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**CE IGCC Repowering Project
Materials for Coal Gasification Environment**

**Topical Report
June 1993**

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CE IGCC REPOWERING PROJECT
MATERIALS TASK

TOPICAL REPORT

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MATERIALS TASK TOPICAL REPORT

I. SUMMARY

A task to develop material requirements and a materials testing strategy was established with the Materials and Water Chemistry Department of the ABB Power Plant Laboratories. This involved examining the requirements for each system under ABB CE scope. The basis for the material recommendations was largely based on in-house test programs under DOE contract and ABB CE experience. Consultants were utilized in a parallel task to assist in the design and material specification for the solids handling systems.

ABB CE experience includes operating data from a former process development unit (PDU) located in Windsor, Connecticut. The unit gasified Pittsburgh seam coal at a nominal firing rate of 120 tons per day. The objectives of the program were to produce clean, low-Btu gas from coal, and to provide the design information for scale-up to commercial-size plants.

The results of the task were used to specify and, depending on scope, design the equipment used in the plant. A detailed document was developed and used to generate a Metallurgical Flow Diagram. Specifications were developed from this diagram. For the equipment designed, these selections were provided to representatives of cognizant design and manufacturing departments. In addition, where appropriate, recommendations were made for operating procedures and for design changes. Specified materials will be again evaluated during detailed engineering.

In some areas the results of the task were not conclusive. Additional investigation will be required. These areas are the types of approaches which can be taken to accommodate product gas sulfidation resistance and solids transport erosion.

II. INTRODUCTION

ABB CE is participating in a \$270 million coal gasification combined cycle repowering project that will provide a nominal 60 MWe of electricity to City Water, Light & Power (CWL&P) in Springfield, Illinois. The ABB CE project will demonstrate Integrated Gasification Combined Cycle (IGCC) technology in a commercial application by repowering an existing CWL&P Plant in Springfield, Illinois. The project duration will be 126 months, including a 63-month demonstration period.

The IGCC system will consist of ABB CE's air-blown, entrained-flow, two-stage, pressurized coal gasifier; an advanced hot gas cleanup process; a combustion turbine adapted to use low-Btu coal gas; and all necessary coal handling equipment. CWL&P's Lakeside Station will be the site for this project. The result of repowering will be an IGCC power plant with low environmental emissions and high net plant efficiency. The repowering will increase plant output by 40 Mwe through addition of the combustion turbine, thus providing a total IGCC capacity of a nominal 60 Mwe. Nearly half of the project will be funded by the United States Department of Energy (DOE), under Round II of the Clean Coal Technology Program, while CWL&P, State of Illinois, and ABB CE will fund the rest.

The IGCC will include ABB CE's slagging, entrained-flow, gasifier operating in a pressurized mode and using air as the oxidant. The hot gas will be cleaned of particulate matter (char) which is recycled back to the gasifier. After particulate removal, the product gas will be cleaned of sulfur prior to burning in a gas turbine.

The proposed project includes design and demonstration of an advanced hot gas cleanup process for removal of sulfur from the product gas to the gasifier. The sulfur removal method features a newly developed moving-bed zinc titanate system downstream of the gasifier. ABB CE intends to use the General Electric (GE) moving bed, zinc titanate sulfur removal system currently being piloted by GE Environmental Systems, Inc.

In this plant, the gasifier will be producing a low-Btu gas (LBG). The LBG will be used a fuel in a standard GE gas turbine to produce power. This gas turbine will have the capability to fire LBG and natural gas (for start-up). Since firing LBG uses less air than natural gas, the gas turbine air compressor will have extra capacity. This extra compressed air will be used to pressurize the gasifier and supply the air needed in the gasification process.

The plant is made of three major blocks of equipment. They are the fuel gas island which includes the gasifier and gas cleanup, gas turbine power block, and the steam turbine block which includes the steam turbine and the HRSG.

III. BACKGROUND

The task for ABB CE has an ultimate goal to determine the most cost effective material selections for a commercial IGCC plant. A combination of data from the demonstration unit, laboratory testing and appropriate industrial experience will be utilized to establish selections for the commercial plant. For the areas of concern the information available to date is insufficient to specify the most cost effective commercial recommendations. The demonstration unit will evaluate both test specimens and the actual installed materials.

The demonstration unit has two areas of materials concern. The first area includes those components which are exposed to syngas and in certain cases to syngas with entrained char. The mechanisms for corrosion in a syngas environment have been fairly well understood. However, the wastage rates over a temperature range for the expected product gas have not been established. The second area are components in the solids feed system which are subject to erosion.

The strategy for specifying materials will be for optimistic selections where corrective actions can be taken. Options will be identified and an appropriate selection of alternatives will be installed. Judgments will be made on which materials should be incorporated into the materials used for construction and those which should be installed as test specimens.

The recommendations which have been made to date have been used for discussion, pricing and scheduling purposes. The work done to date has indicated that additional work will be required to formulate the final selections.

IV. PLANT DEFINITION

The plant for this task was initially defined as:

- Coal Feed
- Gasifier
- Heat Exchanger
- Char Removal
- Char Feed
- Slag Discharge
- Sulfur Removal and Recovery
- Steam System
- HRSG

After an initial review the scope of the task was reduced to those systems which were deemed to require specialized recommendations. These systems are located on the gasifier island and are:

- Gasifier and Heat Exchanger
- Coal Transport System
- Char Collection and Transport System

The needs for the gasifier and heat exchanger, also called a syngas cooler (SGC), include all the components which are subject to the syngas environment. Surfaces exposed to syngas from the gasifier slag tap to the Sulfur Removal System must be protected from sulfidation, hydrogen attack and downtime corrosion.

The coal and char transport system have traditional erosion concerns.

The coal preparation and feed system is designed to pulverize crushed coal, dry and heat it, feed it through a pressure barrier, and meter it into the gasifier. Raw coal discharges from a storage bunker via a volumetric feeder into a pressurized bowl mill pulverizer. The bowl mill pulverizes and dries the raw coal heating it to a temperature of 79 °C (200 °F). A centrifugal fan upstream of the mill provides the mill air used to classify the coal and convey it to a bagfilter. The mill air is heated by duct burners located in the air duct upstream of the coal mill. The receiving bin discharges intermittently and alternately by gravity into two lockhoppers.

Each lockhopper is capable of pressurizing its contents from atmospheric pressure to the gasifier operating pressure and discharging its contents into a feed bin at this pressure. The lockhoppers will be sequenced in such a way that one will be filling while the other is dumping coal into the feed bin. The feed bin will provide a relatively stable inventory of coal which can be metered smoothly to the gasifier. The feed bins continually discharge coal at high pressure into pneumatic conveying lines. Each conveying line from the feed bins splits four ways to supply the four coal burner nozzles located at each firing elevation on the gasifier. Nitrogen is used for pressurizing and transport.

The gasifier and the SGC are utilized to produce a pressurized product gas stream containing char and H₂S. Pulverized coal is delivered and combusted in a deficiency of air. Additional coal and recycled char is introduced. Gasification occurs in an entrained reactor. Sensible energy is removed from the gas in the SGC. The gas exits the system for char removal and desulfurization. Coal ash is fused and tapped from the bottom of the gasifier as molten slag.

The gasifier and SGC are pressurized gas passes which are enclosed in pressure vessels. Located within the SGC is convective heat exchange surface. The product gas is cooled with both water cooled and superheat surfaces. The steam flow generated and the superheating of steam is integrated into the steam cycle. At the outlet of the SGC the waterwalls and pressure shell are joined together with a bellows. The bellows is connected to a transitional housing to which the product gas outlet pipe is connected. The waterwalls, heat exchange surface, bellows, transitional housing and product gas outlet pipe all require considerations for the syngas environment.

In the gasifier, the molten slag continually flows through a slag tap into a slag tank. Quenched slag is periodically let down from this tank. The slag tank is located just below the gasifier.

The char system consists of a cyclone, bagfilter, lockhoppers and feed system. Product gas and entrained char leave the gasifier heat exchanger at 538 °C (1000 °F) and enter a char cyclone that separates a percentage of the char from the product gas. The char discharges the cyclone by gravity into a char seal bin that provides a pressure seal, and proceeds by gravity into the char receiving bin. The product gas and remaining char exits the cyclone and flows into two high pressure, high temperature bag filters arranged in parallel to remove the remaining char from the product gas. The char discharges from each bag filter by gravity to the char receiving bin. The char receiving bin intermittently and alternately discharges by gravity into two lockhoppers. The lockhoppers are pressurized and intermittently discharge to a common char feed bin. The feed bin continuously discharges into one of two conveying lines using superheated steam as a conveying medium. Each conveying line from the feed bins splits four ways to supply the four char reinjection nozzles located at their associated reinjection elevation at the gasifier.

The hot gas desulfurization system that ABB CE is considering to use for this system is being developed by GE. It is a sorbent system as developed by METC. The GE version of this system is known as a moving bed system. Hot product gas enters the absorber vessel at the bottom and is cleaned of all the sulfur species by reacting with a bed of or zinc-titanate. Cleaned product gas leaves the reactor at the top. Spent sorbent is removed periodically from the absorber through a lockhopper and enters the regenerator vessel. The sorbent is regenerated with a stream of hot air and recycled back to the absorber. A stream of SO₂ laden gas is produced which is sent to a sulfur recovery system.

V. MATERIALS DISCUSSION AND RECOMMENDATIONS

A. Basis for Materials Evaluation

Materials for construction of coal gasification equipment must be capable of resisting attack during long periods of exposure to an aggressive environment at elevated temperature. Metallic materials will form oxide scales on exposure to oxidizing environments at high temperature and depending on the alloy composition the scale may provide protection against attack by aggressive species. In alloys containing significant amounts of chromium and/or aluminum protective chromia or alumina scales will be formed and provided these remain adherent, attack by aggressive species such as sulphides will be resisted at least for a period of time. Difficulties arise if, during thermal cycling, all or part of the protective scale should spall or decohere from the alloy surface. In these circumstances the region of the substrate immediately below the scale will be depleted in the critical alloying element (i.e., chromium or aluminum) and rapid attack may result.

Coal gasification environments are characterized by low partial pressures of oxygen and relatively high partial pressure of sulphur - containing gases and in these reducing conditions, the protective nature of oxide scales may be somewhat limited. Also, chromia scales are classified as "leaky" because of their structural characteristics and consequently may not present adequate resistance to sulphide penetration. Alloys containing aluminum or silicon which form alumina or silica based, surface layers show greater resistances to degradation by aggressive species but scales of this type are frequently characterized by poor mechanical properties and low-ductility in particular, so that the performance in thermal cycling conditions may be poor.

In carbon or low-alloy steels the content of chromium is insufficient to form chromia type scales and iron oxides do not provide protection against attack by aggressive species. Consequently, in coal gasification environments iron sulphides would form and the rate of formation would control the degradation characteristics of the components. At low temperatures ($< 300^{\circ}\text{C}$, 572°F) the kinetics of sulphur penetration could be low enough to give acceptable service life in certain circumstances.

Thus, it is clear that the choice of materials for service in these aggressive conditions will depend critically on the precise nature of the gaseous environment, the temperature of operation and the service characteristics of the plant e.g., cyclic operation, process economics, etc.

There have been many investigations of the behavior of metallic materials in coal gasification environments, but these have frequently been limited to specific components or to particular operating conditions. For example, the early work of Perkins et al⁽¹⁾ was concerned mainly with materials for construction of the gasifier vessel and in many cases this will be refractory lined to give adequate protection. Other work, particularly in Europe, has concentrated on materials for the down-stream heat exchanger where the gas would be cooled prior to cleaning and supplying to the gas turbine. In this case the metal temperatures of interest were around 450°C (842°F) and, particularly in the case of work carried out in the UK, the effect of chloride contamination on degradation rates was a major consideration.

In this review the published information on candidate materials for various sections of the ABB gasifier system has been considered in the context of the specific operating conditions (e.g., metal temperatures, coal type, combustion gas analysis) associated with the design study and some emphasis has been given to mild and low alloy steels. In subsequent sections of this report recommendations are made on the basis of this technical evaluation and proposals are presented for a limited experimental program to validate the materials selection.

(i) Thermodynamic Aspects

The combustion environment in a coal gasification system can be particularly severe and will include compounds of oxygen, carbon and sulphur which singly or in combination may attack the materials of construction. In addition, solid deposits may form on metallic components and cause direct corrosion problems or may encourage the formation of micro-environments between the deposit and the substrate so that the rate of degradation will not be controlled by the bulk environment. With some coals, additional contaminants, particularly chlorides or alkali metals may also be present. Operating parameters such as temperature, pressure, load cycling will also have a critical influence on corrosion behavior. However, the situation can be simplified somewhat if corrosion behavior is considered in the context of the two most deleterious elements, i.e., oxygen and sulphur, for a given temperature.

In order to represent the conditions associated with the exposure of multicomponent alloys to multicomponent gases in a relatively simple fashion the concept of the oxide phase-stability diagram has been introduced. In these diagrams, a two-dimensional representation is given of the regions of stability of the compounds of the various metals as a function of two oxidants at constant temperature. An example is given in Figure 1 where stability diagrams for Fe-O-S, Cr-O-S and Ni-O-S have been superimposed at 650°C (1220°F). It must be emphasized that these are simplified diagrams and must be used with some caution but these represent an effective technique for indicating the probable stability of typical oxides and sulphides for a range of oxygen and sulphur partial pressures.

A factor which may be important in determining the rate of degradation in heat exchanger systems is that the metal surface is normally somewhat cooler than the gaseous environment. In these circumstances questions arise about which temperature controls the degradation process (i.e., metal or gas temperature) and also which is the relevant temperature in relation to the sulphidizing (P_{O_2} , P_{S_2}) characteristics of the gas.

One way of handling the latter issue⁽¹⁾ is to calculate "non-equilibrium" values of P_{O_2} and P_{S_2} based on, for example, the CO/CO₂ ratio at the gas temperature but using the equilibrium constant for the metal temperature. The assumption is that the gas does not change composition significantly in contact with the cooler surface because of the slow kinetics of bulk gas reactions.

Figure 1. Phase stability diagrams for Ni, Fe, and Cr oxides and sulfides at 650°C.

The CO/CO₂ equilibrium can be represented as follows:

Where K is the equilibrium constant = $\frac{-\Delta G}{RT}$

ΔG is the free energy of formation of CO₂

T is the temperature in Kelvin

In order to calculate the non-equilibrium value of Po₂ the CO/CO₂ ratio appropriate to 700°C (1292°F) would be used along with a Kp value for 500°C (932°F), based on the value of ΔG at this temperature. A similar procedure would be applied with the H₂/H₂S ratio to calculate Ps₂. This approach has been used to interpret some of the data considered in this review.

(ii) Kinetic Aspects

While the thermodynamics of a system will indicate the phases likely to be stable in given circumstances, the rate at which these phases form is critical in determining the overall corrosion characteristics. Thus it has been found that mixtures of oxides and sulphides can be formed even when from thermodynamic considerations only one compound would be predicted. In these cases, to avoid the formation of sulphides the point representing the gas phase composition must be well within the oxide stability phase field. Accordingly there can be a "kinetic boundary" in addition to a phase stability boundary. This kinetic boundary cannot be predicted and must be determined by experiment.

In simple alloys exposed to clean oxidizing environments the growth of oxide with time will follow a simple parabolic law and rate constants defining the growth kinetics can be derived. However, in more complex multi-component situations where protective oxides may form initially and remain protective for many thousand of hours, breakdown usually occurs eventually and the rate of attack increases markedly (Figure 2). This breakdown may be due to mechanical effects in the oxide e.g.,

- Spalling due to thermal expansion mismatch.
- Oxide fracture as a result of growth strains.
- Dechoesion of the brittle interface regions.

Wt Gain or Metal Loss

Time

FIGURE 2: Schematic showing metal degradation as a function of time

Following failure of a protective oxide the rate of attack frequently increases rapidly because the region of the substrate immediately beneath the oxide layer will be depleted in elements such as Cr and Al which have formed the oxide scale. Thus rapid ingress of corrosive species can occur and the rate of degradation will increase significantly. Whether a protective oxide will re-form will depend on the "pool" of alloying elements available to form an appropriate surface layer.

B. Review of Existing Information
i) Mild and Low Alloy Steels

The information available on steels of this type in aggressive environments is limited because, in many cases, the temperature and impurity level was such that only more highly alloyed materials were investigated. Nevertheless, some data have been published in the open literature^(1,2), particularly for low-alloy steels, e.g., 1Cr-½Mo and 2¼Cr-1Mo in the temperature range 300-500°C (572°F - 932°F).

In the work of Perkins et al⁽¹⁾ mild steel and 1Cr-½Mo (T11) specimens were examined as part of a comprehensive survey of materials behavior in reducing gases containing H₂S. Data from short-term tests (up to 3000h) were evaluated in terms of the corrosion kinetics to give predicted annual degradation rates. It was concluded that mild steel and the T11 material would only give adequate corrosion resistance at temperatures up to 300°C (572°F). Brooks and Meadowcroft⁽²⁾ also examined the behavior of 1Cr ½Mo steel and included work on 9Cr 1Mo (T91) at 400 and 500°C (752°F and 932°F) in an environment simulating combustion in a PC boiler. However, when the combustion gas was evaluated in terms of sulphidizing potential (i.e., Ps₂ and Po₂) the environment was similar to that used by Perkins et al. According to the data of Brooks and Meadowcroft, the samples of both steels showed protective kinetics in tests of up to 1500h duration at 400 and 500°F (752°F and 932°F). When chloride ion was present in the form of HCl at the 400 ppm or 600 ppm level the samples degraded at a linear rate with no sign of the formation of a protective scale.

The data for T11 of Brookes and Meadowcroft for chloride free environments have been replotted with those of Perkins et al for T11 and mild steel in Figure 3 and it is clear that there is reasonably good agreement between both sets of results. However, it does not appear, on this presentation, that protective kinetics were established at 400°C (752°F) as claimed by Brooks and Meadowcroft and a linear degradation rate of 1600µm/year has been calculated for the data from both sources (See Figure 3). The data of Perkins et al for 300°F (572°F) has been included in Figure 3 and although the results are not extensive the annual degradation rate was about 500µm per year.

The compositions of both gas mixtures represented in terms of oxygen and sulfur, are indicated in Figure 4. For the gas composition used in the EPRI work⁽¹⁾ the calculation of Po₂ and Ps₂ was based on the CO/CO₂ ratio at 1100°C (2012°F) and the

B & M = Brooks & Meadowcroft

FIGURE 3: Metal loss as a function of time for plain carbon steel and T11 at 300, 400 and 500°C in gasification environments

equilibrium constant, K_p , for 500°C (932°) to give Ps_2 and Po_2 , ie non-equilibrium values. Although the environment used by Brooks and Meadowcroft is somewhat more sulphidizing (higher Ps_2) than that used in the EPRI work this has not been reflected in a higher rate of degradation. Also, it has been suggested⁽¹⁾ that the non-equilibrium parameters, as used by EPRI, more reasonably represent the real behavior. The proposed IGCC gas composition for the ABB design is also shown in Figure 4 and it is evident that the sulphidizing potential of this environment is similar to that used in the experimental programs. Accordingly it appears that the data generated in references 1 and 2 will be relevant to the ABB operation.

Results from the work of Mayer et al⁽³⁾ for T11 at 400°C (752°F) are shown in Figure 5 and in this case it is evident that a protective scale has formed and the rate of degradation decreased with time. The test environment was a simulated flue gas which was oxidizing and this explains the relatively low rate of attack.

In the work of Brooks and Meadowcroft the results of the laboratory tests were compared with the results of service experience in a 500MW boiler and in terms of both degradation rate and scale morphology there was good agreement with the experimental results.

A similar comparison can be made on the basis of unpublished work^(4,5) carried out at ABB-CE where laboratory testing was carried out with the same gas composition as that used in a gasifier process demonstration limit (PDU) where tube samples were exposed for times up to 2500h. The data from the laboratory tests are shown in Table 1 and the degradation rates at 482°C and 371°C (900°F and 700°F) for mild steel and T11 are somewhat lower than the values from the work of Perkins et al and Brookes and Meadowcroft but the maximum difference is about a factor of two which is not a serious discrepancy for a limited amount of data. When the data from Table 1 are compared with the probe results in Table 2, for the slightly higher temperature of 538°C (1000°F), the agreement for T11 and T9 is very satisfactory.

The overall conclusion from all of these data is that the corrosion resistance of mild and low alloy steels in gasifier environments is poor and certainly inadequate for service applications. Pilot-plant experiment do not always show good agreement with data obtained in the laboratory and Perkins and Bakker⁽³⁾ have investigated some of the factors that could contribute to the differences observed.

These include:

- temperature cycling;
- temperature differential between gases and sample
- surface condition

Fe - S - O System at 500°C

Figure 4 - Stability diagrams for iron-base compounds showing gas compositions from refs 1 & 2.

Metal Loss Data For T11

Synthetic Flue Gas, 0 HCL, 1060°C Flue Gas Temperature, 540°C Metal Temperature

Ref: P. Mayer, A. V. Manolescu, S. J. Thorpe.

FIGURE 5: Metal Loss for Steel T11 in Mildly Reducing Conditions

TABLE 1

Metal Recession Rates Obtained from Laboratory Experiments
Using Pilot Plant (PDU) Gas Mixture

ALLOY	DEGRADATION RATE $\mu\text{m/Yr}$	TEMP °C (°F)	Po ₂	Ps ₂
Mild Steel	1219	482 (900)	8.7×10^{-28}	7×10^{-10}
T-11	1727	482 (900)	---	---
T-9	1143	482 (900)	---	---
Calculated from 30 day exposures, linear kinetics				
AISI 347	330	482 (900)	---	---
Calculated from 15 day exposure, linear kinetics				
Mild Steel	940	371 (700)	3×10^{-28}	6.3×10^{-11}
T-11	533	371 (700)	---	---
T-9	381	371 (700)	---	---
Calculated from 30 day exposure, linear kinetics				

TABLE 2
Wall Thickness Losses (μm)
for Passive Probes
Exposed in Gasifier Pilot Plant (PDU) at
538°C (1000°F)

	800h		2500h		Metal + Recession Rate $\mu\text{m}/\text{yr}$
	Average	Maximum	Average	Maximum	
SA192	---	---	533	737	1812
SA192 Cr**	---	---	152	357	517
SA192 Al***	---	---	430	559	1462
T-22	406	711	1092	1000	3712
T-22 Cr**	76	152	178	254	585
T-22 Al***	279	356	356	254	1210
T-22 CoCrAlY	127	381	203	305	690
T-22 (M444)	914	1880			
T-9	330	1092	356	406	1210
304	76	152	305	790	1037
347	76	254	51	127	173
310	51	127	25	51	85
800	76	280	---	---	808*
671	25	51	---	---	265*

+ Recession rates calculated from average value for 2500h exposure

* Calculated from 800h average data

** Cr = chromized

*** Al = Aluminized

It was found that in each case the rate of attack was increased for mild and low-alloy steels but there was little effect on stainless and higher alloyed material. As an example the annual wastage rate in cyclic temperature conditions was double that in isothermal experiments.

In view of the relatively rapid rates of attack expected in steels with low contents of chromium various surface-treatment measurements have been adopted to provide protection in aggressive environments. One of the most attractive of these is surface chromizing using a pack cementation technique and aluminizing, although less widely used, has also been applied to low-alloy steels. Results for both processes applied to mild steel and T22 from probes exposed in the PDU are included in Table 2 and it can be seen that while chromizing reduced the rate of recession by a factor of about 3 and about 5 respectively the benefit from aluminizing was less.

Further information on the effects of these surface treatment processes is shown in Tables 3 and 4 for T11 material in short-term tests^(6,7). In the case of the data in Table 3 the environment contained Hcl and chromizing reduced the rate of attack at 450°C and 550°C (842°F and 1022°F) with no effect at 500°C (932°F). By contrast with the results reported previously aluminizing greatly reduced the extent of attack at all temperatures. The measurements of surface recession⁽⁷⁾ in Table 4 show similar trends with rates of degradation being reduced by chromizing but with the most significant reductions for aluminized samples which showed no evidence of increased degradation at the higher temperatures.

These results support the view that surface treatments of this type will provide enhanced protection but there are disturbing inconsistencies in the behavior recorded and test durations have been short. Further evaluation would be required to increase confidence in the likely performance of these treatments in the field.

ii) Ferritic and Austenitic Steels
a) High-Cr Ferritic Steels

There appear to have been only a limited number of investigations of the corrosion behavior of ferritic materials with chromium contents of greater than about 15% in gasification environments. Data⁽⁸⁾ for alloy 446 are shown in Figure 6 for specimens tested at 650°C (1200°F). It is evident by comparison with Figure 3 that the rate of degradation is substantially reduced, by more than an order of magnitude compared with the low-alloy materials discussed earlier.

Results for Ebrite⁽²⁰⁾, an alloy with similar composition, are shown along with the data for Alloy 446 in Table 5 in terms of predicted annual rates of degradation and it is clear that both alloys show relatively low levels of attack in the environments used.

Metal Loss Data For Alloy 446 (24% Cr)

FIGURE 6: Degradation Data for Alloy 446 (24%Cr) Exposed at 648°C (1200 °F) in Gasifier Environments at High Pressure

Table 3
Weight Gain After 100h at Temperature Between
450°C and 600°C (842°F and 1112°F) for T11
Coated and Uncoated and T91 Coated (reference 6)

Alloy	Weight Gain mg/cm ² in 100h			
	450°C (842°F)	500°C (932°F)	550°C (1022°F)	600°C (1112°F)
T11	6	6	15	46
T91	5.5	13	14	13
T11 Aluminized	0.1	0.2	0.2	---
T11 Chromized	1.2	6	7	---

Table 4
Metal Loss after 100h Exposure at
Temperatures Between 350° and 500°C (662°F and 932°F)
for T11 Coated and T11 and T22 Uncoated (reference 7)

Alloy	Surface Recession, μm			
	350°C (662°F)	400°C (752°F)	450°C (842°F)	500°C (932°F)
T11	20	23	---	---
T22	20	22.5	---	---
T11 Chromized	5	17	30	22
T11 Aluminized	1	1	1	1

The sulphidizing potentials for both environments are displayed on the phase stability diagram in Figure 7 which confirms that under the conditions of test chromium oxide would be stable and, at least in the short-term, would provide protection against degradation by sulphur penetration.

Consequently, on the basis of this limited amount of data it appears that these high-chromium steels provide adequate levels of protection in this type of environment.

b) Austenitic Steels

There have been extensive efforts to evaluate the performance of austenitic materials in coal gasification environments and alloys AISI 310 and Incoloy 800 in particular have been the subject of much investigation. In the European collaborative program COST 501, these alloys were selected for extensive evaluation at temperatures between 450 and 750°C (842 and 1382°F) in a range of gasification environments for application in heat exchangers downstream of the gasifier and prior to the gas cleaning system⁽⁷⁾. The work involved both laboratory testing for times of up to 5000h, and exposure in small-scale pilot plant. The results for AISI 310 have been summarized in Tables 6-8 for temperatures between 500 and 700°C (932 and 1292°F) and it is evident that as in all data of this type there is considerable variability.

At 700°C the highest rate of loss 1400µm/yr linear, or 335 µm/yr parabolic, is consistent with the sulphidizing conditions in the ABB gasifier ($P_{O_2} = 8.7 \times 10^{-23}$; $P_{S_2} = 3.5 \times 10^{-8}$) and although the linear extrapolation rate is high, the parabolic extrapolation may be more relevant in this case since a protective Cr_2O_3 scale would be expected to form. At the lower temperatures, the conditions most appropriate to the ABB gasifier give parabolic rates between 30 and 52µm/yr at 500°C (932°F). The rates at 500°C (932°F) were based on longer term tests which are likely to give more reliable extrapolations.

Results for Alloy 800 are shown in Tables 9-11 for temperatures between 500 and 700°C (932 and 1292°F) and generally the environmental conditions were similar to those for AISI310, and again parabolic extrapolation data will be considered.

At 700°C (1292°F) for conditions representative of those in the ABB gasifier, loss rates were between 130µm/yr and 450µm/yr from tests of between 150 and 720h duration. However, one set of data, the average of two results gave a very high loss rate of 2090µm/yr. At the lower temperatures, rates were still high for relevant environments ($P_{O_2} = 10^{-24}$ $P_{S_2} = 10^{-10}$) i.e., in the range 960 - 1090µm/yr but were significantly lower at 500°C (932°) in the range 2 - 60µm/yr.

Table 5
Degradation Rates ($\mu\text{m}/\text{yr}$)
Estimated from Linear Kinetics for
High-Chromium Ferritics (reference 8)

Alloy	Temp °C (°F)	Pressure (otm)	pO ₂	pS ₂	Metal Loss
446 (26Cr)	649 (1200°F)	41	1.7×10^{-24}	1.4×10^{-8}	27
	649 (1200°F)	31	3.7×10^{-24}	7.9×10^{-9}	98
Ebrite (26Cr 1Mo)	649 (1200°F)	41	1.7×10^{-24}	1.4×10^{-8}	89
	649 (1200°F)	31	3.7×10^{-24}	7.9×10^{-9}	334
	500 (932°F)	0	4.5×10^{-31}	3.2×10^{-11}	14.7

Table 6
Degradation Rates ($\mu\text{m}/\text{yr}$) Estimated from Both
Linear and Parabolic Kinetics for AISI 310 at 700°C (1292°F) (reference 12)

Time (h)	pO ₂	pS ₂	Linear	Parabolic
500	10^{-23}	4×10^{-9}	1400	335
500	10^{-23}	10^{-10}	---	1.2
1000	10^{-23}	10^{-11}	---	120

Table 7
Degradation Rates ($\mu\text{m}/\text{yr}$) Estimated from
Both Linear and Parabolic Kinetics for AISI 310 at 600°C (1112°F) (reference 12)

Time (h)	pO ₂	pS ₂	Linear	Parabolic
500	4×10^{-25}	4×10^{-10}	1410	340*
1000	4×10^{-25}	4×10^{-10}	500	430
900	10^{-27}	10^{-12}	40	1
900	2×10^{-29}	2×10^{-12}	40	1

* Average of two results

Table 8
Degradation Rates ($\mu\text{m}/\text{yr}$) Estimated from Both
Linear and Parabolic Kinetics for AISI 310 at 500°C (932°F) (reference 12)

Time (h)	$p\text{O}_2$	$p\text{S}_2$	Linear	Parabolic
100	3.2×10^{-31}	10^{-14}	1050	110
1515	7.9×10^{-28}	2×10^{-10}	140	6
2000	2×10^{-30}	1.6×10^{-8}		16
2000	5×10^{-29}	2×10^{-9}		17
3000	2×10^{-28}	4×10^{-11}	50	30
9000	2×10^{-28}	4×10^{-11}		30
15000	2×10^{-28}	4×10^{-11}		52

Table 9
Degradation Rates Estimated from both
Linear and Parabolic Growth Kinetics
for Alloy 800 at 700°C (1292°F) (reference 12)

			Degradation Rate $\mu\text{m}/\text{year}$	
Time (h)	$p\text{O}_2$	$p\text{S}_2$	Linear	Parabolic
100	3.2×10^{-23}	5×10^{-8}	6000	650
100	10^{-23}	3.2×10^{-10}	120*	13*
150	10^{-22}	6.3×10^{-9}	960	130
500	10^{-22}	6.3×10^{-9}	1140	270
500	10^{-23}	10^{-10}	---	0.014
500	10^{-22}	4×10^{-9}	8760	2090**
720	2.5×10^{-23}	8×10^{-11}	510	150
720	2.5×10^{-23}	3.2×10^{-9}	1570	450
1000	10^{-23}	10^{-11}	---	71

* Average of nine results

** Average of two results

Table 10
Degradation Rates Estimated From Both
Linear and Parabolic Growth Kinetics for
Alloy 800 at 600°C (1112°F) (reference 12)

			Degradation Rate $\mu\text{m}/\text{Year}$	
Time (h)	$p\text{O}_2$	$p\text{S}_2$	Linear	Parabolic
100	2×10^{-29}	2×10^{-12}	11	1 *
400	2×10^{-29}	2×10^{-12}	6	1.2 *
900	2×10^{-29}	2×10^{-12}	5	1.6 *
500	4×10^{-25}	4×10^{-10}	4560	1090 *
9500	4×10^{-25}	4×10^{-10}	1000	960
100	7.9×10^{-26}	10^{-12}	20	2.2
400	7.9×10^{-26}	10^{-12}	7	2
900	7.9×10^{-26}	10^{-12}	3	0.8
400	2×10^{-29}	7.9×10^{-14}	4	0.8
900	2×10^{-29}	7.9×10^{-14}	0.6	0.3

* Average of two results

Table 11
 Degradation Rates Estimated from Both
 Linear and Parabolic Growth Kinetics
 for Alloy 800 at 500°C (932°F) (reference 12)

			Degradation Rate $\mu\text{m}/\text{Year}$	
Time (h)	$p\text{O}_2$	$p\text{S}_2$	Linear	Parabolic
100	3.2×10^{-31}	10^{-14}	530	60
150	6.3×10^{-28}	10^{-10}	490	60
1500	3×10^{-28}	4×10^{-11}	5	2
1515	6.3×10^{-28}	2×10^{-10}	75	30
3048	6.3×10^{-28}	2×10^{-10}	33	20
6500	2×10^{-28}	4×10^{-11}	---	4

Cr - S - O System At 650°C

Figure 7 - Phase stability diagram for Cr/CrS/Cr₂S₃/Cr₂O₃ system showing ferritic gas compositions

The relevant gas compositions are represented along with the IGCC gas in terms of sulphidizing potential at 700°C (1292°F) in Figure 8.

In work carried out in Japan⁽⁷⁾ in a synthetic gas atmosphere the rate of recession of AISI310 was reported as 0.22µm/yr at 500°C (932°) and 1.01µm/yr at 600°C based on linear extrapolations from 200h tests. These rates are obviously somewhat lower than the information obtained in the COST program but in this case the gas was considerably more oxidizing ($pO_2 = 10^{-25}$ at 500°C) (932°) than the IGCC composition for the ABB gasifier i.e. 7×10^{-30} at 500°C (932°).

The overall conclusion from these results is that these austenitic materials would perform satisfactorily at 500°C (932°) in coal gasification environments but could probably not be used with confidence at higher temperatures.

iii) Highly Alloyed and Advanced Materials.

In the work carried out in the 1970's and early 1980's, particularly in the USA, the emphasis was on examining the performance of some of the more exotic materials capable of resisting corrosive attack at high temperatures. The alloys examined were mainly Fe-Cr-Ni and Ni-Co-Cr materials and the work has been effectively reviewed by Howes⁽⁸⁾ who developed composite diagrams representing sound metal loss as a function of temperature for the various materials. This information is reproduced in Figures 9 and 10 and illustrates the beneficial effect of higher Cr levels in resisting attack although even at Cr contents of around 25% "breakaway" attack can occur at temperatures above 800°C (1472°F).

Work carried out in Europe around the same time considered some of these materials also but included the characterization of Fe-Cr-Al alloys of the Fecralloy type. Saunders and Schlierer⁽⁹⁾ demonstrated the excellent corrosion resistance of Fecralloy in isothermal exposure in coal gasification environment at 450°C (842°F) with no chloride present.

The protective nature of the oxide in the case of Fecralloy was attributed to the formation of a layer enriched in chromium and aluminum which was effective in preventing the ingress of oxygen and sulphur. Subsequently⁽¹⁰⁾ it was shown that preoxidation would give a further decrease in the rate of attack on Fecralloy, at least in tests of ~1000h duration in a gasification environment at 450°C (842°F).

The behavior of this type of alloy in coal gasification environments containing HCl was studied by Gohil et al⁽¹¹⁾ and it was shown that the degree of protection was influenced by the surface of the samples. Thus, preparation to a SiC grit surface finish effectively cold worked the surface and encouraged an enhanced rate of diffusion of aluminum so that an alumina rich scale was formed in the early stages of

Cr - S - O System At 700°C

Figure 8 - Phase stability diagrams for Cr/Cr₂O₃/CrS system showing austenitic gas compositions.

Figure 9 - Average Trend of Corrosion Rates for Fe-Cr-Ni Alloys
(In coal conversion atmosphere containing >0.5% H₂S)

Figure 10 - Average Trends of Corrosion Rates for Ni-CO-Cr And Ni-Cr Alloys
(In coal conversion atmosphere containing >0.5% H₂S)

exposure. Increased amounts of chromium or silicon also gave enhanced corrosion resistance and while Si was the more effective addition, the influence of increased alloying additions was less than the effect of cold work in giving enhanced protection. Typical data is shown in Figure 11 where the deleterious effect of HCl additions, at least at the 1000ppm level is also evident. This investigation involved relatively short-term tests i.e. up to 1600h at 450°C (842°F) in a coal gasification environment. Work on Fe-Cr-Al alloys of this type also formed a major part of the investigations carried out within the COST 501 Project⁽¹²⁾ on heat exchanger materials and the information obtained has been summarized in Table 12. It can be seen that even at very high sulphidizing potentials recession rates for this material are low. However, in chloride containing environments protection was lost after several hours, confirming the data of Gohil et al. shown in Figure 11.

In more recent work, Lai⁽¹³⁾ has evaluated the performance of the NiCoCrSi alloy HR160 at 871°C (1600°F) in an environment which gave $pO_2 = 3 \times 10^{-19}$ and $pO_2 = 0.9 \times 10^{-6}$ at this temperature and was probably more aggressive in gasification potential than the IGCC gas. The metal recession rate measured in a 500h test was 2040µm/yr which was substantially less than for other commercial alloys exposed in the same conditions. In a field test in the superheater region of a municipal waste incinerator at 700-760°C (1229°F - 1400°F) the metal loss in a two-month test was equivalent to 300µm/yr.

iv) Downtime Corrosion and the Effects of Condensate.

Downtime corrosion has been found to be a significant factor in the wastage of various gasifier components normally operating in a syngas environment. In addition, operation of gasifier components at temperatures below the dewpoint of the surrounding may also result in a similar loss of base metal. This low temperature wastage can result from condensation of acid-forming flue gas constituents contents and/or the hydrolysis of deposit compounds which may result in the formation of acidic solutions which are reactive to the adjacent metal surfaces.

Natesan⁽¹⁴⁾ determined metal penetration or recession rate data under downtime or dewpoint conditions for several materials used as gasifier components in 1000 hour tests with temperature cycling between ambient and 420°C (988°F). The results indicate (Figure 12) that metal recession rates are greater by a factor of 2 even at waterwall temperatures when the gas phase contains condensate. For low alloy steel these rates were significantly larger than the acceptable value of 500µm/yr (0.5mm/yr) for linear kinetics.

FIGURE 11: Gravimetric data for various alloys exposed to coal gasification environment at 450°C, a) CGA + 1000ppm HCl, 1µm finish; b) CGA + 1000ppm HCl, 600 grit SiC finish; c) CGA + 300ppm HCl, 600 grit SiC finish.

Table 12
Degradation Rates - Estimated from Linear
and Parabolic Growth Kinetics for FeCrAlloy (Ref. 12)

Time (h)	Temp °C (°F)	Log(pO ₂)	Log(pS ₂)	pO ₂	pS ₂	Degradation Rate	
						Linear	Parabolic
3,000	400 (752)	31.6	11.5	3.98x10 ³¹	3.16x10 ¹¹	3.6	2
10,000	400 (752)	31.6	11.5	3.98x10 ³¹	3.16x10 ¹¹	---	1
1,000	450 (842)	29.4	11.3	2.51x10 ²⁹	2.00x10 ¹¹	8.8	---
3,000	500 (932)	31.6	11.5	3.98x10 ³¹	3.16x10 ¹¹	3.6	2
10,000	500 (932)	27.7	10.4	5.01x10 ²⁷	2.51x10 ¹⁰	---	2.1
1,000	750 (1382)	19.2	6.7	1.58x10 ¹⁹	5.01x10 ⁶	625	212
1,000	800 (1472)	21.0	9.0	1.00x10 ²¹	1.00x10 ⁹	---	56
1,325	800 (1472)	21.0	10.0	1.00x10 ²¹	1.00x10 ¹⁰	---	33
1,630	800 (1472)	21.0	10.0	1.00x10 ²¹	1.00x10 ¹⁰	---	32
900	800 (1472)	22.0	10.0	1.00x10 ²²	1.00x10 ¹⁰	---	6

* Average of two results

Natesan⁽¹⁴⁾, Perkins⁽¹⁵⁾, and Bakker⁽¹⁶⁾ have all reported test data on metal recession rates under both cyclic and isothermal conditions with and without moist gas flow under downtime conditions. In general, the results indicated that penetration rates were greater with thermal cycling than with isothermal exposure and the presence of moist gas or air during downtime accentuated the metal recession rate over and above the values reported for cyclic conditions alone (Figure 13).

The effect of both H₂S and HCl on the dewpoint of syngases has been the subject of laboratory investigations⁽¹⁷⁾. HCl appears to have the greatest influence even at ambient pressure when the addition of 0.3% HCl increased the dewpoint by 8 to 10°C (46-50°F). At high pressure the effect of HCl additions was more pronounced and the addition of 700ppm led to an increase of 60°C (140°F) in the tabulated dewpoint of a typical syngas (Figure 14).

The major findings of the work of Perkins et al⁽¹⁸⁾ and of Bakker and Perkins⁽¹³⁾ have been summarized below.

- Condensation of HCl from raw syngas from combustion of coal with even 0.05 to 0.1% chloride can produce an aggressive acid on the metal surfaces. The reaction product (FeCl₂) can be stable in the expected range of HCl concentration.
- Chromia and/or chlorides have been detected in grain boundaries or surface sites indicating penetration of the metal surface.
- Initial iron reaction products FeCl₂ and FeSO₄ along with alkali chlorides are hygroscopic and may deposit on metal surfaces as acidic (pH4) films. Extensive wastage can occur during downtimes or initial startup due to concentration of the acidic layer.
- As noted earlier, addition of HCl in the product gas will increase the dewpoint requiring an increase in outlet temperature. Evidence of dewpoint corrosion has been found in pilot plant components believed to be operating above the calculated syngas dewpoint.
- Deposits found on convection section surfaces are not totally removed and usually these deposits contain sufficient quantities of water soluble sulfates and chlorides to cause corrosive attack.
- Materials in gasifiers which are susceptible to sulfidation during operation also suffer from aqueous corrosion during downtime in areas where the temperature of a component is below the dewpoint of the syngas. General corrosion and pitting as well as intergranular and transgranular stress corrosion cracking were observed.

FIGURE 12: Effect of Downtime Condensate On Metal Recession Rates Metal Temperature: 420°C, Gas Temperature: 900°C, 1000 hours, Mixed Gases

FIGURE 13: Metal Recession Rates for Fe - 1 1/4Cr - 0.5 Mo Steel

FIGURE 14: Effects of HCl Additions on Dewpoint of Syngas at 4.2 MPa (600 psig)

- Low alloy steels suffer from general attack while pitting is usually observed on stainless steels during downtime particularly in conjunction with carbon containing deposits. Pitting is also exacerbated by the presence of chloride in the deposits. The severity of pitting was found to increase as the concentration of HCl in the syngas increased.

The laboratory studies⁽¹⁷⁾ showed that 1000ppm HCl was required for accelerated pitting of stainless steels while pilot plants suffered downtime pitting while producing syngas with as little as 200ppm HCl.

Chloride in deposits appears to be directly related to surface pitting since the severity of pitting increases as the concentration of chlorides increases in surface salt solutions. Following downtime saturation of deposits with chloride-containing species condensate samples exposed to HCl containing syngas were pitted to an extent one order of magnitude greater than those exposed in moist air at the same temperature.

It appears that pitting attack can be initiated during either cool down or startup since the laboratory studies confirmed such wastage can be initiated between 25 and 150°C (~75-300°F). Within minutes pitting was induced in the presence of chloride containing deposits in moist air at 35°C (150°F) in one such study⁽¹⁶⁾. The authors suggested that downtime wastage could be controlled by use of alternate materials such as 2-6% Mo steels or use of chromized components. Additional laboratory studies were also recommended. The main form of attack in high-alloy steels at the Cool Water IGCC plant was pitting and this was attributed to downtime acidic attack.

The majority of problems described as downtime corrosion are in fact related to deposits and/or condensates which adhere to component surfaces whenever the boilers or gasifiers are removed from service. Operational changes which avoid deposit and or condensate accumulation would of course ameliorate the problem. Experience with down time corrosion in individual boilers firing miscellaneous fuels which result in hygroscopic deposits forming acids or which leave an acidic condensate provides certain guidelines for minimizing such attack.

Keeping boiler surfaces dry will generally alleviate these problems and in more severe cases an alkaline wash upon shutdown followed by air drying of metal surfaces is appropriate.

Downtime wastage may also be controlled by use of chromized components or substitution of 2-6%Mo steels in lower temperature service.

v) General considerations for materials selection

It is evident from the survey of the published literature that a wide range of alloys has been evaluated for service in coal gasification environments and, although the gas compositions vary considerably, there is less variation when the compositions are

compared on the basis of sulphidizing potential. A feature of the data has been the strong emphasis on austenitic materials with high levels of chromium and while these alloys frequently show low rates of attack in aggressive environments, cost considerations would limit applications in a gasifier of the design proposed by ABB-CE. On the other hand, it is equally clear that mild or low-alloy steels with at best only limited amounts of chromium, show rates of attack which would be unacceptable in service applications.

Clearly, the choice of material for the aggressive conditions proposed for the ABB plant would involve alloys with sufficient chromium or aluminum to form protective surface oxides. For large areas of exposed metal surfaces materials costs will clearly be a critical parameter in construction of a commercially viable unit. Equally important however, will be the long-term reliability and on-line availability of a commercial installation and normally a five to ten year period of reliable operation would be required. This requirement highlights one of the fundamental difficulties in materials selection for aggressive environments in that test pieces have rarely been exposed for periods of greater than 5000h and in most cases exposure times have been much shorter i.e. 500-1000h. This comment relates to both laboratory experiments and to the evaluation of samples in pilot-plant.

Throughout this review, rates of metal loss have been described in terms of annual recession rates based for the most part on a linear rate of degradation for material such as mild steel where it was unlikely that a protective scale would form. For austenitic materials extrapolations have been based on parabolic kinetics. However, it is important to appreciate the limitations of this approach and the implication in comparing different materials. Thus linear extrapolation of short-term data to give annual recession rates:

- generally over estimates corrosion rates if the scale provides some degree of long-term protection
- takes no account of the effects of scale spallation
- assumes a constant rate of attack throughout the exposure time.

On the other hand, extrapolation based on parabolic kinetics will not be conservative if protection breaks down (breakaway attack) or if spalling of the protective oxide occurs. In the latter case, if sufficient alloying addition (e.g., Cr) is present beneath the spalled layer, the oxide may "heal" and protection would be restored.

While these factors represent serious limitations there is no viable alternative in the absence of either reliable long-term data for relevant alloy systems or a good predictive model to allow short-term data to be extrapolated to service conditions.

With this background and using the information generated in this review, recommendations have been made for materials for gas touched components in the proposed ABB gasifier.

CONCLUSIONS

1. Unprotected mild or low-alloy steel will not give adequate corrosion resistance in typical coal gasification environments at 400 and 500°C (752 and 932°F).
2. Surface treatments such as chromizing and aluminizing will greatly improve the corrosion resistance of mild or low-alloy steels but only data from short-term tests appear to be available. Longer term data would be essential to establish the degradation kinetics.
3. Austenitic and high-chromium ferritic materials show improved corrosion resistance at 500°C - 650°C (932°F - 1202°F) and some longer term data (e.g. 5000h) are available.
4. Alloys of the FeCrAlloy type have shown good resistance to attack in coal gasification environments at least in the absence of chloride.
5. There is some uncertainty about the appropriate sulphidizing potential when a hot gas is in contact with a cooler surface and the use of a pseudo-equilibrium requires justification. Also, the kinetics are not understood and must be determined experimentally.
6. Condensate corrosion can be avoided if the gasifier walls are maintained dry and in extreme conditions given an alkaline wash and air dried.

C. Materials Recommendations.

The end result of the investigations is a specification for materials for each component of the plant. The development of the specification is in three phases. The first phase is the evaluation of the process. The second phase is the development work. This phase involves inputs from the following disciplines: process, systems, metallurgist, specification engineer, and projects. The third phase provides the following outputs: piping and equipment metallurgy, coincident pressures and temperatures both normal and design, corrosion allowance, code compliance, environmental requirements, fluid state, fluid category, chemical material, concentrations, thermal cycles, charpy impact test requirements, stress relief requirements, and maximum line sizes. This output is provided to the customers system engineer, the metallurgical engineer and the specification engineer. The following areas required special consideration.

i) Coal Feed

The coal feed system has traditional erosion concerns.

The recommendations are:

1. The pulverized coal receiving bin, lockhoppers, and feed bin have material selected for strength with protection for erosion. The shells and hoppers are carbon steel. The options for erosion protection are: Tp 309 cladding, extenalloy surface treatment, or a Tp304 liner sleeve which is not bonded.

- The selection for erosion protection is a Tp304 liner which is not bonded. The same selection was made for the coal Kinetic Extruder discharge and feed bins.
2. Flow feed lines should be carbon steel with erosion protected elbows.
 3. Fuel nozzles should have silicon carbide linings.

ii) Gasifier and Heat Exchanger

Carbon steel is subject to severe sulfidation by H_2S , elemental sulfur and Na_2S in the presence of CO_2 (and CO to a lesser extent) when subject to continuous exposure. Fundamental studies in ABB Power Plant Laboratories (KDL) provided wastage curves which have been confirmed both in chemical recovery units and the PDU (Process Development Unit) in Windsor.

Many methods have been used to protect tube metal surfaces in similar gas environments. Studs and refractory, weld overlay, metallizing, composite tubing and chromizing are considered to be among the more effective approaches. Each approach has its advantages and disadvantages. The final approach and degree of protection required has not been absolutely established.

Chromizing is one of the more recent developments that has been used to protect steam generation/heating surface. Chromizing is a high temperature diffusion coating process in which a chromium rich metal surface is produced by solid state diffusion resulting in a structure that is resistant to corrosion in a variety of environments. It results in the surface of components (particularly pressure part tubing) being modified with the diffusion of chromium into the metal surface. Test and experience data has shown that it is a practical and cost effective alternative to other methods of protection. Carbon steel and numerous alloys can be chromized including the following steam generation tubing materials: SA-192, SA-213 T-11, T-22 and T-91. Up to 40% of the iron in the outer 0.020 inches of the tubing can now be replaced by chromium to provide a wastage resistant surface. The outer layer contains up to 30 to 40% chromium at the surface. The process as developed can accommodate large heat exchangers i.e., waterwall panels, superheater assemblies and other tubular components that are used in many industries to generate or superheat steam. This process has been demonstrated in operating utility and chemical recovery boilers.

The O.D. and /or I.D. surface of these tubular components can be chromized but, more importantly, the attachments, fins and welds that are fabricated before chromizing are also chromized which provides protection to the total surface. The enrichment occurs "in" and not "on" the surface, consequently, application of the coating does not change the physical dimensions of the component. Being an integral part of the base metal, the metallurgically bonded, diffused chromium structure is not subject to peeling or spalling.

Chromizing carbon steel and low alloy tubular steam generator components is thus a unique way to convert the surface of tubular steam generator components to the equivalent of a high chromium, ferritic stainless steel. Being ferritic, the thermal

expansion properties of the corrosion resistant structure are nearly identical with the ferritic base metal thus eliminating the tolerances and expansion considerations that must be made when a totally austenitic or austenitic/ferritic co-extruded tubing is used. The 30-40% chromium in the chromized coating is significantly higher than the 18-20% chromium level in commonly used austenitic alloys, and thus is considered to be equal to or perhaps more resistant to sulfidation than the 18-8 austenitic stainless steels. Welding is a simple, straight forward procedure. Butt welds on chromized components are made with single weld preps that are machined after chromizing. Filler metal is the same as if welding non-chromized tube. If protection from wastage is desired, an E309 electrode is used as a cover pass. Attachments that must be made to the chromized surfaces utilize the same procedure that would be specified for welding non-chromized surfaces.

In the early 1980's under an EPRI sponsored program, the quality of the diffused coating was extensively evaluated for use on a commercial basis as protection of tubular steam generator waterwall panels and convection pendant assemblies for coal gasifiers. These studies showed that the chromized components had properties that were suitable for commercial use including: ductility of coating, uniformity of coating thickness/composition and various other aspects that impact commercial scale use. Associated studies in the EPRI sponsored program showed that the diffused coating had substantial resistance to sulfidation in the hostile coal gasification environment.

Another method for the practical prevention of wastage in waterwalls in the syngas environment is weld overlay with Tp309L or fabrication from Tp430. Inherent stresses in the overlaid tubing and possible post weld heat treatment for Tp430 may require safe ending of the waterwall panels prior to welding to the carbon steel tubes in the gasifier.

Experience in substoichiometric reducing environment in both fossil fired boilers and chemical recovery units as well as in municipal solid waste incinerators has shown the studs and refractory design will protect against such wastage. Operating experience in the coal gasification PDU as well as pulverized coal and chemical recovery units show that use of Tp430 studs prevent stud burnback, thus minimizing replacement while providing wastage protection primarily while retaining a layer of frozen slag which usually replaces the refractory during oxidation. Silicon carbide refractory is preferred in incinerators to avoid a reduction in lower furnace heat transfer thus avoiding overloading superheaters. If insulating properties are required use of Emerald Ram or some other Al_2O_3/CR_2O_3 refractory may be selected.

For convective sections the maximum requirements for material selection is chromized surfaces whose base material has been selected for traditional strength considerations. The use of alloys with increasing chromium content, reinforced by surface chromizing, is based on the results of laboratory and pilot plant testing by CE for the Department of Energy (ERDA) during the 1977-81 test period as well as this successful use of chromized tubing in sulfidizing atmospheres in operating fossil fuel and chemical recovery boilers. Options include: for the evaporator, T-91; for low and

intermediate superheater, Tp304 or 800H; and for the high temperature superheater, HR3C (Modified Tp310) or Composite 10/T22.

Sections in the gas pass which are uncooled such as brackets, guides and supports can be made of IN671 for high temperatures and either 310 Niobium stabilized or HR3C for lower temperatures.

Downtime corrosion is addressed by both operating procedures to keep the gasifier and SGC (syngas cooler) dry during downtime and the use of materials that are resistant to chloride enhanced corrosion. The operating procedures may not fully eliminate the problem, but they are recommended. The procedures will ensure dry out of the system during down time to prevent pitting due to hydrolysis of acid forming ash deposits. The use of materials is considered the best approach to control downtime corrosion. The materials selected for sulfidation meet the requirements for downtime corrosion prevention.

For protection from hydrogen attack use of chromium has been found effective. The surface treatments specified for sulfidation protection also ensure protection for the temperature and partial pressure of the hydrogen in the syngas.

The recommendations are:

1. For the Gasifier, Crossover and SGC pressure vessels which are not gas touched, the recommendation is 516 GR70 Carbon Steel. During the detailed engineering alternative carbon steels will be evaluated.
2. Gasifier waterwalls by process design are required to provide a minimum heat loss. To allow for this the walls must be lined with refractory and allow for the accumulation of a build up of solidified slag and or for running slag. The recommendation is for the waterwalls to be made of traditional boiler materials as SA192 with Tp430 studs and a insulating chrome alumina refractory.
3. For the convection surfaces traditional boiler materials with chromizing were recommended. The following material limits were established: SA192 to 425°C (800°F), T-11 to 454°C (850°F), T-22 to 510°C (950°F) and T-91 to 565°C (1050°F). The design of the superheater requires use of stainless steels to compensate for differential movements, for this Tp304 was selected.
4. For uncooled members Tp304 Niobium stabilized was selected.
5. Refractory coverage was selected for erosion protection in the gas pass.

iii) Char Removal

The char removal system consists of a cyclone and baghouse. Both components are exposed to the syngas environment. The cyclone is subject to erosion.

The recommendations are:

1. The char primary cyclone material was selected as Tp304 or Tp310.
2. The material for the char removal baghouse, char transport screw, primary cyclone char control valve and char rotary valves was selected as Tp310 or Tp321 or refractory lined carbon steel.

iv) Char Feed

The char feed system has traditional erosion concerns with the exception that this system is exposed to a higher temperature than traditional solid feed systems. In addition to recommendations by ABB CE, an independent consultant was used. Options were selected and J.R. Johanson conducted high temperature friction tests on the more promising materials, and stainless steel alloy that best satisfied all the requirements was found.

The recommendations are:

1. The char lockhoppers should have material selected for strength and clad with either Tp309 or refractory lined carbon steel.
2. Flow feed lines should be stainless steel.
3. The char nozzles should be lined with silicon carbide.
4. The char receiving bin and char lockhoppers were selected as either T91 CR, Tp310 or Tp430Ti, or refractory lined carbon steel.
5. The char control valves, char stream splitters, char pick-up T's and char feed Bin were selected as either Tp310 or Tp430 Ti HP10.

v) Additional Recommendations

1. It is recommended that integral test sections of all alternate materials be included in the convection section as well as integral panels in the waterwall, Figure 15. These can then be inspected at six month intervals and measured ultrasonically to determine wastage rate and provide the basis for estimated service life.

In addition to integral tube installation a materials testing program should include:

- ° Cooled and non-cooled (passive) probe tests.
- ° Coating and alloy test rods welded to membranes on gasifier walls.
- ° Studs on tube surfaces as test specimens.
- ° Plates of various alloys welded in place in non-cooled surfaces in the gasifier system.

2. Bench scale screening of suggested materials options will provide a ranking of alternative materials in comparison with the recommended procedure, i.e.:
Chromized T-91 vs.
SA192 Overlayed Tp309
3. Confirm if possible the pilot plant experience with chromized tubing (CE produced).
4. Consider erosion protection for:
 - a. Cross-over waterwalls - studs and refractory vs alternate alloy Tp430Ti.
 - b. Baffle wall in Heat Exchanger Section - Tp430 or studs and refractory.
 - c. Transport piping - see Fuel and Char System discussion.
5. Include instructions for drying gasifier during down time to prevent pitting due to hydrolysis of acid forming ash deposits.

VI. UNRESOLVED ISSUES

Final material selections will be made in the detail design phase of the project. There are questions about the practicality of some of the recommendations made. While the recommendations expressed in this report are based primarily on metallurgical reasons, there are other concerns which may cause these recommendations to be altered.

The cost effectiveness of some of the selections is the primary concern. The plant needs to be designed with the most cost effective material selections both for considerations of the demonstration plant costs, and for consideration of future commercial plants. For this reason, an ongoing investigation into alternate materials is continuing. A testing program will be proposed below to address the needs of material selections.

In some instances, the selection is impractical because of the design configuration. For example, The use of extendalloy was mentioned for fuel lines. This may be impossible in some of the smaller lines since current manufacturing techniques may not apply in the size range required. The cost of this coating will also be a factor. Currently The design of the fuel lines is being reviewed to find a practical installation.

For the gasifier and SGC the issues which require further work involve protection from sulfidation. The recommendation for chromizing is still under review. Additional research into previous studies and possible laboratory testing may be done.

In general it is expected that as the design of the plant proceeds there will be a number of areas which will require a modification to the material recommendations listed here.

VII. RECOMMENDATIONS FOR FUTURE WORK

A. Bench Scale Corrosion Studies

As noted in the preceding discussion confirmatory testing in the laboratory of the various materials options is recommended. Also, as the literature review has shown, there is little long-term information on materials performance particularly for the surface protected alloys which would be widely used in the ABB unit.

Bench testing will be conducted to provide the basis for selection of materials to be included in strategically placed test panels and controlled temperature corrosion probes in the first IGCC repowering unit which ABB is designing for the city of Springfield, Illinois. Materials selected in this subtask will be fabricated in the form of coupons of approximately one square inch total surface area. After polishing, these coupons will be weighed and measured prior to exposure in laboratory bench facilities for extended periods in well defined environmental conditions.

Accelerated weight-loss tests will be carried in small Vycor tubular electric furnaces (Figures 16 and 17). These furnaces will be arranged to allow passage of the controlled atmosphere across previously weighed metal coupons embedded in powdered ash or deposit constituents. Metal coupons will be about 38mm (1 1/2-inch) long, 3.2mm (1/8-inch) thick, and 8mm (5/16-inch) wide, with an exposed surface area of approximately 750mm² (1.2in.²). Each furnace will be regulated at the desired temperature with a thermocouple-actuated temperature controller in the thermocouple hot junction located inside the furnace. Exposure times of 7 days and 30 days will be used.

A total of three separate runs are planned to compare the candidate alloys and modified surface against standard boiler materials under anticipated conditions for the Springfield IGCC boiler. Both waterwall and superheater conditions will be simulated.

Since the test materials will be carefully examined microscopically, weighed and measured prior to testing, these same measurements following exposure will allow assessment of wastage potential. Duplicate samples will be examined metallographically if significant wastage is observed due to physical measurements.

It is anticipated that final selection of alloys and materials to be exposed in test panels or controlled temperature probes in the IGCC field unit can be made on the basis of test results from this bench scale screening experience and in consultation with an independent expert.

FIGURE 16: LABORATORY TEST FURNACE

FIGURE 17: CORROSION TEST FACILITY

B. Field Monitoring of Fireside Corrosion

i) Background

Fireside corrosion in coal fired boilers is generally associated with areas of localized higher heat transfer and/or build-up of slag and deposits. Molten phase attack may also occur on waterwalls under reducing conditions or in high temperature superheaters. Specific regions of high wastage may vary from unit to unit depending on operating conditions and variations in fuels. The waterwalls just above the burner and the finishing superheater bends are particularly vulnerable when firing corrosive fuels.

Experimental work to pinpoint the causes of various problems and to study proposed solutions will include field studies with controlled temperatures corrosion probes in operating boilers supplemented with laboratory studies designed to simulate actual furnace conditions.

ii) Field Studies

In order to determine the effectiveness of any method of reducing or eliminating corrosion, it is essential that it be evaluated under service conditions. Relevant test data can only be obtained in the following circumstances:

- (i) With test surfaces of the same shape as actual furnace components.
- (ii) In a temperature range high enough to fix the maximum service temperature, and
- (iii) In an environment comparable to that of actual service.

Items (i) and (ii) can be controlled in laboratory tests very effectively, and together with the best simulated furnace environments, item (iii), provides means of screening materials and permits preliminary evaluation of new methods of corrosion control. However, in order to completely fulfil item (iii), testing must be carried out under actual operating conditions.

Various field methods have been used to evaluate alloys and coatings, as well as to study the effectiveness of additives, fuel treatment, and design and operation changes. These include:

- (a) installing test tubing as integral parts of walls and superheater circuits;
- (b) use of probes fabricated of materials suitable for present or future furnace tube construction.

The welding of test specimens into a circuit has the advantage of subjecting them to exactly the same pressure-temperature environment as that of a permanently installed tube in the same position. In this sense, it is the ultimate in evaluation procedures.

However, this method has several disadvantages:

- (i) The specimen cannot be inspected for metal wastage until the unit comes off the line and, therefore, the time of exposure may not be conveniently governed.
- (ii) The installation is rather expensive and there is little or no control over the metal temperature except at that temperature fixed by the steam temperature. For these reasons, this method is used primarily for materials which have been screened previously in some other manner. Specific tests of this type are discussed later.

Probes have been used in many investigations because temperature and time of exposure can be controlled and their location is limited only by the position of access doors to the unit. Because of these advantages, it was decided that properly developed probes would yield more data in a shorter period of time than any other method.

Figure 18 shows a horizontal probe. It consists of cylindrical test specimens screwed together and cooled with compressed air or N₂ regulated by thermocouples embedded in the specimen walls. Specimens are machined in 50mm (2-in.) ID tubular sections and are 6.25mm (¼-in.) thick and 38mm (1 ¼-in.) long. The details of a typical test cylinder and a diagram of the installed probe are shown. Note that the thermocouple well in the cylinder wall is drilled to within 1mm (0.040-in.) of the outer metal surface, thus providing for accurate metal temperature measurements.

Figure 19 is a schematic diagram of the complete experimental apparatus. The apparatus consists essentially of three parts.

1. Probe to which the test specimens are attached.
2. A mechanism for regulating air flow to the probe for control of specimen temperature, and
3. A temperature recorder.

The probe is divided into two sections; one which is water cooled and serves as an arm to hold the other section which is air or N₂ cooled. The two sections are 50mm (2-in.) diameter and may be any length desired within practical limits. Test specimens are attached as previously described to the cooled section in three or more groups, each group containing up to six specimens. Temperatures are recorded but for those specimens not containing thermocouples estimates are made from the plot of temperatures as a function of location.

Regulation of the air flow to the probe controls the temperature of the specimens. The temperature gradient along the length of the probe permits the testing of a given alloy at several temperatures during a single test.^(21, 22) Control of the air flow is accomplished by means of a manually operated valve plus two bypass solenoid valves which are activated by change in temperature of the centrally located thermocouple.

FIGURE 18: Horizontal Corrosion Test Probe

FIGURE 19: Pneumatic Temperature Control Circuit

Where waterwall corrosion is anticipated or observed, the probe design and manner of installation are changed in an effort to closely simulate actual unit wall construction. In this modification five cylindrical 50mm (2-in.) diameter test specimens of different alloys or castings are screwed together to form a probe. This probe is mounted vertically in the plane of the furnace wall usually through a strategically located observation door. Therefore, only half of the sample surface is exposed to the furnace interior. Vertical probe construction and general installation is shown in Figure 20. The temperature control system is identical to that described for horizontal probes.

Previous work²³ in moderately substoichiometric conditions showed only minimal material losses for carbon and low alloy steel after exposure for two years in a coal-fired environment.

iii) Tube Corrosion Measurements.

Tube Corrosion rates could potentially change within the IGCC systems due to changes in waterwall slagging conditions and/or changes in furnace stoichiometry/oxygen level. Therefore, both the shakedown operation and the long term performance test of the gasifier system, boiler tube corrosion/wastage rates will be ascertained. To evaluate waterwall corrosion rates, or changes therein, a relatively long period (1,000 to 8,000 hours) of consistent boiler operating is required. Since the primary purpose of a demonstration evaluation is to assess corrosion rates under low stoichiometry firing conditions, that phase is discussed in detail.

The two methods used to assess the tube corrosion potential of the IGCC system are discussed below.

1. Direct measurement of the secondary furnace waterwall tube thickness is recommended by a ultrasonic thickness (UT) wall monitoring technique both prior to and after the one year long term performance test. During each of these tests up to one thousand (1000) tube locations should be measured. The measurement positions will be selected based on discussions with Performance Design Engineering. Wastage locations observed in other coal gasification systems will be reviewed. Nominally, the six elevations selected represent: (1) the fuel inlet zone or air nozzle elevations (2) midpoint of combustion reburn zone; (3) combustion zone outlet or additional air nozzle evaluation; (4) the gasifier outlet plane; (5) the crossover duct; (6) mid point of leading heat exchanger tubes; (7) bottom of leading heat exchanger tubes. Test tube numbers and locations shall be accurately recorded for future reference and repeatability. The locations will be reviewed with the plant operators and the co-sponsors prior to final selection. Tube wastage while operating with the gasifier system is determined as the difference in tube wall thickness between the baseline and performance tests. Wastage rates are determined by dividing the calculated wastage by the actual number of hour of gasifier operation during the test period. Wall thickness measurements during baseline testing

will be compared with those obtained during the long-term performance tests. Boiler outages of up to one week duration may be required for the UT mappings.

2. Indirect measurement of furnace waterwall wastage rates can be determined by corrosion probe. Four waterwall locations shall have probes installed for periods of 30 hours, 300 hours, and 1000 hours during the long term performance testing. Additional periods of 2000, 4000 and 8000 hours may be monitored during the long term tests.

It is anticipated that the exposure of corrosion probes during baseline testing would be for a minimum of 1000 hours. The three elevations for the probe testing are: (1) the reburn zone inlet (four locations at this elevation); (2) the midpoint of the reburn zone (2 locations); and (3) the furnace outlet plane (2 locations).

The eight special waterwall ports will be installed in the gasifier and cross over waterwall as shown in Figure 21. It is anticipated that following each of the above exposure periods the wall thickness of each probe would be measured ultrasonically after mechanical (wire brush) cleaning and then reinserted into the gasifier boiler. Upon completion of the full test period, the coupons will be cleaned, weighed and measured as described below. An additional superheater probe is planned for installation in the heat exchanger area. Final selection of the probe location is subject to the approval of plant personnel and the cosponsors.

Corrosion probes are air or N₂ cooled temperature controlled cylindrical test specimens. Cooling requirements will be reviewed with Springfield personnel. Figures 22-23 present schematics of an as-installed waterwall corrosion probes. As noted the probe contains specimens or coupons of various tube wall materials. For both baseline and long term performance test periods the following examinations will be conducted on each specimen prior to and after exposure and testing in the furnace.

1. Weight, microhardness, outside diameter and wall thickness
2. Chemical composition and/or mill report of each specimen
3. Cross section metallographic examination to determine microstructure and surface condition of selected samples based on severity of wastage.

In addition upon completion of a probe test, the probes shall be carefully removed from the furnace to avoid disturbing any slag deposits formed. These deposits shall be examined for species which enhance tube wall corrosion and for corrosion by-products. During actual testing, once a probe is in place and the automatic temperature controller and recorder is operational minimal care is required. Visual observation of the normal unit walk-downs and removal of

FIGURE 21: Test Probe Location

FIGURE 20: Vertical Corrosion Test Probe - Design

a probe if the high temperature alarm is actuated will be discussed with the plant operating personnel.

It is considered that the outlined test program when fine-tuned will provide ample early warning of any significant wastage and allow optimization of a technique for minimum wastage.

FIGURE 22: Overall Design of Vertical Probe

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IX. APPENDIX - NON PROPRIETARY MATERIAL

A. Coal Gasification PDU Materials Studies

Passive corrosion probes containing six different alloys and twelve coatings were exposed in Combustion Engineering's Coal Gasification Process Demonstration Unit between July 1978 and January 1981. Operating at gas temperatures sufficient to provide skin metal temperatures of 600, 820 and 1000°F these materials were exposed for 2500 total gas making hours. A second probe series was exposed over 800 hours (see Figure A1).

Calculations of equilibrium pO_2 and pS_2 are similar for this pilot operation and for the Springfield IGCC operation. Thus wastage would be expected to be similar.

The results of the first series indicated that increasing chromium content in ferritic alloys or substitution of austenitic alloys provided increased corrosion resistance. In addition, four of the twelve coatings on carbon steel showed sufficient resistance to warrant further study.

The second series included SA192 carbon steel, T-11, T-22, T-9, Tp304, Tp310, Tp347, In671, In690, In800 as well as chromized and aluminized T-22 and spray coatings Metco 444 and CoCrAlY.

This second exposure showed that at 1000°F all ferritic alloys up to 9% chromium suffered metal losses at the same wastage rate. The austenitic alloys were attacked at only about 10% of this rate. The chromized, aluminized and CoCrAlY afforded protection while the Metco 444 was a total failure (see Figures A2 and A3). Metallurgical examination showed undercutting of the CoCrAlY in some places and the chromized surface was damaged by sootblowers.

Penetration measurements showed the properly chromized surface was less subject to wastage than the aluminized surface in this gasifier environment.

Downtime Wastage

As shown in Figures A4 and A5, the open ended construction of the original passive probes allowed accumulation of highly acid condensation. Since the PDU was cycling often, particularly during the early period of operation, pitting of significant magnitude was observed during this time and the task force recommended end caps on the probes to prevent further condensation.

TABLE 1
Wall Thickness Losses (inches)
Passive Probe 1000°F PDU

	800 Hours		2500 Hours	
	Average	Maximum	Average	Maximum
SA192	---	---	0.021	0.029
SA192 Cr	---	---	0.006	0.014
SA192 Al	---	---	0.020 0.015	0.022 0.021
T-22	0.016	0.028	0.038 0.049	0.040 0.084*
T-22 Cr	0.003	0.006	0.007	0.010
T-22 Al	0.011	0.014	0.014	0.017
T-22 CoCrAlY	0.005	0.015	0.008	0.012
T-22 (M444)	0.036	0.074	missing	missing
T-9	0.013	0.043	0.014 0.026	0.016 0.075*
304	0.003	0.006	0.012	0.031
347	0.003	0.010	0.002	0.005
310	0.002	0.005	0.001	0.002
800	0.003	0.011	---	---
671	0.001	0.002	---	---

* = Erosion

TABLE 2
Wall Thickness Losses (inches)
Passive Probe 1000°F PDU

	800 Hours		2500 Hours		
	Average	Maximum	Average	Maximum	
SA192	---	---	533	737	1812
SA192 Cr	---	---	152	357	517
SA192 Al	---	---	430	559	1462
T-22	406	711	1092	1000	3712
T-22 Cr	76	152	178	254	585
T-22 Al	279	356	356	254	1210
T-22 CoCrAlY	127	381	203	305	690
T-22 (M444)	914	1880			
T-9	330	1092	356	406	1210
304	76	152	305	790	1037
347	76	254	51	127	173
310	51	127	25	51	85
800 *	76	280	---	---	808*
671	25	51	---	---	265*

* = Calculated from 800h average data

FIGURE A1: Drawing of PDU Showing Unit Elevation at Sites of Coating and Probe Tests

Second Series

FIGURE A2: Weight Loss of Coated T-22 Test Pieces

FIGURE A3: Weight Loss of Alloy Test Pieces

3	T-22	4	T-9	5	Tp347	6	Tp304	7	Alonized	8	Tungsten Carbide	9	CocRA1Y	10	Wallex 50	11	Colmonoy 8	12	Chromium	13	C-E Multi	14	METCO 45	15	XP 24
Coatings on SA-192

FIGURE A4: Cleaned Exposed Test Specimens

FIGURE A5: Pitting Attack to I.D. Surface

B. Other Materials Experience

i) Yuubari 40TPD

A 40 tpd fluidized bed pilot plant gasifier was constructed and operated in Yuubari City, Japan. This plant was built as part of the Japanese National Program. The plant operated from 1981 until 1990. It was dismantled after the end of its program. The components from the plant were inspected and a research program was initiated to gather materials data.

The Yuubari plant ran a series of 68 tests with an overall run time of 8325 hours. This gives a relatively long term evaluation of materials in a gasification environment. The original intent of this work was to provide information for a 200 tpd fluidized bed IGCC scale-up, however the information is useful for other processes as well. While the operating conditions are not exactly the same as in the entrained flow gasifier, there are many similarities.

The information on this plant was presented in a paper presented at the U.S./Japan Joint Workshop on Surface Coal Gasification Meeting held October 13, 1992. The paper entitled "Materials Inspection of 40 tpd Fluidized-bed IGCC Pilot plant Gasifier" was presented by N. Nishimura of Mitsubishi Heavy Industries, Ltd.

The materials research covered components in the gasifier, heat exchanger, coal system, char system, ash system, and product gas system. Results were obtained from field inspection of the components and from sampled specimens.

The results of the field inspections showed that refractory can be effective in resisting corrosion. Refractory was installed in the gasifier, in the 'L'-valve and its' nozzle, and in the pipe between two cyclones. Only a little corrosion was noticed in these areas.

Corrosion in the heat exchanger tubes in the gas pass was about equal to the corrosion in the waterwall tubes leading them to conclude that gas flow doesn't influence corrosion.

Erosion was heavy in the char piping and in certain parts of the gasifier.

Stainless steel parts in the coal and char system showed some pitting and microcracks.

The sampled specimens in the gasifier vessel showed some metal loss from general corrosion but they could not detect hydrogen embrittlement. In the high temperature heat exchanger corrosion was observed but cracking and changes of metal properties was not.

In the coal system, transgranular cracks about 1mm. deep were found in the water-cooled jacket of the coal feeder.

The char injector and transport pipe eroded heavily and there was some corrosion in the char nozzles.

The ash system showed metal reductions and cracking on the inner and outer surface of a small water cooled nozzle.

There was an expansion joint in the product gas system made of 304 stainless steel. This component showed severe intergranular corrosion and cracking.

The 40 tpd results led to several recommendations. Specifically, there should be consideration given to dew point corrosion in carbon and low alloy steels. In stainless steels, the main problem was stress corrosion cracking. Erosion resistance is important in high velocity regions. Water cooled jackets should be designed to alleviate thermal stress. Components should be designed to allow inspection of critical components.

In general, the results of the Yuubari plant study seem to be consistent with the recommendations given in this report. From a qualitative standpoint, the results are what one would expect. It is impossible to compare these results in a quantitative manner, however, because exact numbers and operating conditions are not available. It should be noted that several differences exist between the Yuubari plant and the one designed for the ABB CE IGCC project. The fluidized bed gasifier operates at temperatures in the combustor that are generally lower than in the entrained flow gasifier. The heat exchanger conditions are probably similar. Gas compositions and pressures are not known for the Yuubari plant and these may affect the corrosion rates. Erosion rates in the gasifier are probably not comparable, but the erosion rates in the coal and char lines probably are comparable.

ii) DOE Experience

Several materials test programs have been carried out in gasification pilot plants with Department of Energy sponsorship. The aim of the work was to test candidate materials in operating conditions similar to those of a commercial unit.

Among the pilot plants included in the program were: Hygas, Conoco Coal, Synthane, Bi-gas, Peakgas, Battelle, U-Gas, Westinghouse (now KRW), GEgas, and Mountain Fuel Resources. Overall the project covered most of the major process areas of coal gasification. In all cases the gasifier vessel was protected by insulating layer of either frozen slag, if the vessel were water-cooled, or of refractory designed to minimize heat loss and to resist the gasifier environment. The gasifier vessel was fabricated in mild or low-alloy steel and where condensate attack was anticipated weld-overlay with Type 347 was used to give protection.

The resistance to sulphidizing attack was assessed by exposing candidate alloys in the freeboard areas of the gasifiers and extensive work was carried out in the Westinghouse unit ($pO_2 = 1.7 \times 10^{-24}$, $pS_2 = 1.4 \times 10^{-8}$) at temperatures between 837 and 1030°C (1588 and 2174°F) with exposure times of about 800h with thermal cycling. The results showed that alloys with greater than 24% chromium (e.g. 617,310) performed well in the short term tests and showed linear corrosion rates of less than 1 mm/yr. Armco 18SR showed a similar rate of attack and this alloy contains only 18% Cr but the additions of 2% Al and 1% Si presumably improved corrosion

resistance in this case. The high-Ni alloys (Fe-Ni-Cr) did not perform well and gave corrosion rates of more than 500 mm/yr in some cases.

In the temperature range 540 to 870°C (1004 to 1598°F) in the Hygas and Synthane gasifiers high-chrome ferritics (e.g. 430) and austenitic alloys (321, 316, 310, Alloy 800) performed well. Aluminizing or chromizing alloys 310 and 800 gave improved performance. In the first stage of the Hygas plant where operating temperatures were in the range 510-620°C (950-1148°F) alloys with 15-20% Cr performed well. Overall these results are consistent with the findings of the experimental work referred to in this review and confirm the need for Cr levels of 18% or more for good resistance to sulphidation. Also the pilot plant exposures have shown the benefits of aluminum and silicon additions in combating corrosive attack although aluminized alloys appear to exhibit better performance in the laboratory than in more service-related environments. This may be associated with the more cyclic operating conditions in pilot plant. Techniques such as weld overlay and the use of co-extruded tubing will give good protection but chromizing appears to be an attractive and relatively inexpensive method for providing high levels of chromium at the surface of critical components. For applications such as hot gas clean-up, metallic filters have generally performed poorly; and in situations where large surface areas are exposed to the hot gas, problems of corrosion attack can be anticipated.

In gas quench and heat exchanger applications the austenitic steels (304 and 316) performed well but no details of metal temperatures were given. Experience quoted with the CE gasifier indicates that unprotected mild steel was satisfactory although it was emphasized that exposure times were short and long service lifetimes were not required in the pilot plant. The "Ebrite" alloy (26% Cr) gave the best performance in the Westinghouse unit. Soot and ash deposits contributed to poor corrosion resistance in some cases and the low alloy materials T22 and T91 gave unacceptably high local rates of attack.

At the Mountain Fuel Resources (MFR) 30T/day process development unit (PDU) the 800H superheater tubes were subject to stress corrosion cracking at 600°C (1112°F) gas temperature and 432°C (810°F) steam after some 250 hours of operation during shakedown. While subject to significant surface oxidation or gas phase attack, the adjacent T22 tubing did not fail during the operating period. Aluminized T-22 was ordered as replacement tubing.

There have been instances of stress-corrosion cracking by polythionic acids in austenitic steels in piping and transfer lines as a result of reaction between sulphide scales and condensates. Higher alloy material may be substituted to overcome the problem or metal wall temperatures can be maintained above the dewpoint value.

SUMMARY

- In strongly sulphidizing environments at temperatures in the range of 620 - 870°C (1148 - 1598°F) alloys with >24% chromium were required for reliable performance at temperatures between 510 and 620°C lower chromium ie 15-25% alloys were satisfactory.

- For less sulphidizing environments alloys with more than 17% Cr were generally acceptable.
- Additions of aluminum and silicon were shown to be beneficial in improving the sulphidation resistance of austenitic steels.
- Ebrite (26Cr1Mo) and high-Cr austenitics were the most satisfactory materials for gas quench and heat recovery applications. Lower Cr alloys showed some pitting attack as did the ferritic materials 410 and 430.
- Deposits and dew point corrosion can give enhanced rates of attack at high temperatures.
- The results from pilot plant exposures are consistent with the results of laboratory studies and are in accord with the predictions of oxide and sulphide phase stabilities.

iii) **Experience of Materials Performance in the Cool Water IGCC**

Little detailed information has been published and data on materials performance has been classed as proprietary. The following information is available.

- Aluminized coatings do not perform well in high sulphur, high chloride coals, although the quality of the aluminized layer was not optimized
- Pitting attack developed on high alloy steels apparently as a result of condensate attack during downtime
- The results indicate that with the best material evaluated a 25 year tube life could be expected when burning a low-sulphur coal but similar predictions for high-sulphur conditions would require a longer exposure time
- -Exposure in highly sulphidizing environments containing chlorides accelerated the corrosion of low and high-alloy steels and recession rates were up to two orders of magnitude greater than those in less sulphidizing conditions.

iv) **Pilot-Plant Exposure**

(Ref: Bakker & Perkins: Corrosion-Erosion-Wear Berkeley, 1990, NACE, ed M. Levy)

In recent work conducted by EPRI the apparent inconsistencies between laboratory results and plant experience have been investigated. It was claimed that corrosion rates of <0.2 mm/yr as predicted from laboratory testing at 500-550°C (932-1022°F), which is a satisfactory rate of degradation for a commercial plant, were not achieved in practice in operating units and pilot plants where much higher rates of loss were recorded. For nearly all materials, recession rates were higher than expected and in the case of aluminized coatings on low-alloy steel little attack

occurred in the laboratory, but in plant conditions the materials suffered severe degradation in less than 2000h.

The EPRI work focussed on the influence of trace elements, particularly chlorides, and deposits on rates of degradation although the deleterious effects of these factors has already been well established in work in Europe. Not surprisingly the work has shown that chloride can have an important effect in increasing rates of attack and will tend to concentrate in the presence of deposits forming CaCl_2 for example. Chlorides can also influence dew points and therefore effect down-time corrosion. The results provided by the research at EPRI have shown that there is a significant influence of chlorides on dew point in high pressure environments with an increase of up to 60°C (108°F) with 700 ppm of HCl in gas at 41 atm.

This effect could have a major influence on corrosion behavior in plant and a factor which is at best poorly understood. Trace amounts of metal such as Zn, Pb, As & Ge have also been found in deposits on tube surfaces but there was insufficient information to determine the effect, if any, on the protective nature of chromia scales. In corrosion experiments on low-alloy steel it appeared that the addition of 600 ppm of HCl to the gas atmosphere reduced the rate of recession by 2/3 at atmospheric pressure. However, at high pressure the rate of attack was increased by HCl additions and was greater by an order of magnitude than that of the same gas at atm pressure. The rate of attack was such that an uncoated low-alloy steel could not be used for commercial application (with or without HCl) above 300°C (572°F).

Similar results were obtained with aluminized low alloy steel when about 1/3 of the coatings were consumed by oxidation-sulphidation in 1000h at 350°C (662°F) with 1000 ppm of HCl at 41 atm pressure. Corrosion rates were further enhanced by adding downtime cycles. Thus these experiments simulated operational experience where aluminized materials have performed poorly.

Work on austenitic steels, while incomplete in many respects has shown that downtime corrosion results in the formation of less protective scales (lower Cr, higher Fe) at higher temperatures and that vanadium can be a beneficial trace addition for high temperature corrosion resistance. If this proves to be generally true there might be some justification in using CrMoV rather than $2\frac{1}{4}\text{Cr}$ steels or in the chromizing of steels with a pack which includes vanadium.

In work on high Cr austenitic (e.g. alloy 800) the more rapid rates of attack in pilot plant were attributed to the presence of HCl, surface deposits, high pressure and downtime corrosion although no good supporting evidence was provided. Overall the results from the EPRI program confirm the deleterious effects of chloride and of deposits and the damaging influence of downtime corrosion. In addition, it is clear that investigations conducted at atmospheric pressure may be inadequate to present high pressure operation.

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