Four materials were evaluated: 1010 carbon steel, Corten, 317SS and Hastelloy C-276. The results show that acidic conditions result in higher corrosion rates than alkaline conditions for all the materials. The carbon steel, Corten and stainless steel show moderate to heavy pitting attack in the acidic environment. For the alkaline conditions, the corrosion rates of carbon steel and Corten were higher than the stainless steel or Hastelloy C-276. Also, the corrosion rate of abraded specimens were four times those of unabraded specimens in the flue gas.

It is probable that areas of wall-wetting and plugging in the duct injection process will exhibit high rates of corrosion for the carbon steel, Corten, and stainless steel materials. General corrosion and pitting corrosion will predominate. Additionally, abraded duct areas will corrode at a significantly higher rate than unabraded duct materials.

1.0 INTRODUCTION

Duct Injection systems remove the sulfur dioxide from flue gas streams by injecting a wet or dry sorbent in the flue gas. B&W is participating in a cooperative effort coordinated by the U.S. Department of Energy to evaluate and design advanced duct injection systems. These systems involve chemical reactions to neutralize and precipitate sulfur dioxide in the flue gas. Calcium hydroxide is injected as a sorbent which reacts with sulfur dioxide in the flue gas to form a calcium sulfite compound. This reaction:

SO_2 Absorption: $SO_2 + Ca(OH)_2 \rightarrow CaSO_3 \cdot 1/2H_2O + 1/2\ H_2O$
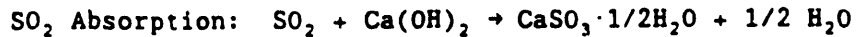
The calcium sulfate is collected in the ash hoppers and either disposed at landfills or recycled as construction materials. Appendix A is a review of operating experience, corrosion problems and anticipated corrosion problems in these dry flue gas desulfurization (FGD) systems. The major material concerns are:

- Corrosion from condensing flue gas (wall wetting) and underdeposit damage from deposited fly ash and calcium sulfite. Weld corrosion is also a concern.

- Erosion from slurry injection of the chemical sorbent.

- Cracking of ceramic components from thermal cycling. Some components have a ceramic coating, such as aluminum oxide to provide protection from the highly erosive environment at the slurry injection sites. These components crack and fail prematurely because of thermal cycling.

Specifically this test program was designed to determine the corrosion rates of the duct injection construction materials in a range of environments. Initially, a survey of the literature was completed to determine what materials should be included in the test program. Carbon steel and Corten A are alloys presently used as the ductwork material. Because the majority of installations of duct injection systems will be retrofits, it is appropriate to evaluate carbon steel and Corten corrosion behavior in this test program. Stainless steel (300 series) is a bolt and hanger material in existing duct structures and also a possible duct material. Hastelloy C-276, a nickel-based alloy, is being used in highly corrosive areas of wet scrubbers.

2.0 EXPERIMENTAL PROCEDURE

A two-part test program was designed to meet the goals of this test program. First, retort tests were used to evaluate the corrosion behavior of materials under conditions closely simulating expected service environments. Second, electrochemical corrosion tests were performed to evaluate the effect of chlorides, oxygen, and pH upon corrosion rates.

In the retort tests, carbon steel, Corten, 317 SS, and Hastelloy C-276 were exposed in a simulated flue gas atmosphere. This test technique has been used in other fossil environment materials evaluations.(1) Each of the four material types were exposed in the five different environments or conditions shown in Table 1. Also, the effect of abrasion upon corrosion was determined for materials exposed in the flue gas, with no deposits.

Table 1. Retort Test Parameters

Materials: Hastelloy C-276, Corten A, 317 SS, Carbon Steel

Simulated Flue Gas:

Composition: 3.5% SO_2, 9.0 CO_2, 7.2% O_2, 12.1% H_2O, N_2 balance
Flow Rate: 351.3 ml/minute
Temperature: 150°F
Time: 1000 hours

Environment	Unabraded	Abraded
No Deposit	x	x
Slaked Lime	x	
Hydrated Lime	x	
Fly Ash	x	
Fly Ash + Hydrated Lime	x	

Potentiodynamic and polarization resistance methods were used to evaluate corrosion behavior in aqueous environments. Polarization resistance is a technique which electrochemically determines the corrosion rate. The oxygen content of the solutions was controlled by sparging with either nitrogen or with air. The pH of the solutions were adjusted by adding either sulfuric acid or sodium hydroxide. Chloride additions were as sodium chloride. The electrochemical test matrix is shown in Table 2.

Table 2. Electrochemical Test Environments

Environment	1010 CS	CORTEN	317 SS	C-276
• pH 2.5 deaerated		x	x	x
• pH 2.5 aerated 10 ppm Cl	x	x	x	x
• pH 12.5 deaerated	x	x	x	
• pH 12.5 aerated	x	x	x	
• pH 12.5 deaerated 10 ppm Cl	x	x	x	x
• pH 12.5 deaerated 1000 ppm Cl	x	x	x	

2.1 Retort Tests

2.1.1 Retort Test Facility

The retort test system used in this test is shown in Figure 1. The retort or reaction vessel is placed in a furnace. The simulated flue gas is delivered to the retort from pre-mixed bottle gas. The water is metered as a liquid and converted to steam before injection to the combustion gas stream. The gas is brought into thermal equilibrium before being delivered into the test retort. The effluent is connected to a chemical scrubber to prevent sulfur fumes from escaping. A partitioned tray holds the ceramic crucibles containing the corrosion specimens and the deposit mixtures. Figure 2 shows this capsule and specimen tray.

2.1.2 Test Specimens

Four different alloys were evaluated in this test. The chemistry for each of the alloys and the reported physical properties are listed in Table 3. Rectangular specimens (0.5 inch x 1.0 inch x 0.0625) were made from each material. The specimens were measured and weighed before the test exposure and reweighed after each test exposure. Before the final weighing, the specimens were chemically cleaned to remove scales and oxide deposits. The abraded specimens were prepared by grit blasting the surface. The abraded surface roughness was measured at 20 to 25 RMS (root mean square) by a profilometer.

2.1.3 Retort Test Procedure

The specimens were placed in alumina crucibles, covered with deposit (where applicable), and then placed into the retort. The retort was then placed into a controlled furnace. Finally, the furnace was heated; and the gas and water flow were established for the remainder of the test. In this program the combustion gas environment was simulated using the gas mixture shown in Table 4.

Table 4. Simulated Flue Gas

SO_2	3.5%
CO_2	9.0%
O_2	7.2%
H_2O	12.1%
N_2	Balance

Gas Flow Rate	351.3 ml/minute
Water Flow Rate	1.8 ml/hour

2.2 Electrochemical Tests

2.2.1 Electrochemical Test Apparatus

The low temperature (90°F) corrosion measurements were performed in electrochemical glass cell assemblies. Figure 3 shows a schematic of this assembly. The specimen (commonly called the working electrode) is suspended in the test solution. The graphite rods are used as counter electrodes and
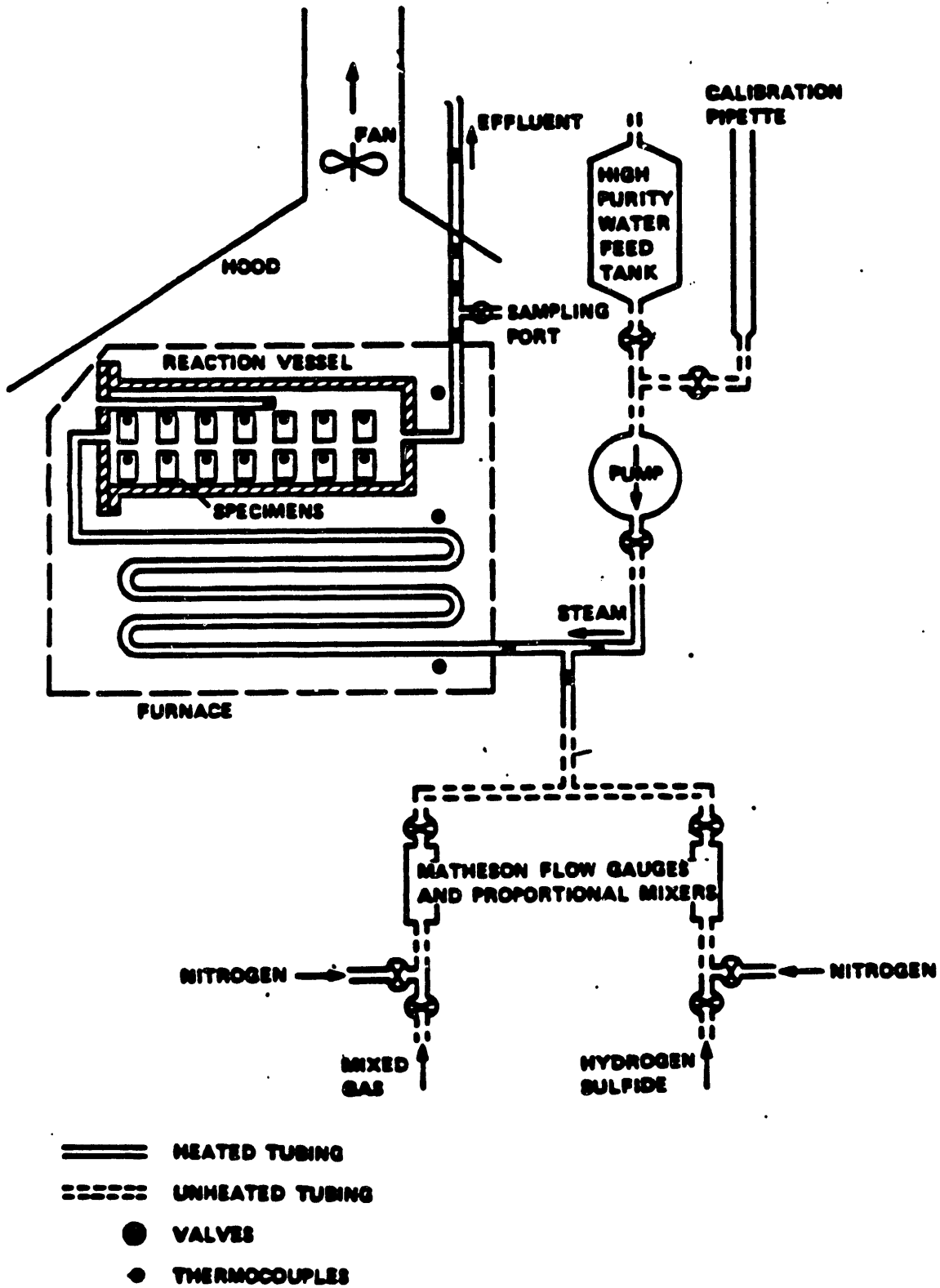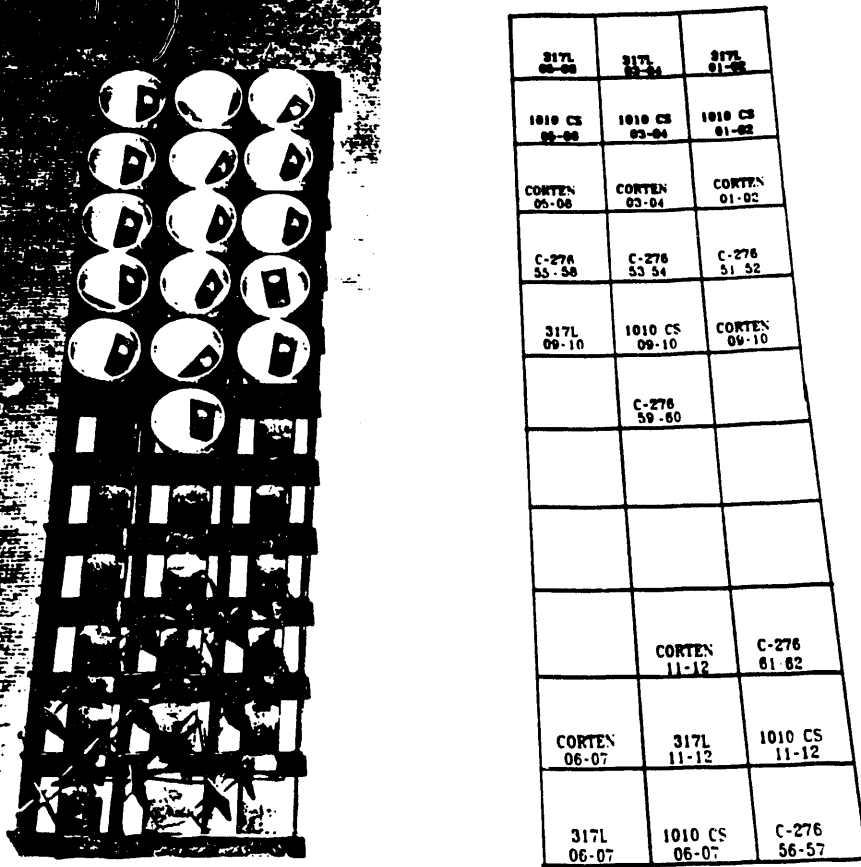
Figure 1.   Schematic of retort test facility.

Figure 2. Specimens and rack.
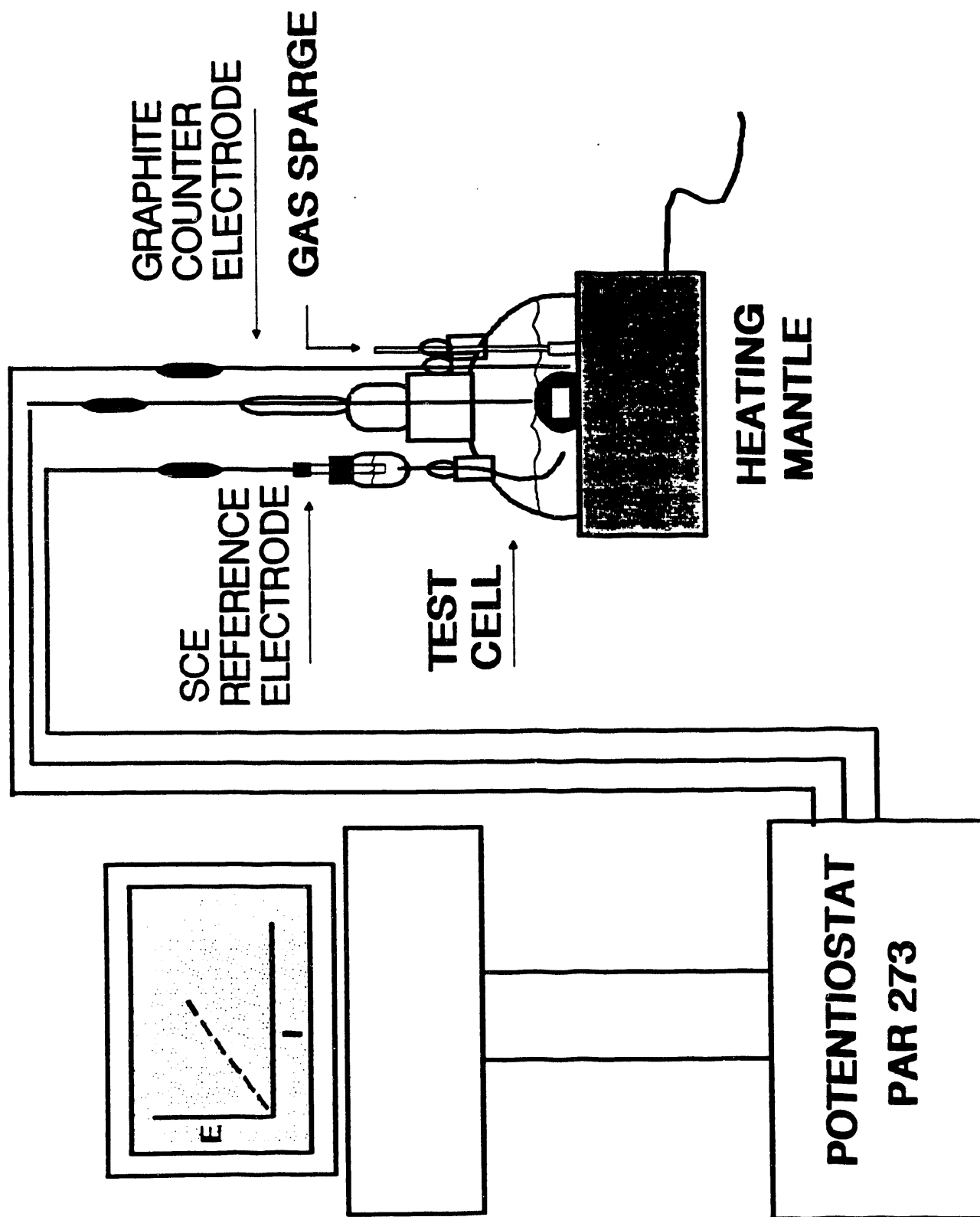
Figure 3.   Electrochemical test assembly.

Table 3. Chemical Compositions and Mechanical Properties of Test Materials

Material	Mill/Heat	C	Mn	P	S	Si	Cu	Ni	Cr	Fe	Mo	W	V	Nb	N_2
Corten A	U.S. Steel/D023	.09	.39	.10	.012	.38	.26	.14		Bal					
317L SS	USINOR/D637	.02	1.66	.026	.006	.50		12.96	18.32	Bal	3.01				.038
CS 1010	Lapham-Hickey P815	.11	.36	.01	.015	--									
INCO C276	Huntington E796	.01	.45	.008	.001	.05		56.4	15.97	5.80	16.2	3.92	.20	1.01	

Material	Heat	Tensile Str.	Elong.	Hardness	Yield Point
Corten A	D023	79.5 ksi	24.0%	80 Rb	54.0 ksi
317L SS	D637				
CS 1010	P815				
INCO C276	E796	115 ksi	63% (2" dia)	88 Rb	52.9 ksi

'Furnished by Metal Samples Co.

supply the current flowing to the working electrode during the test. The reference electrode is a saturated calomel electrode (SCE). A gas sparge tube was used to equilibrate the solution with the cover gas. The temperature was maintained using heating mantles and voltage controllers.

2.2.2 Electrochemical Test Procedure

A linear polarization resistance technique was used to determine the corrosion rates of the materials in an aqueous environment. The procedure used is as follows:

1. Apply a small potential on both sides of the open circuit potential ($\sim$10 - 30 mv).

2. Measure the current change over for this potential range.

3. Calculate the slope on the linear part of resulting potential-current density plot.

The corrosion current, i_{corr}, is related to the slope of the plot:

$$\frac{\Delta E}{\Delta i} = \frac{B_A \, B_C}{2.3 \, (i_{corr})(B_A + B_C)}$$

Thus,

$$i_{corr} = \frac{B_A \, B_C}{2.3 \, (B_A + B_C)} \frac{\Delta i}{\Delta E}$$

Where,

$\Delta E / \Delta i$ = slope of the Linear Polarization Plot.

B_A, B_C = anodic and cathodic Tafel constants.

B_A = 100 millivolts/decade of current

B_C = 100 millivolts/decade of current

i_{corr} = corrosion current, μA

The corrosion current can be related directly to the corrosion rate using the following:

$$\text{Corrosion rate (mpy)} = \frac{0.13 \, I_{corr} \, (E.W.)}{d}$$

where E.W. = equivalent weight of the corroding species, g/f
   d = density (g/cm^3)
   I_{corr} = current corrosion density, μA/cm^2

3.0 TEST RESULTS

3.1 Retort Test Results

Table 5 lists the results of the retort furnace tests. These results are presented graphically in Figures 4-9.

Table 6 shows the chemical analysis of the environments before and after the one-thousand hour exposure. The slaked and hydrated lime become the same environment after a short time due to the water vapor in the flue gas. The reaction which transforms lime to hydrated lime and slaked lime is:

$$CaO + H_2O \rightarrow Ca(OH)_2$$
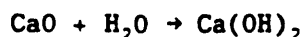
This reaction occurs quite rapidly as evidenced by the similar corrosion behavior in both the slaked and hydrated lime.

In the lime deposits corrosion is general corrosion or wastage. However, in deposits containing fly ash, pitting is the dominant corrosion mechanism. During exposure to the flue gas, the deposits containing fly ash become quite acidic. In these acidic fly ash deposit environments, the 317L SS show the highest corrosion rates because of its sensitivity to pitting. However, the corrosion rates for all the materials in these two acidic environments were consistently above 10 mpy.

Several general statements concerning the corrosion of the four test materials in simulated duct injection environments can be made:

- Corrosion rates generally increase with time for materials not covered with deposits in the simulated flue gas.

- In the deposit free simulated flue gas, the corrosion rate of the 317 stainless steel is low and the corrosion rate of the Hastelloy C-276 is negligible.

- Corrosion rates generally increase when specimen surfaces are abraded prior to flue gas exposure.

- The corrosion rate of the Hastelloy C-276 is much lower than the other three materials in all the environments except those with fly ash in the deposits, where 1010 carbon steel had a lower rate. However, the corrosion rate calculation does not adequately account for pitting attack; 1010 was pitted, C-276 was not.

- In the two caustic environments, slaked lime and hydrated lime, the corrosion rates of the 317L stainless steel and Hastelloy C-276 were considerably less than the Corten and carbon steel.

- The fly ash and the hydrated lime plus fly ash mixture become acidic when exposed to flue gases; all the materials have higher corrosion rates in these acidic environments compared to the alkaline environments.

- In fly ash and hydrated lime plus fly ash environments, the 1010 carbon steel, Corten, and 317L showed moderate to heavy pitting. C-276 was essentially pit-free.

Table 5. Furnace Results – Corrosion Rates

Condition	Material	Corrosion Rate (mpy) 500 Hours	Corrosion Rate (mpy) 1000 Hours
Bare in Wet Flue Gas	1010 CS	1.42×10^{-1}	1.07×10^{-1}
	Corten A	5.89×10^{-2}	1.00×10^{-1}
	317L SS	0*	4.00×10^{-2}
	C-276	0*	1.14×10^{-2}
Abraded in Wet Flue Gas	1010 CS	3.56×10^{-1}	4.78×10^{-1}
	Corten A	4.56×10^{-1}	4.37×10^{-1}
	317L SS	0*	2.36×10^{-1}
	C-276	1.83×10^{-2}	3.40×10^{-2}
Slaked Lime	1010 CS	7.57×10^{-1}	1.98×10^{-1}
	Corten A	1.01	8.18×10^{-2}
	317L SS	5.26×10^{-2}	4.66×10^{-2}
	C-276	0*	1.82×10^{-2}
Hydrated Lime	1010 CS	5.32×10^{-1}	6.06×10^{-2}
	Corten A	5.71×10^{-1}	8.51×10^{-1}
	317L SS	6.91×10^{-2}	3.07×10^{-2}
	C-276	8.89×10^{-3}	1.36×10^{-2}
Hydrated Lime + Fly Ash	1010 CS**	8.08×10^{-1}	2.40×10^{-1}
	Corten A**	8.98×10^{-1}	3.26×10^{-1}
	317L SS**	9.15×10^{-1}	1.84
	C-276	6.69×10^{-1}	1.16
Fly Ash	1010 CS**	1.43	2.03
	Corten A**	3.23	8.27
	317L SS**	9.16	5.09×10^{1}
	C-276	3.13	2.70

* Weight gain observed; therefore corrosion rate taken to be zero.

** These specimens were moderately to heavily pitted, pitting attack is generally not accounted for in corrosion rate calculation.

Table 6. Pre and Post Test Chemistries

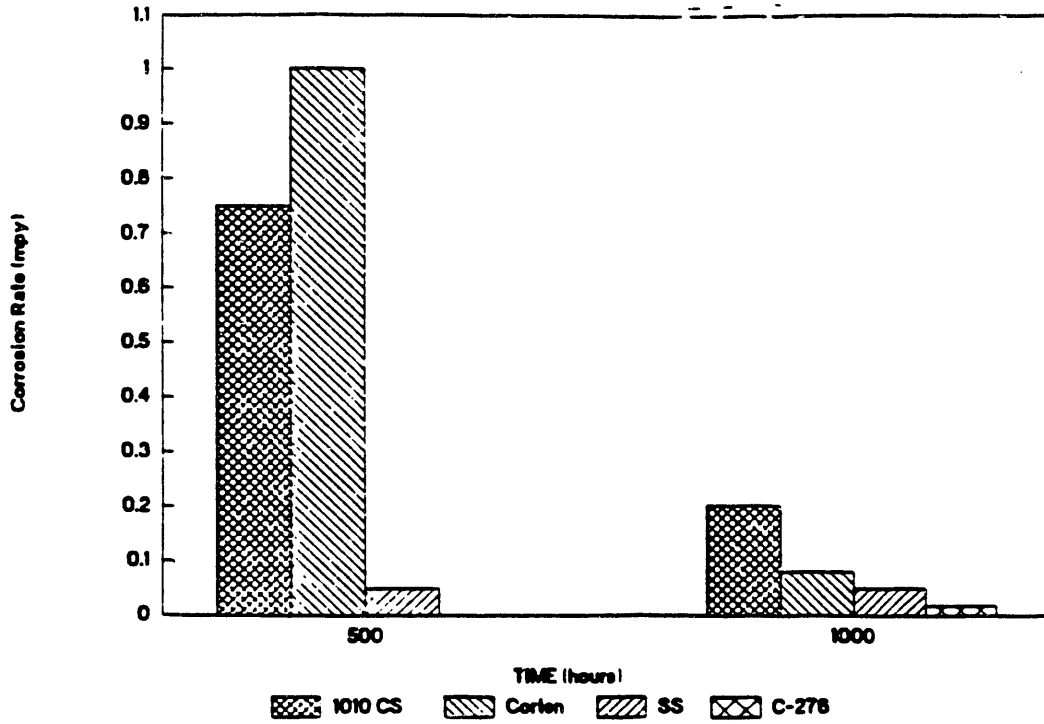| Analysis	Fly Ash Pre-	Fly Ash Post-	Fly Ash + Hydrated Lime Pre-	Fly Ash + Hydrated Lime Post-	Hydrated Lime Post-	Slaked Lime Post-
pH	10.4	1.37	12.6	2.0	12.6	12.5
Ca (%)	1.1	0.5	28.3	15.0	44.1	37.4
S (%)	0.31	16.4	0.36	17.7	7.8	10.1
iron (%)	9.1	4.13	4.35	2.58	7.8	10.0

Figure 4.   Corrosion rate of Corten A, 1010CS, C-276 and 317L SS in a slaked
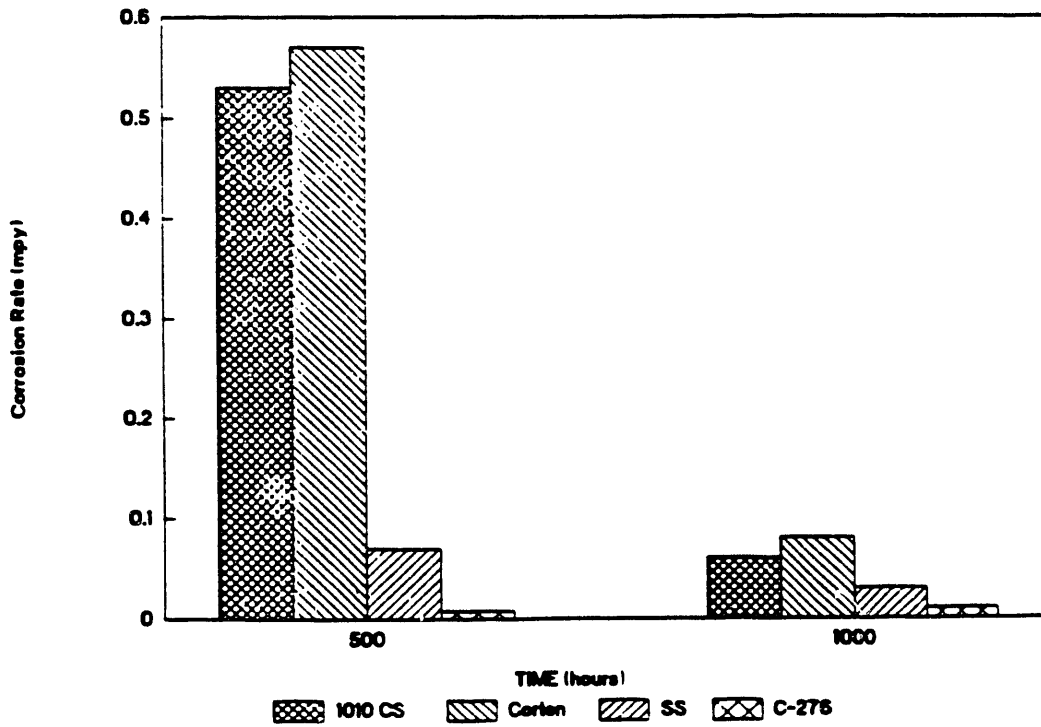   lime environment.

Hydrated Lime

Figure 5.   Corrosion rate of Corten A, 1010CS, C-276 and 317L SS in a
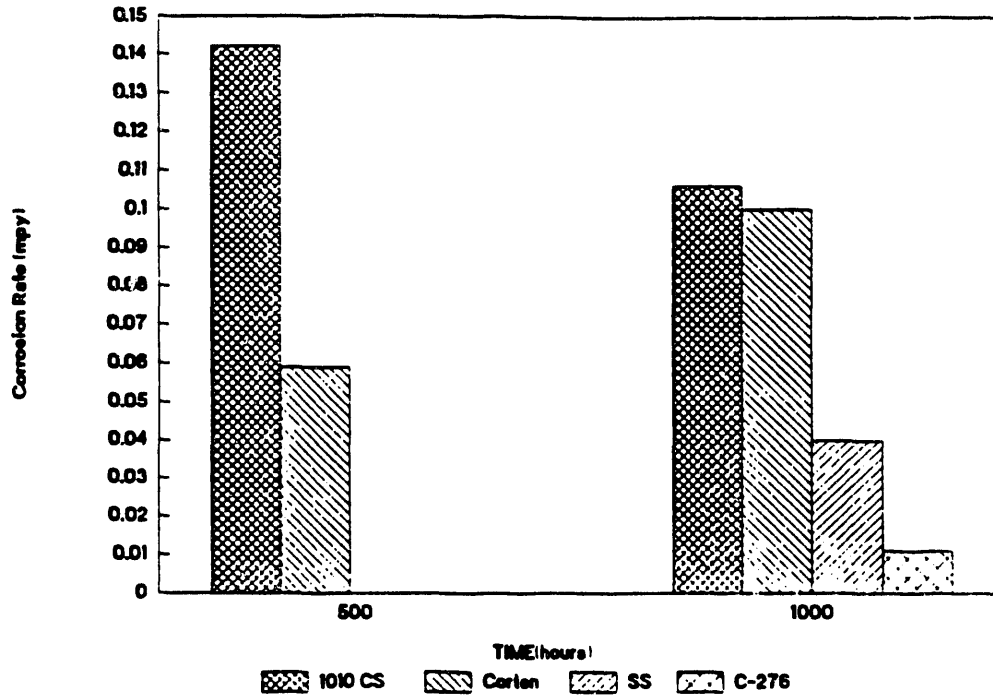   hydrated lime environment.

Wet Flue Gas

Figure 6.   Corrosion rate of Corten A, 1010CS, C-276 and 317L SS in vet flue
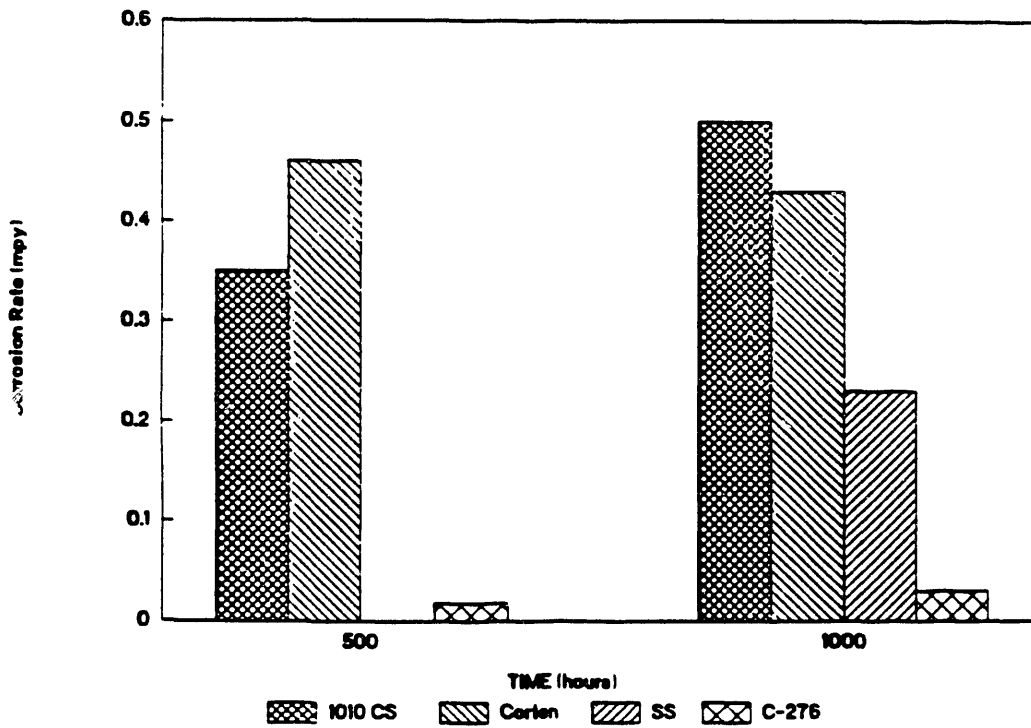gas.

Abraded + Wet Flue Gas

Figure 7.   Corrosion rates of abraded 1010CS, Corten A, C-276 and 317L SS in
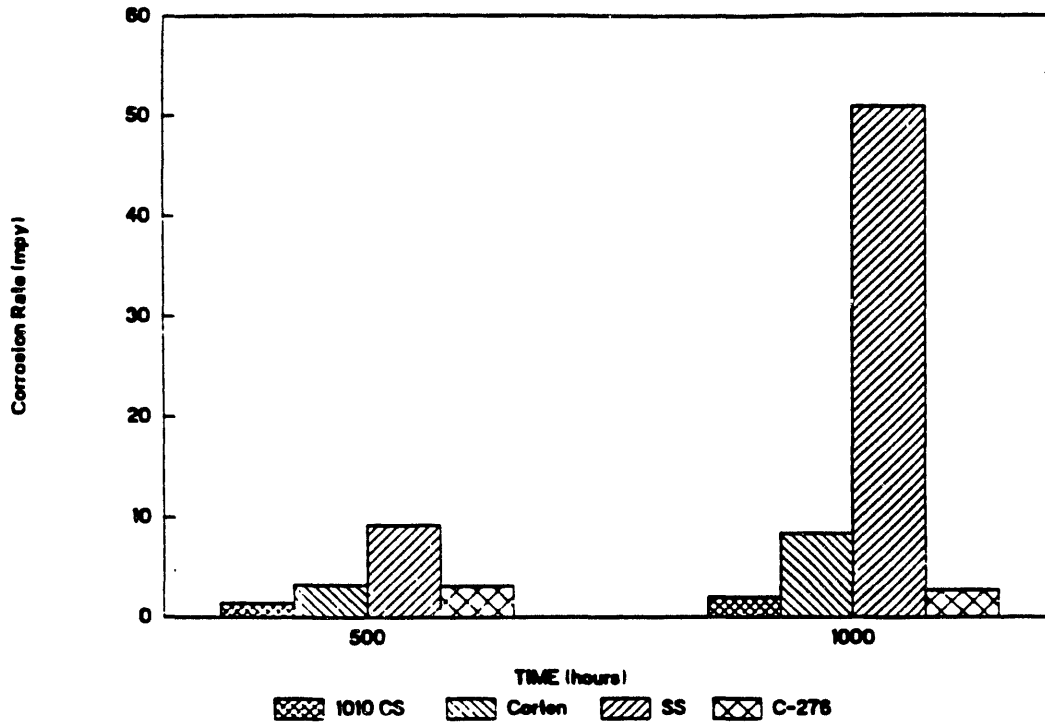vet flue gas.

Flyash

Figure 8.   Corrosion rate of Corten A, 1010CS, C-276 and 317L SS in fly ash.
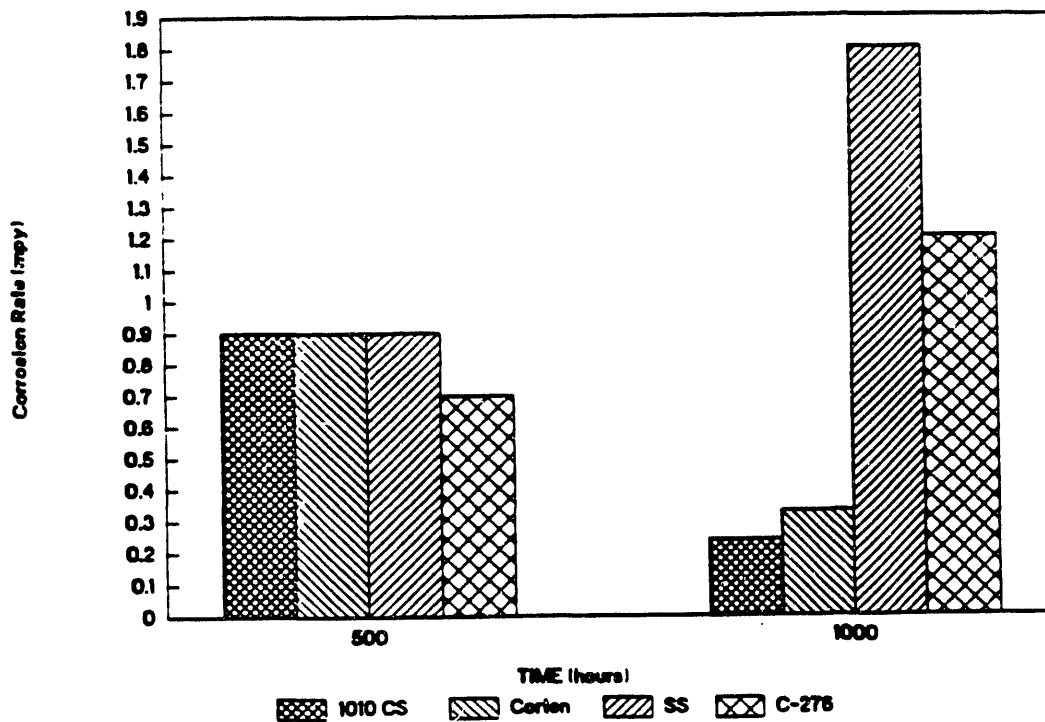
Lime + Flyash

Figure 9.   Corrosion rate of Corten A, 1010CS, C-276 and 317L SS in hydrated lime and fly ash.

3.2 Electrochemical Test Results

Table 7 lists the corrosion potential (E_{corr}), the corrosion current density (I_{corr}), and corrosion rate (mils per year, mpy) for six electrochemical tests. The results of the electrochemical testing show the following:

- Corrosion rates increase when replacing nitrogen with air as a cover gas in acidic environments.

- 1010 carbon steel and Corten are the most sensitive materials to air ingress.

- In a caustic environment the corrosion rates are low whether the cover gas is nitrogen or air.

- The addition of chloride increases the corrosion rate for carbon steel, stainless steel and Corten A in the low pH solution.

- Chlorides increase the corrosion rate of 1010 carbon steel but have no effect upon 317L stainless steel on Alloy C-276 in the high pH solution.

4.0 DISCUSSION

4.1 Retort Test Results Discussion

The retort test results show that any upset condition which causes wall wetting or wet ash plugging can result in acidic underdeposit conditions. An acidic environment causes pitting and heavy wastage corrosion. All four materials in this test program are attacked in acidic flue gas environments. Depending on fuel chemistry, deposit chemistry, and operating conditions, the environment at the metal wall will range from strongly acidic to strongly alkaline. When the local environment is alkaline, there is little corrosion concern. When the underdeposit chemistry becomes acidic the corrosion rates are higher than those in alkaline environments for all materials investigated. Sulfur dioxide and oxygen can condense or diffuse into deposits and cause them to become neutral or even acidic.

The deposits can become quite corrosive with time, unless they are removed and refreshed with unreacted calcium hydroxide.

Figure 10 and 11 shows the effect of temperature and sulfuric acid condensation on the corrosion rate of carbon steel.(2,3) Under ideal conditions in the dry scrubber or duct injection environment the corrosion rate of carbon steel or Corten A will be relatively low. The ideal environment would be dry unabraded walls with no deposits, or where deposits are continually removed and refreshed; also no temperature cycling and no condensation should be allowed to occur. However, the ideal is difficult to maintain and many duct injection pilot tests have experienced wall wetting and plugging.(4,5) This experience suggests that high corrosion rates will be experienced in localized regions where moisture or deposits can collect.

4.2 Electrochemical Test Discussion

These results show that the introduction of air in acidic environments significantly accelerates the corrosion rate. There is not a large effect of air upon corrosion rates in high pH environments.

An increase in chloride concentration causes an increase in corrosion rates for 1010 carbon steels, Corten and 317L SS in low pH environments. This trend has been seen elsewhere (6). Stainless steels are used as supports, hangers, or joint connectors in fossil back end gas containment flues. Therefore, if acidic condensing environments with chlorides exist, then 317L SS will suffer from crevice corrosion. Hence, there is considerable concern about the life expectancy of these parts.

It is likely that corrosion rates seen in this study will occur, at least in some localized areas. The corrosion mechanism for localized acidic areas is pitting. Pitting attack is statistical in nature and can be difficult to quantify and predict time-to-failure. Metal loss is small but localized when pitting occurs. The averaged weight loss generated corrosion rates presented in this report do not indicate the depth of pitting. A more detailed pit depth distribution analysis could aid the prediction of component life times.

Corrosion in dry scrubber or duct injection environments was initially assumed to be much lower, compared to wet scrubber environments. There are two reasons for these conclusions: 1) ideally no wall wetting or plugging will occur and, 2) the neutralization of the acidic flue gas condensation by the basic lime will make conditions less corrosive. However, under less than ideal operating conditions wall wetting, surface erosion, and plugging do occur in duct injection systems. If wall wetting occurs the underdeposit environment can be acidic, even when the fly ash and bulk deposits are highly alkaline. Although some speculate the inherent alkalinity of the ash would neutralize the acid condensate, this work and others (7) suggest that acid conditions will exist under deposits. The acidic condensate flue gas constituents are continually supplied to a static deposit, causing it to be completely reacted and become acidic. The chemical aspects of deposits or poultice formation and corrosion is still uncertain and depend on fuel chemistry, diffusion rate of the acid gases and condensate through the ash, and the amount of deposit. Conservative designing would dictate a resistant nickel-chrome alloy in areas of potential localized corrosion. Areas where fly ash plugging and condensation occur have a potential for corrosion rates comparable to the wet scrubber environment.

5.0 CONCLUSIONS

The conclusions from this laboratory program are:

● In areas where static ash deposits occur or where the wall is wet, the chemistry will vary from strongly acid to alkaline.

● For materials evaluated in this program, significant corrosion rates can occur, if the localized deposit chemistry is acid.

Table 7. Electrochemical tests – Corrosion Rates – MPY

Environment: pH 2.5, 90°F, H₂

Material	E_{corr}, mv	I_{corr}, μa/cm²	MPY
1010 CS			
Corten A	.41	.11	.05
317L SS	.41	.11	.05
C-276	.20	.14	.07

Environment: pH 12.5, 90°F, H₂

Material	E_{corr}, mv	I_{corr}, μa/cm²	MPY
1010 CS	.547	.69	.32
Corten A	.392	16.8	8.8
317L SS	-.377	.22	.1
C-276			

Environment: pH 2.5, 10 ppm Cl Air

Material	E_{corr}, mv	I_{corr}, μa/cm²	MPY
1010 CS	-.540-.547	72.9	33.7,88.8
Corten A	-.558-.560	237,357	110,169
317L SS	.082	*	.93
C-276	.690	.57	.28

Environment: pH 12.5, 90°F, Air

Material	E_{corr}, mv	I_{corr}, μa/cm²	MPY
1010 CS	-.383	.69	.32
Corten A	-.419	.24	.11
317L SS	-.440	.31	.14
C-276			

Environment: pH 12.5, 90°F, 10 ppm Cl, H₂

Material	E_{corr}, mv	I_{corr}, μa/cm²	MPY
1010 CS	-.579	.62	.29
Corten A	-.505,-.505	.27,4.8	.14,2.27
317L SS	-.478	.31	.14
C-276	-.470	.011	.013

Environment: pH 12.5, 90°F, H₂, 1000 ppm Cl-

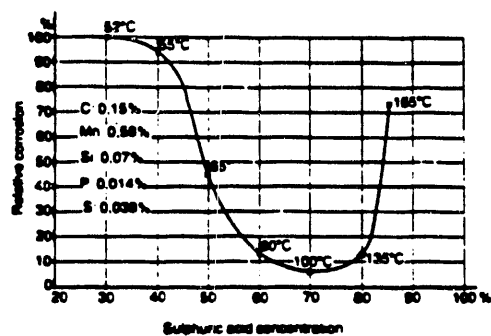| Material	E_{corr}, mv	I_{corr}, μa/cm²	MPY
1010 CS	*	*	5,20
Corten A	-.420,-.280	.45,.39	.21,.10
317L SS	*	*	.04
C-276			

*Test not performed.

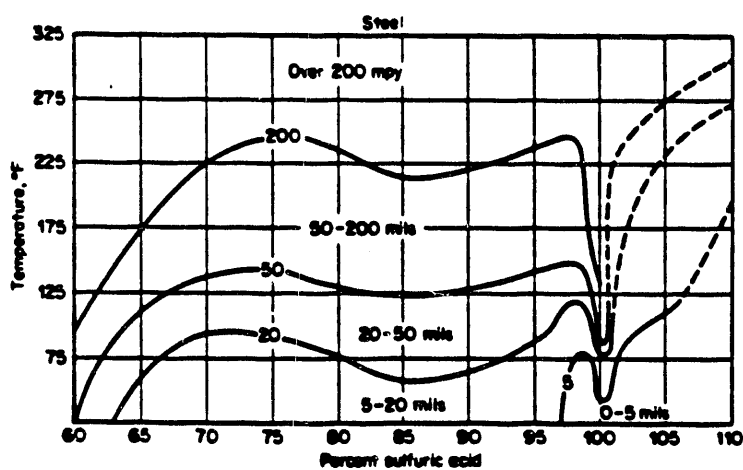**Figure 10.   Sulfuric acid concentration.**

Figure 11.   Corrosion of steel by sulfuric acid as a function of concentration and temperature.

o Abrasion or erosion of surfaces can accelerate corrosion rates.

o Stainless steel (317L) and Hastelloy C-276 have lower corrosion rates than carbon steel and Corten A in alkaline environments.

o Chloride ions will accelerate the corrosion when the wall chemistry is acidic and oxygen is present.

6.0 RECOMMENDATIONS

Based on this test program, the following recommendations are made:

o Unless wall wetting and deposition can be completely avoided, material alternatives or coatings should be considered.

o A more quantitative comparison of pitting attack is recommended for future studies of materials in acidic flue gas environments.

Additional recommendations for the duct injection systems are presented in Appendix A.

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                  Group Supervisor

Approved by: _____
                  B. P. Miglin
                  Section Manager

gea

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APPENDIX A

o   P. V. SMITH - CHEMICAL ENGINEERING SECTION, ARC

rom   S. L. HARPER - MATERIALS PERFORMANCE SECTION, ARC

ust.

File No.
COLD-END CORROSION

ubj.   CORROSION OF MATERIALS IN FLUE GAS PATH

Date DECEMBER 11, 1989

This letter to cover one customer and one subject only

Attached, please find the "Corrosion of Materials in Flue Gas Path" design review topical report.

S. L. Harper

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Attachment

CORROSION OF MATERIALS IN FLUE GAS PATH

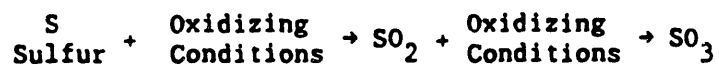### INTRODUCTION

Introduction - Statement of Topic

This is a review of the operative back-end corrosion processes of a coal-fired steam generator. A brief review of operating experience and corrosion problems in dry scrubbers is also presented. A review of the corrosion problems expected in duct injection sites/dry scrubbers is presented.

Identification of Potential Corrosion Problems

Cold-end condensation is the major corrosion problem in the boiler back-end. Sulfur and chlorine constituents of the combustion gas condense and rapidly corrode exposed metal surfaces. There are many variables that affect the cold-end corrosion. A description of these corrosion processes is presented in subsequent sections of this paper.

Corrosion from Sulfur in Flue Gas[1]

In sulfur-containing fuels, the sulfur is oxidized to sulfur dioxide and then sulfur trioxide as shown below:

$$\begin{array}{c} S \\ Sulfur \end{array} + \begin{array}{c} Oxidizing \\ Conditions \end{array} \rightarrow SO_2 + \begin{array}{c} Oxidizing \\ Conditions \end{array} \rightarrow SO_3$$

The factors that influence the sulfur trioxide content are:[2]

- sulfur content of the fuel
- excess air
- presence of catalysts
- presence of impurities

Sulfur trioxide (SO_3) readily reacts with water vapor present in a gas process stream to form sulfuric acid. Below the boiling point of sulfuric acid (620°F), most of the SO_3 will combine with the available water to form this acid.

$$SO_3 \ (g) + H_2O \ (g) \rightarrow H_2SO_4 \ (g).$$
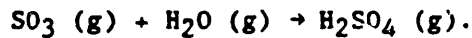
When hot flue gas comes in contact with a metal surface, the liquid in the gas will condense as a film on the cooler metal surface. The temperature at which the sulfuric acid condenses is called the acid dew point which is primarily dependent on the partial pressure of water vapor and SO_3 gas. Thus the percent concentration of the sulfuric acid as a gas is a critical factor in determining the concentration of the sulfuric acid condensing on the metal surface.

Operation Variables Affecting Dew Point Corrosion

Variation in water content of the flue gas depends on several factors, such as air inleakage from the condenser side or leaks in upstream water washing equipment. Other factors that can contribute to an increase in flue gas moisture content are:

- instrumentation leaks
- boiler tube leaks
- forced draft fan ingestion
- steam coil air preheater leak
- excessive boiler or air heater soot blowing

At the dew point, liquid condenses as individual drops or a continuous film, depending on the surface tension characteristics of the liquid.

The heat flux through the film is defined by factors such as flow configuration and tube dimensions. The heat flux along with the mass velocity of the gas defines the turbulence of the film. There are a multitude of factors affecting the film formation and localized cold-end corrosion behavior in each specific boiler location. The film formation is also important in maintaining an adequate heat transfer on the cooling surface, since a thick film will have a measurable temperature gradient across its depth.

Variables that Affect Amount of Film Condensation

The variables that effect film condensation are: temperature, velocity of the flue gas, water partial pressure, design factors, and inert substances in the flue gas. The water partial pressure affects the equilibrium concentration of the condensing acid. This equilibrium concentration of the sulfuric acid is directly related to the metal temperature and ranges from 50 to 70% at 82°C (180°F) to 80 to 90% at 149°C (300°F) (Figure 1).
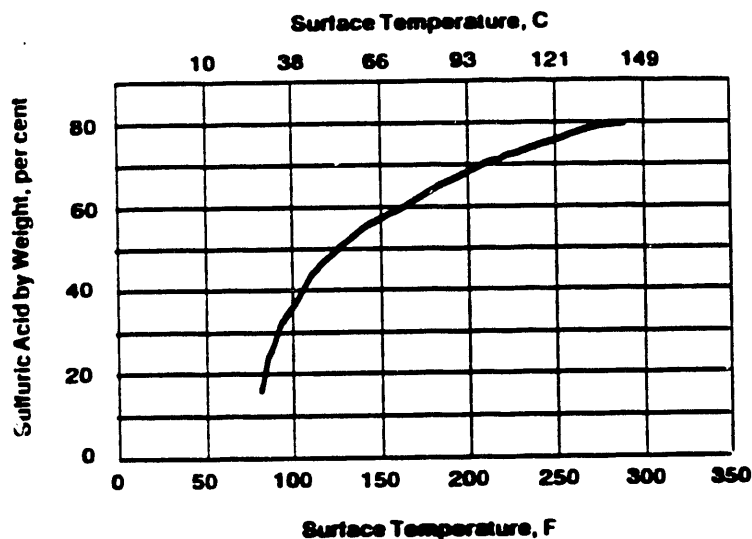

Figure 1. Relationship of concentration of condensed sulfuric acid to temperature of condensing surface (100 ppm SO_3 and 8.3 percent H_2O) [2].

The presence of other ions also affects cold-end corrosion. Chlorides and fluorides from coal can cause severe corrosion to many materials. Chlorides can form hydrochloric acid. Fluorides can form hydrofluoric acid or react with siliceous material fillers and reinforcements used in linings.[3]

It is appropriate to mention secondary factors that modify the condensation-corrosion mechanisms. These factors are:

- time of exposure
- material composition
- presence of corrosion products
- fuel ash
- temperature cycling
- air-in-leakage
- hydrogen chloride
- effects of cleaning systems.

To illustrate the time of exposure effects, laboratory work [2] indicates that the initial corrosion rate for mild steel is much higher than long-term corrosion rates (Figure 2).
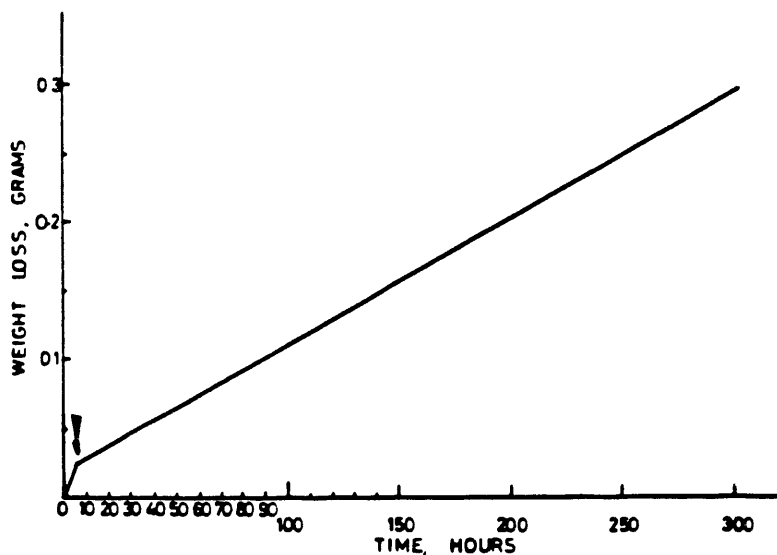

Figure 2. Cumulative weight loss over 300 hours in laboratory rig
(SO$_3$ 26 ppm, excess O$_2$ 8%, coupon temperature 105°C (221°F))
[1].

Another factor is the type and amount of the corrosion product. Corrosion products are different for each alloy. Carbon steel gives a relatively dense thin layer of oxides and sulfides which is not protective; but its presence after a few hours of exposure appears to reduce the rate of corrosion (as illustrated in Figure 2).

The influence of the metal temperature on the rate of both acid deposition and corrosion is shown in Figures 3 and 4. The corrosion rate measured immediately below 150°C (302°F) corresponds to metal temperatures just below the dew point. Figure 5 shows another high corrosion rate which is at the water dew point (~40°C). The water dew point is the temperature below which water condenses; the corresponding acid which condenses is sulfurous acid.

The leakage of air into the back-end of the coal-fired unit significantly increases the corrosion. Air leakage:

- chills the flue gas increasing the condensation of a more dilute acid

- locally increases the moisture content which decreases the acid dew point

- accelerates the metal loss because increased flue gas oxygen produces ferric ions [5].

The effect of increased oxygen is demonstrated by Figure 6 [5]. Even though the data are from an oil-burning unit, the same effect would occur in a coal-fired plant: i.e., increased oxygen increases the acid dew point.

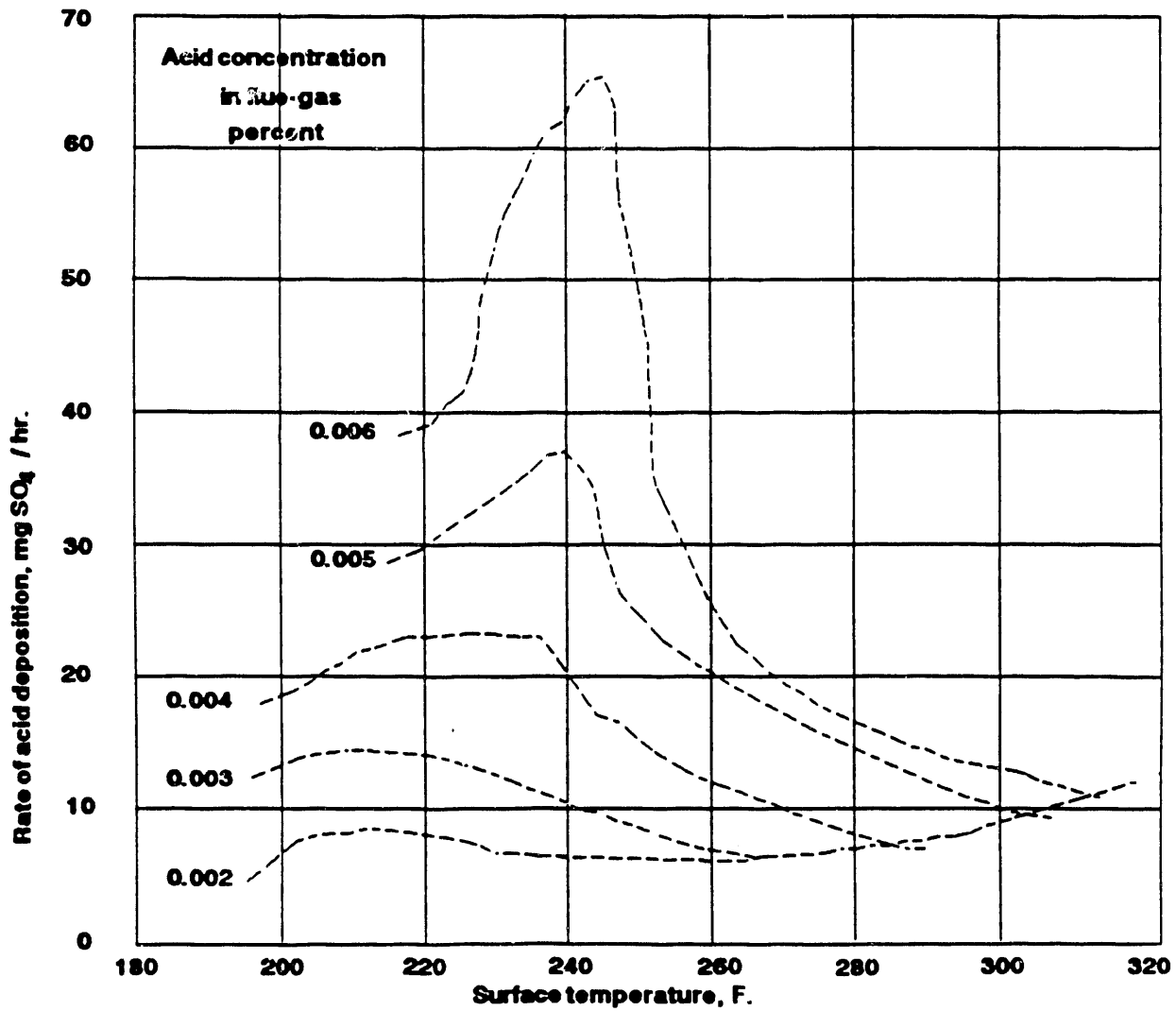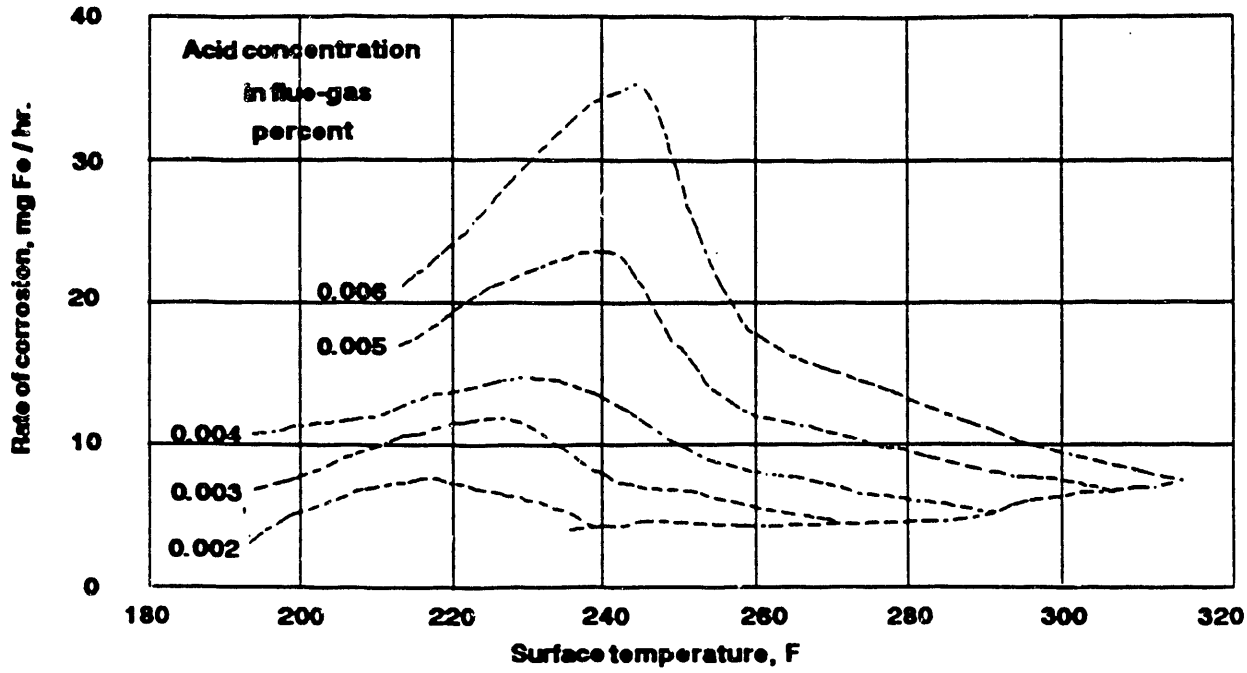Figure 3. Corrosion rate versus surface temperature and acid concentration.

Figure 4. Rate of deposition vs. surface temperature.
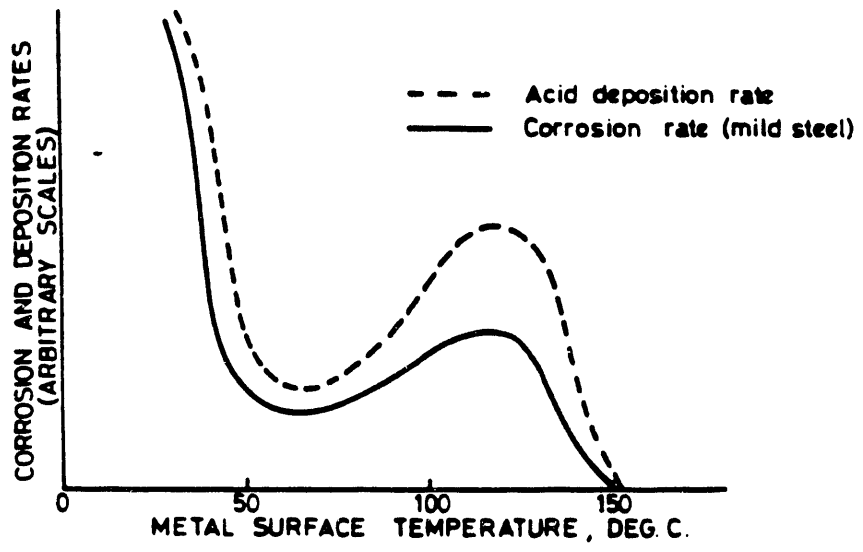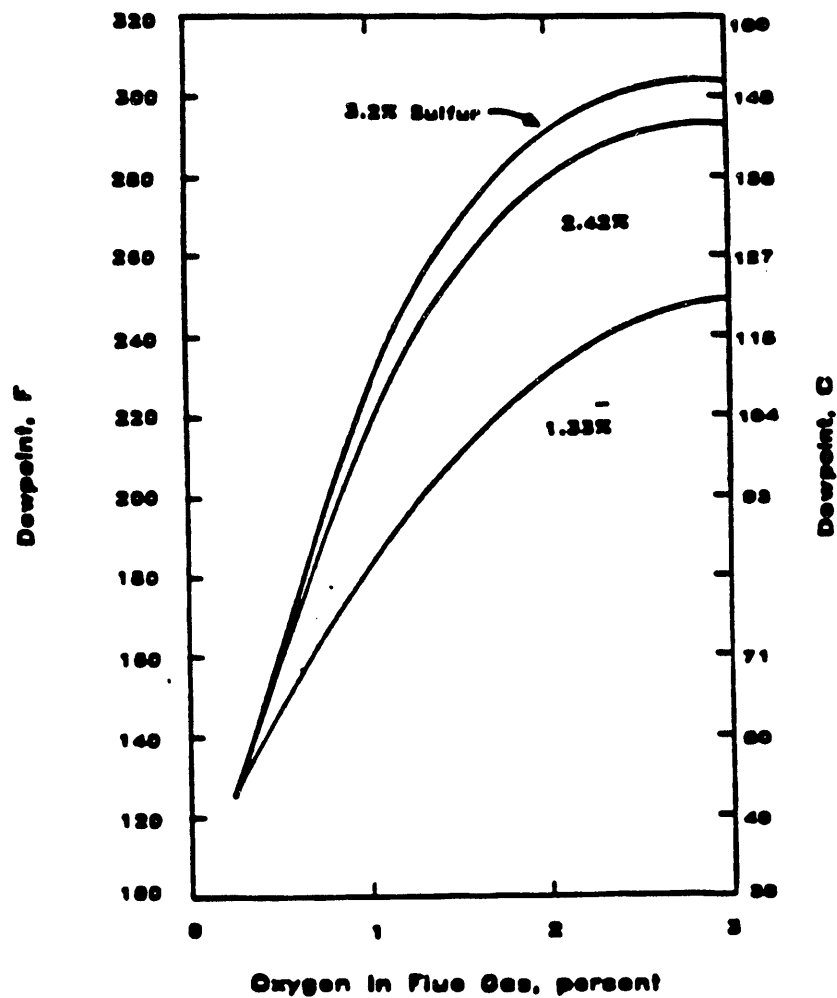
Figure 5.

Figure 6. Decrease in dew point with low excess air in an oil-fired
furnace [5].

The role of fuel ash in the coal-fired cold-end corrosion is complex and
depends on the type of ash, the ash deposition, and the cyclic load condition.
For instance, an ash that is high in pyrite oxide may increase the formation
of sulfur trioxide through catalytic effect of the uncombined iron oxide.
Calcium and magnesium containing ashes may absorb some of the sulfur trioxide,
thus reducing the acidity of the condensate. Too much fly ash causes the
presence of warm, moist, ash-packed areas which readily causes under-deposit
corrosion. These ash deposits are hydroscopic and, at lower temperature
conditions, caused either by design or off-load conditions, will absorb

will absorb moisture. This deposit will greatly increase the rate of
corrosion if the alkaline ash has absorbed enough sulfur trioxide for the
adhering wet mass to deplete the alkalinity and become acidic.

As previously mentioned, the sulfuric acid dew point depends on the
concentration of acid within the system. The concentration of the acid
depends on the water vapor partial pressures and the amount of sulfur trioxide
present. Therefore, the moisture variation within the flue gas influences the
acid dew point. Figure 7 demonstrates that as moisture in the flue gas
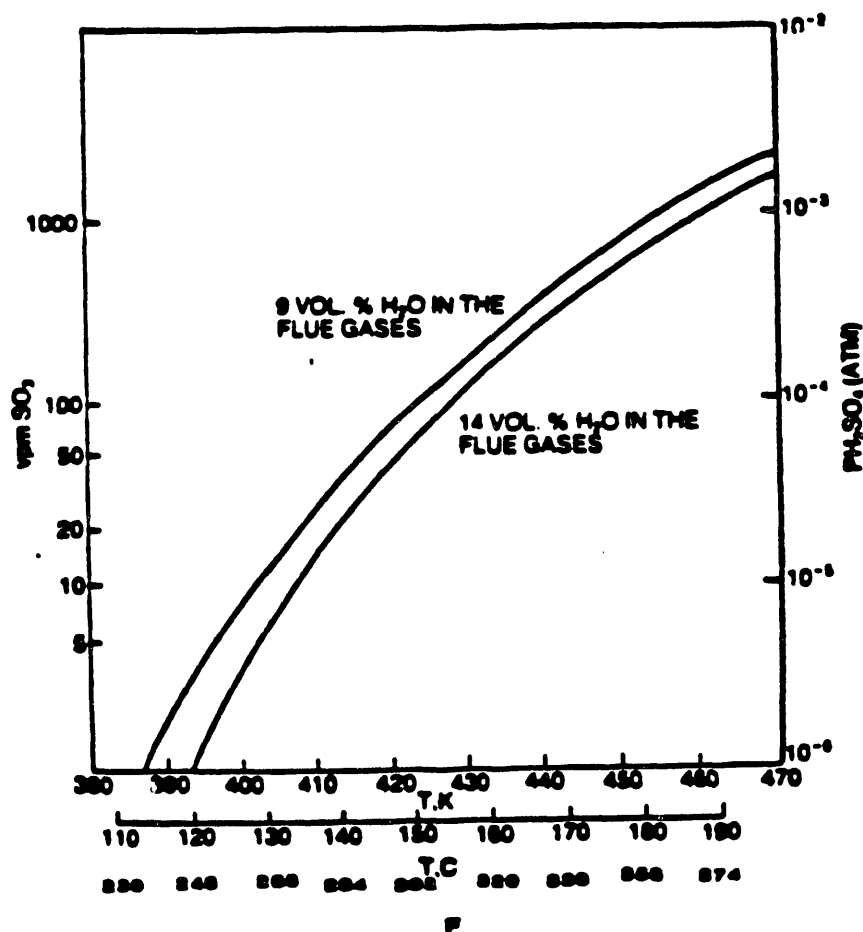increases, the acid dew point decreases.[4]

Figure 7. Effect of percent water on acid dew point [8].

Corrosion from Condensation of Chlorine Compounds

Chlorine compounds in the flue gas are a major contributor to corrosion in the flue gas path. The chlorine content (in the form of chlorides) of U.S. coals ranges from 0.1% to 0.5% (1000-5000 ppm). Also the water used in boiler operations contributes to the chlorine compounds present in the flue gas.

At the sulfuric acid dew point, the presence of chloride in the flue gas translates to a 1% HCl concentration in the deposit.[7] But below the water dew point the situation changes. Hydrochloric (HCl) acid readily condenses such that the concentration of the HCl in the condensate is ~85% of that in the flue gas. This study also reported a 200% increased short-term corrosion loss for a flue gas with 100 ppm HCl at the water dew point.

Precipitating chlorides and low pH will promote crevice attack and pitting under scale deposits. Chlorides also cause stress corrosion cracking of austenitic stainless steels over a wide range of pH.

Areas of Boiler Affected by Cold-End Corrosion

Air-Heater Elements, Framework and Seals. Acid deposition causes adherent deposits and corrosion of the element packs. This impairs gas flow and often reduces the amount of combustion air available. Element failure can often lead to air-heater seal damage, giving rise to high levels of air-heater leakage, increasing flue gas losses.

Ductwork and Expansion Seals. Duct and seal penetration due to acid dew point corrosion will increase the induced draught fan requirements due to air inleakage, thereby reducing plant efficiency, and in some cases the maximum plant output. Complete seal or duct failure can lead to an expensive plant outage and repair.

Precipitators. Isolation dampers can corrode, rendering them inoperable and preventing on-line precipitator maintenance. Corrosion of precipitator structural concrete can lead to roof collapse, while corrosion of precipitator wires, frames and plates can lead to precipitator zones failing, increasing dust emissions. This in turn will require a reduction in load to comply with emission requirements.

Chimney Stacks. The concrete or limestone concrete aggregate flues are generally lined with a corrosion resistant brickwork, but often metallic components (e.g., flashing, chimney tops) are used. Failure of brickwork or metallic components may lead to attack of the flue, thereby threatening its structural integrity. Acid penetration of the flue can be monitored by conductivity probes embedded at various depths into the concrete. Significant increase in conductivity above the norm is an indication of acid penetration.

Duct Injection Technology [8, 9]

Duct injection technology encompasses a wide variety of processes for the removal of SO_2 from flue gas. The major difference between the flue gas desulfurization duct-injection processes is the type of sorbent/gas mixture design. Figure 8 demonstrates the two types of duct injection processes and variation on the humidification model. One process humidifies the gas by injecting a slurry of calcium-based sorbent. The moisture in the slurry evaporates and humidifies the flue gas. The other process injects dry particles into the flue gas either before or after the gas is humidified by spraying a fine mist of water into the ductwork. The variation concerns whether the sorbent (dry) is injected before or after the injection of water. The humid gas wets the particle surface producing the reaction between the sulfur dioxide and the sorbent. When the sorbent is injected the particles are wetted, which improves the SO_2/sorbent reaction.
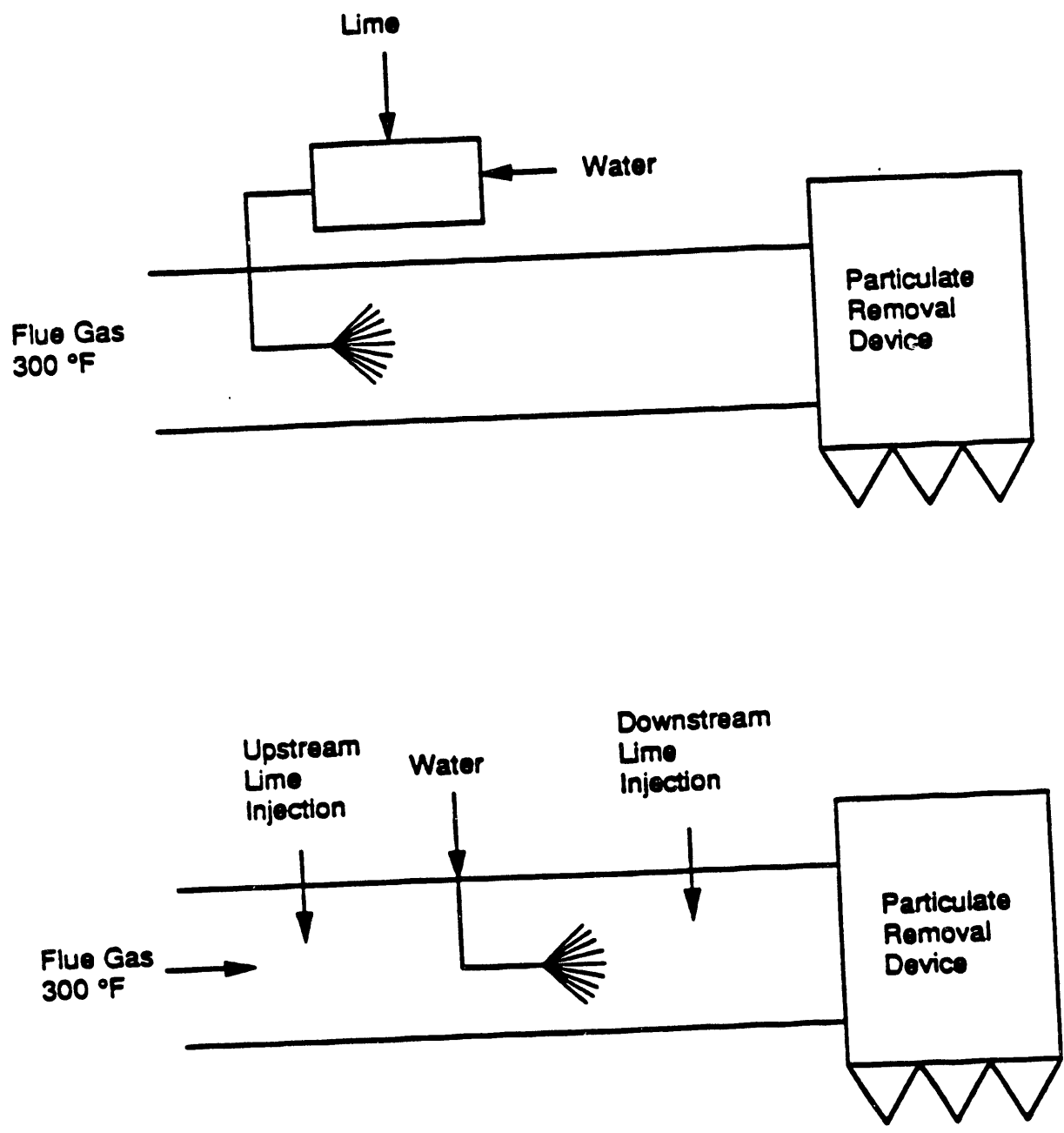
Figure 8. Humidification Locations for Various Duct Injection Processes[8]

The sorbents used are either calcium ($CaCO_3$, $Ca(OH)_2$) or sodium (NaOH) although the calcium type is heavily favored. The calcium types are many, and continuing laboratory studies are investigating many other variations including: high surface area limes, pressure hydrated limes, and limes with a variety of chemical additions. One variation is using recycled fly ash which contains silicon dioxide. This silicon dioxide reacts with the calcium sorbent to yield a calcium silicate. Calcium silicate is even more reactive with the SO_2 in the flue gas. Sodium hydroxide is another experimental additive that increases the reactivity of the calcium based sorbent. The design differences in the variety of processes encompasses the number of nozzles, the nozzle design, and material. The atomizing pressure, size of the flue duct, and component flow rates are other process variables.

The most important variable affecting the SO_2 removal and sorbent utilization is the approach to saturation temperature i.e., the lower the approach temperature, the higher the of SO_2 removal. For the dry sorbent/humidified gas, the lower approach temperatures produces wetter particles which are more reactive towards SO_2. A lower approach temperature with the slurry injection process means an increased drying time for the droplets and a longer reaction time with the sulfur dioxide which increases the amount of SO_2 removed. However, the lower the approach temperature, i.e., closer to the adiabatic saturation temperature the greater probability of wet solid deposition on the walls. This is because the drops do not dry completely before hitting the walls of the gas duct. The increased amount of wall deposits will increase the amount of SO_2 removed from the flue stream because of the longer time available to react with the SO_2.

Duct Injection Process Corrosion

Ideally, duct injection technology promises very low corrosion rates compared to the wet scrubber technology. The mixture of lime with the flue gas in duct injection technology yields a basic pH. The wet scrubber environment is acidic and rapidly attacks carbon steel. The environment in the ductwork at the injection and mixing site will be less corrosive because temperature of the walls, the flow rate, and design factors. But, ideal conditions that prevent corrosion and erosion are difficult to achieve while trying to get a good SO_2 removal.

The most significant influence on the corrosion of carbon steel is the pH.[15] At higher temperatures (300°C) the corrosion rate increases at the higher pH.[15] Most duct injection prototype investigations have had problems with solid deposition on the walls of the ducts[8, 9] The regions where deposits wet the walls is where the temperature drops. Wall deposits threaten the ductwork materials corrosion integrity with both underdeposit localized corrosion and wastage mechanisms operable. In this cooler area the SO_2 combines with the condensing water to form sulfuric acid resulting in acidic conditions adjacent to the wall. Besides the corrosive conditions at the wall, the lime water deposit can, under some conditions, form a concrete-like deposit which can build until the duct plugs completely. Gas flow distribution is also a factor in the presence of wall deposition and erosion.

Not surprisingly, the factors that affect the SO_2 removal efficiency also affect the amount of wall wetting, deposition and abrasion damage. One factor is the residence time of the sorbent/gas components in the ductwork. The longer the dwell in the ductwork the higher the SO_2 removal efficiency. But, this also means an increased likelihood of wall wetting and deposition. Also the flow rate, i.e. dwell time influences the amount of abrasion or erosion damage in the ductwork and delivery nozzle.

CONCLUSIONS

1. Severe corrosion results from a close approach to saturation temperature. Even if lime is present, the continued condensation lowers the pH[2] under the deposit.

2. Hotter temperature (higher approach) would ensure low corrosion rates.

3. Avoid temperature cycling, i.e., oscillating process temperatures, below and above saturation temperature.

4. Stainless steels are not suitable for downstream of a spray drying application. Stainless steel is susceptible to cracking where chlorides can condense.

5. Hastelloys and Inconels (Ni-Cr-Mo alloys) are most resistant to acid
    condensation corrosion.

6. Downstream of the spray dryer, coated carbon steel or corrosion-
    resistant alloy clad of carbon steel can be used as a protection against
    dewpoint corrosion.

7. Measure gas conditions (sulfur presence, temperature) downstream of the
    precipitator to determine if reheat is necessary.

RECOMMENDATIONS [1-14]

Based on the present experience in dry scrubber units and overall back-
end experience, the following design recommendations are made:

o Provide means for monitoring temperature and velocity to avoid
  corrosive condensation.

o Measure corrosive components of the process streams to estimate
  process stream corrosiveness.

o Insulate outlet ducts, avoid cold spots.

o In the ESP or baghouse and downstream to the stack, avoid crevices,
  dead legs, or other stagnant areas. Insulate properly.

o It is desirable to bypass the baghouse or preheat system during start-
  up (until the gas stream reaches operating temperature) to avoid
  excessive condensation and flyash plugging.

o In joints, corners, and other areas where condensation is possible,
  avoid contact of galvanically dissimilar materials; uncoated carbon
  steel and stainless steel or carbon steel and graphite impregnated
  rubber.[6]

- Keep flow velocities within specification and provide means for removing ash build-up and deposits such as sweeping or vacuuming. Sweeping or vacuuming is preferable to flushing or washing.

- In the Spray Dryer Modules all parts exposed to slurry should be abrasion resistant i.e., bushings, wheel body, wear plates, etc. (SiC)

- Brace components to avoid excessive vibration (fans).

DISCUSSION

Time spans for pilot plant operations are too short to make definitive predictions about corrosion. Pilot testing is not always a good measure of corrosiveness in a plant. The test spans are too short and the process variables change frequently depending on the process data required.

The corrosion and erosion damage at operating units using dry scrubber or duct injection technology is shown on Figure 9. [2, 10, 11, 12] In Region A where a slurry is sprayed all parts are exposed to severe abrasion. When the material wears appreciably this affects the pattern of the spray and upsets carefully calculated mixing variables. In Region B, the seals around the isolation dampers plug frequently with ash. This area has to be cleaned frequently. In Region C significant corrosion has necessitated replacement of the door seals of the baghouse compartment doors. Also the areas around the bag hangers and the walls between the bags have displayed corrosion. Region D is the reverse air fan and fan housing. Carbon steel and stainless steel in this assembly have exhibited severe corrosion, both pitting and chloride cracking. The most severe potential for corrosion is the region between the fan and out the stack. Currently, a fiber reinforced plastic (FRP) liner is used to protect the stack walls.

Additional recommendations can be made as the body of field experience, pilot testing, and laboratory test programs increases.
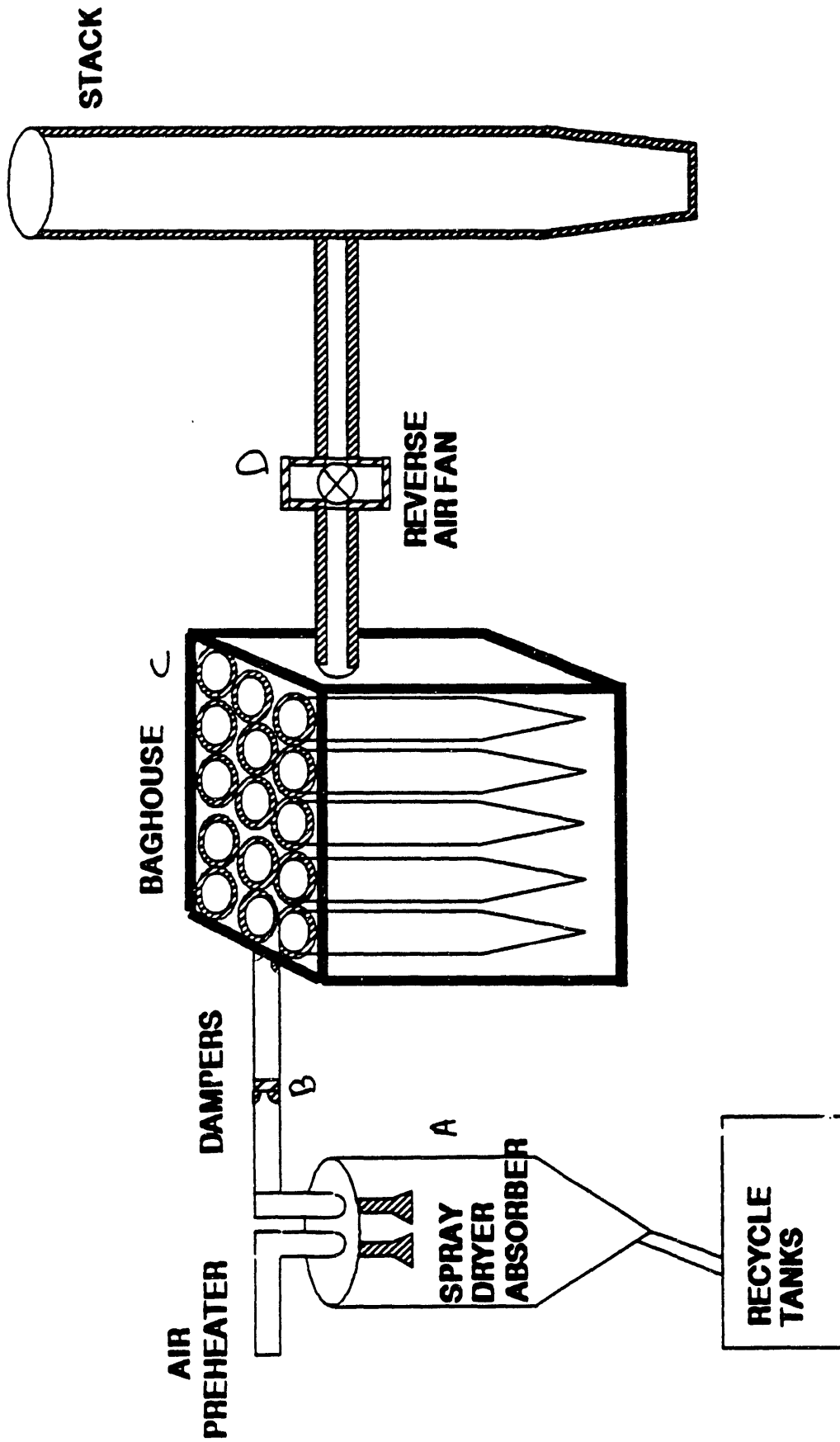
Figure 9. Composite damage at dry scrubbers.

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