MATERIALS FOR GASIFIER HEAT EXCHANGERS

PROJECT SUMMARY 302

CLEANER FOSSIL FUELS PROGRAMME
– CLEANER COAL R&D PROGRAMME

OBJECTIVES

- To assess the potential corrosive effects of deposits formed on coal-fired and coal/waste co-fired gasifier fuel-gas/syngas heat exchangers in Air Blown Gasification Cycle (ABGC) and Integrated Gasification Combined Cycle (IGCC) systems.
- To determine the composition ranges of deposits in ABGC and IGCC fuel-gas/syngas heat exchangers.
- To quantitatively assess the rates at which these deposits cause downtime corrosion and the effectiveness of proposed preventative measures.
- To assess the potential for the deposits to cause synergistic degradation (at high and low temperatures), and to measure the resulting increase in material damage rates.
- To identify exposure/operating conditions/ materials which could lead to rapid heat exchanger failures.

SUMMARY

A wide variety of gasification systems are continuing to be developed around the world, including Integrated Gasification Combined Cycle (IGCC) and the UK developed Air Blown Gasification Cycle (ABGC) systems. Originally, these systems were developed to be fired on various grades of coal, but there is now interest in using a more diverse range of solid fuels (eg co-firing coal with waste or biomass, using low grade coals and heavy fuel oils) in order to reduce environmental impact and fuel costs.

All gasification technologies require a heat exchanger (often called either a syngas cooler or fuel gas cooler) between the gasifier and the gas cleaning system. The duty required from this heat exchanger varies depending on the type of gasifier, gas-cleaning requirements (eg hot dry cleaning or wet scrubbing) and steam cycle needs.

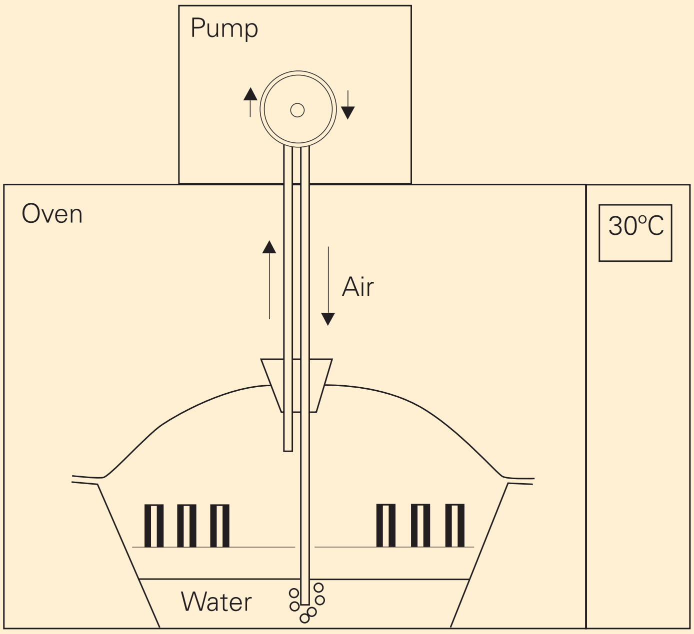

Figure 1. Downtime corrosion exposure system

However, gasifier hot gas path environments are potentially very aggressive for materials both during plant operation and off-line periods. This has the effect of imposing a temperature window for the safe operation of these heat exchangers (with current materials restricting their use to modest steam conditions and preventing their use as superheaters with commercially viable lives) and dictates that downtime corrosion control precautions are required during off-line periods. There are significant differences in the hot gas path environments between the various gasification systems and with different fuels, but unfortunately these just have the effect of changing the balance between different potential degradation modes arising from the gasification environments.

The project has assessed the potential corrosive effects of deposits formed on coal-fired and coal/waste co-fired gasifier fuel-gas/syngas heat exchangers in ABGC and IGCC systems. This has included determining the ranges of deposit compositions formed on heat exchangers with different fuels and quantitatively assessing effects of such deposits on downtime corrosion (including the effects of potential preventative measures) and synergistic interactions. These activities have led to the identification of combinations of fuels, operating conditions and materials that could produce rapid heat exchanger failures due to interactions with the deposits formed during the heat exchanger operation.

The following candidate gasifier heat exchanger alloys were investigated: AISI 316L, AISI 310, AISI 347H, Alloy 800, Sanicro 28, Haynes 160, Esshete 1250, Haynes 556, IN625 and T23. In terms of cost and performance Sanicro 28 appears to be the best choice for evaporative heat exchangers in the range of test conditions investigated.

BACKGROUND

A number of coal gasification systems have been developed based on different types of gasification processes. Once generated, the fuel gases need to be cooled and cleaned before being burnt in gas turbines. It is possible to carry out the gas cleaning by water scrubbing the cooled fuel gases, but this leads to lower cycle efficiencies and requires the provision of a scrubbing and wastewater treatment facility. The first generation gasification systems have been built to use water scrubbing for gas cleaning. Hot dry gas cleaning, using barrier filters to remove particulates and catalysts/sorbents to remove gaseous species offer higher cycle efficiencies as well as lower capital and operating/ disposal costs. However, hot dry gas cleaning is still at the developmental stage and so only parts of these processes are included in the latest demonstration plants, often as parts of sidestreams.

There are many significant differences between the various gasification systems. From the perspective of materials performances and the optimum materials selection, the component operating conditions and the environments produced in each of the systems are critically important. Minor and trace gas species are very important in determining materials performances, both through direct reaction and indirectly through deposit formations and subsequent reaction. The levels of the minor and trace gas species in these gasification systems are not readily available.

All gasification technologies require a heat exchanger between the gasifier and the gas cleaning system. The duty required from this heat exchanger varies depending on the type of gasifier, gas cleaning requirements and steam cycle needs. However, gasifier hot gas path environments are potentially very aggressive for materials both during plant operation and off-line periods. This has the effect of imposing a temperature window for the safe operation of these heat exchangers (with current materials restricting their use to modest steam conditions and preventing their use as superheaters with commercially viable lives). Thus, in different gasification systems evaporators are used to produce saturated steam at 10MPa/320°C with metal temperatures of 320-400°C depending on the fuel gas temperature. It is expected that evaporator steam conditions will be raised to 18MPa/350°C, with corresponding metal temperatures of 380-450°C. Even at these steam conditions, highly alloyed materials such as alloy 800 (Fe-32Ni-20Cr) or Sanicro 28 (Fe-31Ni-27Cr-3Mo) need to be used to give economically viable heat exchanger lives. However, some gasification cycles would be more efficient (and viable) if at least some superheating could be carried out by a heat exchanger in this location in the hot gas path: this would involve steam at temperatures of 500-550°C with corresponding metal temperatures of 550-600°C.

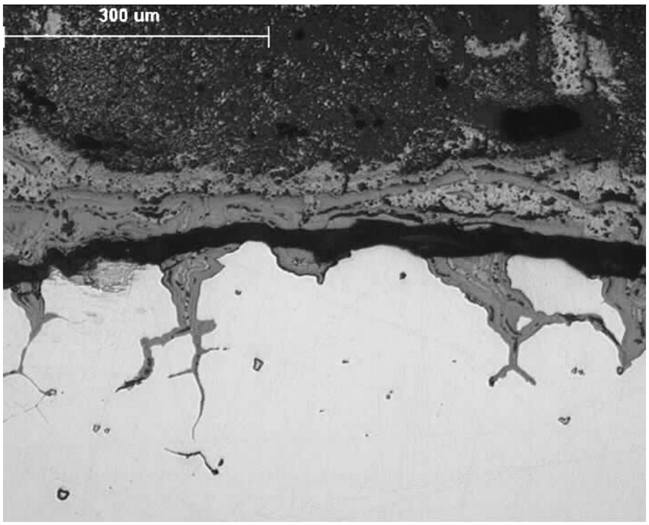

Figure 2. Surface features of Alloy 800 after Synergistic Test

DEPOSIT FORMATION ON GASIFIER HOT GAS PATH COMPONENTS

A literature search was carried out to gather together reported information on the formation of deposits in gasifier fuel gas/syngas heat exchangers. In light of the limited information on deposit compositions found in the literature and available from COST522 partners, this data gathering was extended to cover the volatilisation and condensation of trace element species in gasifier fuel gas paths, as this is the major route by which chemically aggressive deposits could be formed on heat exchanger surfaces. This yielded more useful information on potential heat exchanger deposit compositions. However, there were still obvious limitations in the information gathered, so a thermodynamic study was carried out to provide consistent data on the effects of pressure and gas compositions in ABGC and Prenflo IGCC systems.

The thermodynamic study considered a number of variables:

- Two gasifier processes: an oxygen blown entrained flow process (Prenflo) and an air blown fluidised bed process.
- Atmospheric and pressurised operation.
- Temperature ranges covering gasification and hot gas cleaning.
- A range of sulphur and chlorine levels to cover the potential ranges of coal and coal/biomass fired systems.
- The elements As, B, Ba, Be, Ca, Cd, Co, Cu, Hg, K, Mn, Mo, Na, Pb, Sb, Se, Sn, V, Zn.

The elements Cr, Ni and Fe were not investigated as they are major alloying elements used in materials used throughout the fuel gas path.

The study found that trace and alkali metals are more volatile in gasification systems and that the same broad classification of volatility used for combustion gases is not valid as different species are volatile. Sulphur and chlorine levels (both absolute and relative), as well as operating pressure and gasification process can influence the volatility of trace and alkali metal species. Hg, Pb, Zn, Cd, Se, Sb and Sn (and As, B and V in some systems) can pass through the gasifier system, as well as alkali metals. Depending on the heat exchanger surface metal temperature Pb, Zn, Cd, Sn, Na, K potentially can condense onto the heat exchanger from the gas stream.

DOWNTIME CORROSION TESTING

Tests to investigate downtime corrosion (DTC) of materials in coal gasification environments have utilised different simulations of gasifier heat exchanger deposits. These compositions have been produced by EPRI and KEMA, from their experience of entrained gasification processes, and British Coal, from their experience of a fluidised bed partial gasifier.

Two types of testing have been carried out (electrochemical and DTC) using a range of candidate materials for gasifier heat exchangers.

Electrochemical testing using a triple electrode system in naturally aerated solutions at 30°C has been used to measure the pitting potential, repassivation potential and hysteresis of the candidate materials. The test method is based upon ASTM G61.

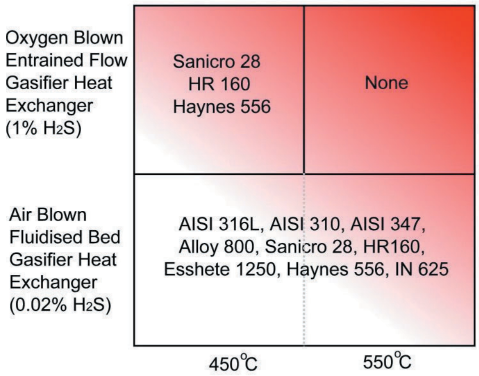

Figure 3. Example of Summary Materials Degradation Map

DTC testing was carried out using a modified EPRI test. Specimens were coated with a deposit consisting of 6.26% $FeCl_2$, 3.74% NaCl and 90% char. Specimens were exposed to water saturated air at 30°C for 25 hour cycles. After exposure the deposit was removed and the specimens cleaned and examined before repeating the test. Damage was assessed by visual inspection, weight loss and depth of attack.

The pitting resistance equivalent number (PRENW [including tungsten]) was calculated from the materials nominal compositions. It has been established that the pitting behaviour of stainless steels can be broadly related to composition using empirical relationships such as PREN. Crevice corrosion is influenced by many factors and therefore PREN is generally not so useful for prediction of this type of behaviour. The ranking of the overall resistance of the materials to the electrochemical and DTC tests matched the PRENW ranking well.

DOWNTIME CORROSION TESTING AND PREVENTATIVE MEASURES

A series of tests assessed the effectiveness of candidate preventative measures against downtime corrosion. The candidate preventative measures include the use of dry atmosphere (such as dry nitrogen), washing deposits off heat exchanger surfaces (with and without corrosion inhibitor) and mechanical removal of deposits. The majority of these tests have been carried out on clean samples, but one test was carried out using pre-oxidised/ sulphidised samples.

Tests have shown that for simulated deposits applied to clean specimens that mechanical removal of deposits and/or washing deposits off heat exchanger surfaces will reduce corrosion rates. The addition of a corrosion inhibitor to the wash solution would further reduce corrosion.

SYNERGISTIC TESTING

The conditions used for synergistic tests produced a range of simulated gasifier environments for heat exchangers in IGCC and ABGC systems. For the IGCC system, the gas composition was chosen on the basis that it is an oxygen blown entrained flow gasifier with no sulphur removal prior to the heat exchanger. For an ABGC system, the gas composition was chosen on the basis that it is an air-blown fluidised bed gasifier with in-bed sulphur retention.

Specimens were exposed for 7 x 100 hours at 450 or 550°C in either the IGCC or ABGC simulated gases with and without the corresponding simulated deposit. For each test condition (ie gas/temperature combination) one of the pair of alloys were exposed to DTC for 25 hours at 30°C.

The IGCC environment was more aggressive than the ABGC environment, as would be expected with the higher H_2S level.

At 450°C there are still a number of alloys that give satisfactory performance even in the presence of deposits. At 550°C most of the alloys can not be considered due to poor high temperature gaseous corrosion (HTGC) performance and even the best performing alloys are borderline in terms of HTGC and DTC performance.

To allow easier interpretation of the results generated by this project, summary materials degradation maps can be produced e.g. Figure 3.

CONCLUSIONS

- Limited information is available on the formation of deposits on gasifier heat exchangers and the fate of the trace element species found in gasifier fuel gases.
- Data from theoretical studies and plant observations indicate that trace element partitioning between condensed and vapour phases is significantly different in gasification and combustion systems.
- In all gasification systems, many more trace elements are volatile and many have the potential to be transported along the fuel gas path and condense onto heat exchanger surfaces. Plant observation of significant levels of Pb, Zn, As, Cd, Se, Sb and Ge on heat exchanger surfaces confirms these predictions.
- Important parameters that affect the behaviour of trace elements in the fuel gas paths have been highlighted as sulphur and chlorine levels, operating pressure and gasification process.
- Electrochemical tests have been carried out to produce baseline data for the candidate heat exchanger materials which were then ranked in terms of predicted DTC resistance. The EPRI DTC test has been modified to more accurately simulate real deposits observed in service. Alloy ranking given by this DTC test and electrochemical

studies have shown a strong correlation with that predicted by PRENW.

- Mechanical removal of deposits and/or washing deposits off heat exchanger surfaces will reduce corrosion rates.
- Synergistic tests that simulated a range of gasifier environments for a heat exchanger found that Sanicro 28, HR 160 and Haynes 556 gave the best performance over all the conditions tested.
- The data generated has been used to identify safe operating windows where factors do not combine to produce rapid heat exchanger failures. Aspects such as candidate heat exchanger materials, gasifier type, fuel and fuel gas compositions, deposit compositions and heat exchanger operating conditions have been investigated.

POTENTIAL FOR FUTURE DEVELOPMENT

The test programme has demonstrated that gasifier hot gas path environments are potentially very aggressive for materials both during plant operation and off-line periods. Current materials are restricted to modest steam conditions. Many gasification cycles would be more efficient if at least some superheating could be carried out by the fuel gas heat exchanger. Alloy research and development is required to produce materials with extended lives at temperatures below 450°C and viable service lives at temperatures above 450°C. Alternatively the use of coatings and/or co-extruded heat exchanger tubing may provide a route to achieve this target. This research area would also require investigation of the weldability of the new materials/coatings and the resulting mechanical properties, strength, high temperature corrosion-fatigue etc., in the parent material and weld region.

COST

The total cost of this project was £99,903 with the Department of Trade and Industry (DTI) contributing £49,951 and COST522 partners/Cranfield University providing the remainder of the balance.

DURATION

36 months – May 2000 to April 2003.

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FURTHER INFORMATION

For further information about this project see contractor report Materials for Gasifier Heat Exchangers available from the Helpline.

Further information on the Cleaner Fossil Fuels Programme, and copies of publications, can be obtained from:
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