

Materials challenges and gasifier choices in IGCC processes for clean and efficient energy conversion

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In the 1970 and 1980s, gasifiers were envisaged for synthesising substitute natural gas (SNG) as well for IGCC (integrated gasification combined cycle) systems. Component temperatures were above 700°C, but stainless alloys did not have the required corrosion resistance. Experimental alloys developed in the UK were alumina formers, incorporating Ta, W, and Mo as gettering elements for sulphidation resistance. Sulphidation corrosion is solvable, but attack by HCl in gasification environments seems intractable. The supposed materials problems of gasification, plus the complexity of IGCC, have led to them being sidelined for power generation. However, commercial IGCC plants are not dependent on high temperature materials and offer higher efficiency than Rankine cycle steam. Best near term prospects for IGCC are for CO₂ capture, but this constrains the type of gasifier. Gasifiers incorporating carbon capture and storage produce hydrogen, or with less capture, SNG. Such systems will supply SNG for space heating as well as electricity, and can cope with the intermittency of wind energy. High efficiency IGCCs will need very advanced gas turbines with 100 bar, 1500-1600°C turbine inlet conditions. Key requirements will be thermal barrier coatings and catalytic combustor materials. Such gas turbines would offer efficiencies of 70% in straight CCGTs, or 50% when used in carbon capture IGCCs.

Keywords: IGCC, Gasification, Sulphidation, Synthetic natural gas, Flexible power plant operation, Gas turbines, HCl high temperature attack, Reviews

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Introduction

The general arrangement of an integrated gasification combined cycle (IGCC) plant modified for carbon capture and storage (CCS) is shown schematically in Fig. 1.¹ The figure does not fully convey the complexity of IGCC, since the gasification process results in streams of grey and black water containing fine ash, unconverted char and ammonium salts that have to be treated before discharge. On some types of gasifier, tars, phenols and liquid hydrocarbons containing sulphur compounds have to be dealt with and recycled back to the gasifier. But modern steam plant is also complex, needing processes for dealing with wet ash, particulates from the air preheaters, and the contaminated calcium sulphate from the flue gas desulphurisation system.

A great deal of effort has been put into trying to design and build IGCC plants which are more economic than conventional steam plant and, as with steam plant, the aim has been to raise operating temperatures. This appeared to require the determination of temperature limits for off-the-shelf materials in coal gasification environments, and it must be admitted that even highly alloyed stainless materials have proved disappointing – hence, as will be described, the formulation of innovative alloy compositions using the ‘gettering’ principle. Some of these developments may have good prospects for gasifiers producing a synthetic or substitute natural gas, but they are more likely to be used as coatings than structural materials.

It seems worth stating at the start that much of the work which has been done on IGCC materials was a hangover from the early days of coal gasification, when steam, air, oxygen and sometimes hydrogen had to be heated up by raw syngas, preparatory to being reacted with coal. Materials resistant to a sulphiding and carburising syngas were obviously needed. In contrast, most gasifiers and associated plant which are or would be used in IGCCs have no such requirement, as high temperature heat exchange for steam superheating is not a necessity. Even in those IGCC processes where superheating is useful, it is arguable whether steam temperatures in excess of 500°C are needed.

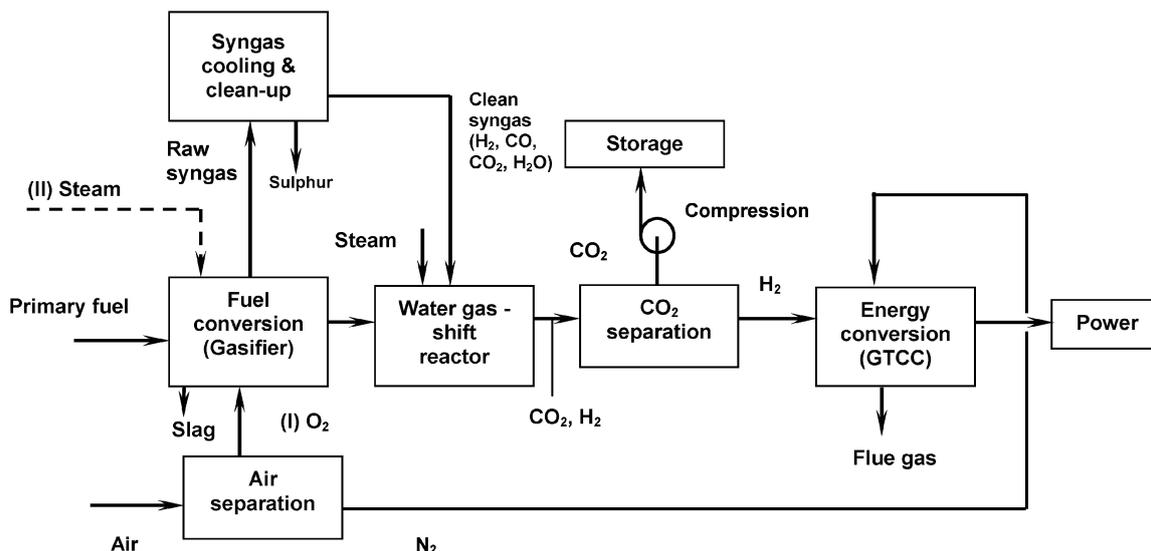
The view that IGCCs do require a monumental amount of materials work, alongside the supposed complexity of the plants, has meant that conventional steam plants have always been more attracted to investors, even though these are in a struggle to obtain improvements in heat rate, and where carbon capture is still unproven. Nevertheless, if there really was serious concern about CO₂ and global warming, IGCC based plants would be under construction today. The units needed to capture CO₂ for a ‘standard’ IGCC are add-on processes of the same type that have been used on ammonia and hydrogen plants for over 50 years. If governments really believed in Global Warming, they would, despite the high capital cost of IGCC plus CCS, be insisting that these plants be built, now, not by 2020! Instead, all the R&D funding for CCS seems to be going into steam plant based pilot plant activities.

The figures in Table 1, taken from a Department of Energy/National Energy Technology Laboratory (DOE/NETL) sponsored study in 2007, support this judgement. In the study² three types of entrained flow gasifiers were compared with a supercritical steam plant, with a

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1 Schematic diagram of IGCC based plant incorporating CO₂ capture (after Ref. 1)

steam temperature 593°C. The costs are somewhat out of date, but the trend is well shown. Supercritical plants, without carbon capture, easily beat IGCC on costs. The efficiency of non-CCS supercritical plants is about the same as GE–Texaco and E-Gas IGCC plants, but is significantly worse than a Shell based IGCC. When CCS is included the electricity cost comparison is more uniform, but the efficiency of the supercritical plant falls disastrously. Compared with GE–Texaco, coal consumption would be over 10% higher, and electricity about 1% more expensive. Further, CO₂ emissions, even after CCS, are much worse than the IGCC processes. It should be noted that these figures do not correlate very easily with practice in Northern Europe. The use of higher heat value (HHV) efficiencies pushes down the figures by ~2%, but there is also another 1–2% reduction because average air and cooling water temperatures are higher in the USA. And over here, we are opting for an 85% capture rate from steam plant since above this level, in steam plant, efficiencies plummet and costs soar.

The post-2020 timescale for widespread application of CCS does imply that politicians have other priorities than global warming. But European governments should be concerned with a nearer-term issue. There is a need to make the best use of coal, the majority of which is imported into Europe, even today. The UK, for example, imports two-thirds of power station coal and, if coal continues to be used, imports will rise, despite the protestations that there are billions of tonnes still to be mined. Accordingly, since IGCC is basically a gasifier combined with a modified combined cycle gas turbine (CCGT), it will be shown below that – using all the developments of which *combined cycle* technology is

capable – coal to electricity efficiencies of 50% can be achieved, even with carbon capture. It is unlikely that even ultra-supercritical coal plant will reach this target.

These two subjects, CO₂ capture and high efficiency IGCCs, will form a major section of this review. The history of IGCC and related gasification projects also receive attention, since, during the 1970s and 1980s, these became major challenges to materials technology. One of the present authors (FS) was responsible for much of the materials development for SNG-type gasification processes within British Gas, and how these activities differed from the mainstream activity is reviewed. Most of the gasifier projects geared to producing SNG were discontinued, partly because of materials issues, and this history still influences current perceptions of IGCC’s prospects. IGCC concepts that have survived to reach a commercial stage have been based on well proven hardware, in which the focus of the development work was getting the equipment to work on bituminous coal.

Integration and plant flexibility

Integrated gasification combined cycle is a form of power generation in which coal, lignite or heavy oil is first gasified to produced a ‘syngas’ which, after purification to remove H₂S, COS, HCl and particulates, is burnt in a conventional CCGT to generate electricity. The operative word is ‘integrated’, which is usually taken to mean that steam generated from the gasifier and gas purification and upgrading processes is integrated with that in the heat recovery steam generator (HRSG) of the CCGT, minimising capital costs and improving efficiency.^{3,4}

Table 1 Comparison of efficiency, cost and CO₂ emissions for USA based IGCC and supercritical power plants at 2007 cost levels²

	Gasifier							
	GE–Texaco	GE–Texaco	E-Gas	E-Gas	Shell	Shell	Low supercritical	Low supercritical
Capture rate/%	0	90	0	90	0	90	0	90
Efficiency (HHV)/%	39.0	32.0	39.7	31.0	42.1	31.2	39.3	28.4
Capital costs/\$/kW	1813	2390	1733	2431	1977	2668	1575	2870
CO ₂ emissions/kg MWh ⁻¹	783	92	777	99	725	99	803	111
Electricity cost/\$/MWh	76.3	105.6	74.0	110.3	81.3	119.4	58.9	106.5

Integration can be taken much further. Most IGCC systems need oxygen at 95% purity, requiring a cryogenic oxygen plant and associated heavy duty air compressors. The capital and running cost of these, which is high, can be significantly reduced by taking air off from the gas turbine compressor of the CCGT, and using this as a 'feed' to the cryogenic plant. Clearly this will reduce the flexibility of the IGCC scheme and can make start-up more difficult.

The issue of flexibility in any type of fossil fuel generating plant cannot be over-emphasised.⁵⁻⁷ This is especially true for countries like the UK that have plans to increase wind and nuclear capacity. Spain, which already has ~20 GW of windfarms, uses its hydroelectricity to compensate for times when there is no wind power. Denmark, which also has much wind energy, in proportion to its size, plus a great deal of combined heat and power, has to continually import and export electricity to keep its grid in balance. And to give a different example, France, which gets over 70% of its electricity from nuclear. In point of fact, to meet daytime demand, France has to use a combination of imports, plus 36 GW of indigenous hydropower and pumped storage to enable nuclear to run at near constant output. Britain (and especially England, as Scotland moves towards energy independence) has neither the hydro-power reserves nor the high voltage direct current connections which allow other European countries to function with large amounts of wind and nuclear power. Its fossil fuel based plants have to be highly flexible.

In this respect, most IGCC plants, except those relying on fixed bed gasifiers, are (like nuclear plants) not capable of being shut down at night and starting up the next day, i.e. operating in a true two shifting regime. This is an issue that must be acknowledged in any objective review of the merits of IGCC plants. There are ways round this issue, in which the IGCC plays a fuller part of the European energy scenario, producing substitute natural gas as well as electricity. These aspects will be discussed towards the end of this review. Today, the IGCC at Buggenum, in The Netherlands, is used for daytime load following as its power output can be ramped up and down very rapidly. Good load following is a saleable commodity, and in this case completely offsets the fact that IGCC efficiency falls away at low loads. The reduction of efficiency is a feature of some of the older gas turbine models (Buggenum dates from the mid-1990s). In being modified to run on syngas, the gas turbine is not able to maintain turbine inlet temperatures, once it moves away from the design load. Efficiency also falls because of the high demand from the plant ancillaries, which do not drop off in line with the load on the gasifier. Newer gas turbines, which incorporate more sophisticated compressors, using several rows of variable stator blades, are more able to maintain gas turbine efficiency when the load falls away.

Environmental issues and global warming

Integrated gasification combined cycle as a method of generating electricity has come in and out of fashion. It first came to prominence in the 1970s when it was seen as a method of eliminating SO_x emissions and combating acid rain. When coal is gasified, the hydrogen sulphide



2 Granton plant for CO₂ removal from synthetic natural gas (SNG) syngas using Benfield process in 1978: 'steam' is mixture of CO₂ and water vapour

formed is easy to remove from the syngas. Integrated gasification combined cycle faded when it became apparent that flue gas desulphurisation systems could be retrofitted to existing steam power plants.

More recently, IGCC has been promoted as a proven method of capturing CO₂. It is with some amusement that those with practical experience in the gas and petrochemical industries, read about the millions of pounds, euros and dollars being put in pilot scale 'demonstration' projects for removing CO₂ from flue gas streams. Figure 2 shows a plant at Granton, Edinburgh in which CO₂ was removed from the gasification stream to ensure that the gas had the correct calorific value. And there are scores of ammonia plants in which it is essential to remove CO₂ from the 'synthesis gas' to permit hydrogen and nitrogen to react to form ammonia.

For the authors, however, the merit of IGCC is the prospect of hitting efficiencies significantly higher than any practical coal fired steam plant. Recall that the IGCC at Buggenum, commissioned in 1994, runs with an efficiency of 43.2%, which for an inland site using river water for cooling is a very acceptable figure.⁸ Water is needed for the gasification reactions, of course, but since most of the power is generated by the gas turbines, the cooling water requirement for condensers is rather less than that with supercritical steam. Even for CO₂ capture, where the downstream treatment requires steam to convert all the carbon monoxide in the raw syngas to hydrogen, the balance is still in favour of gasification. The DOE/NETL report² showed that gasifiers need ~2 t water per hour for each megawatt of output, whereas supercritical needs 3 t h⁻¹ MW⁻¹. Presumably, the high water demand of the supercritical plant is a result of the relatively low efficiency of electricity generation, which requires more carbon being burnt for the same output.

Corrosion of materials in gasification environments

Early US work

Following the 1973 energy crisis, a major effort was made in the USA to produce oil and gas from coal. The USA was already a major importer of oil, and there was concern that natural gas reserves were also running

short. Efforts were needed to produce a substitute or SNG. In fact, the real issue was that the price of natural gas had fallen to such a low level that development of new fields had declined.⁹ Nevertheless, there was general concern about the future of gas supplies and, to ensure compatibility with natural gas, any coal to gas process would have to produce a gas containing at least 90% methane.

A 90% methane target was a serious chemical engineering challenge. In practice most organisations adopted a multistep route, in which the preliminary step was the reaction of steam and oxygen with coal or coal char to produce a gas which contained a fairly high proportion of hydrogen, along with excess steam, carbon monoxide and carbon dioxide, and (depending on the pressure and temperature) some methane plus unreacted steam. In an extremely good, succinct review of 1970s gasification processes,^{10,11} Bodle and colleagues pointed out that some of these gasifiers could be air rather than oxygen blown, producing a 'low Btu' fuel gas for power production. Where fuel gas was being produced, for the firing of gas turbines, it was advantageous to keep the gas reasonably hot before it was combusted, so there was a need for filtration of particulates and sulphur removal at high temperatures.

Because of its high nitrogen content, low Btu gas had a caloric value of about 150 Btu ft^{-3} (5.6 MJ m^{-3}), whereas 'high Btu' gas, intended for SNG production, has a caloric value of $\sim 300 \text{ Btu ft}^{-3}$ (11.2 MJ m^{-3}). The main syngas reaction can be written as



Having obtained a gas mixture rich in CO and H₂, a standard treatment was to remove H₂S and then to perform a series of catalytic reactions on the purified syngas to form a straight substitute natural gas. These steps are of the exothermic type, occurring at about 300–400°C, and are suitable only for medium pressure steam raising. Since the intention was to produce a SNG, not electricity, steam production was regarded as a drawback. In more sophisticated processes the unpurified or 'raw' syngas was reacted still further with the coal itself. Here the 'organic' constituents in the coal would react with hydrogen to form more methane at temperatures in the 700–900°C range. The portion of the coal that did not react was transported to another part of the equipment, as a 'char', and reacted with steam and oxygen to provide the raw hydrogen rich syngas.

Many of these processes were of the fluidised bed type, in which the temperatures were in the 700–1100°C range, whereby the ash in the coal did not melt. Movement of coal char from one reactor to another required transfer lines in which the red hot char moved at high velocity. In other parts of the process cyclones were required to remove entrained ash and char. Erosion corrosion at high temperatures was a serious issue. In addition, the gas streams exiting these processes were hot, and it was beneficial to utilise this heat for preheating reactants to a very high temperature.

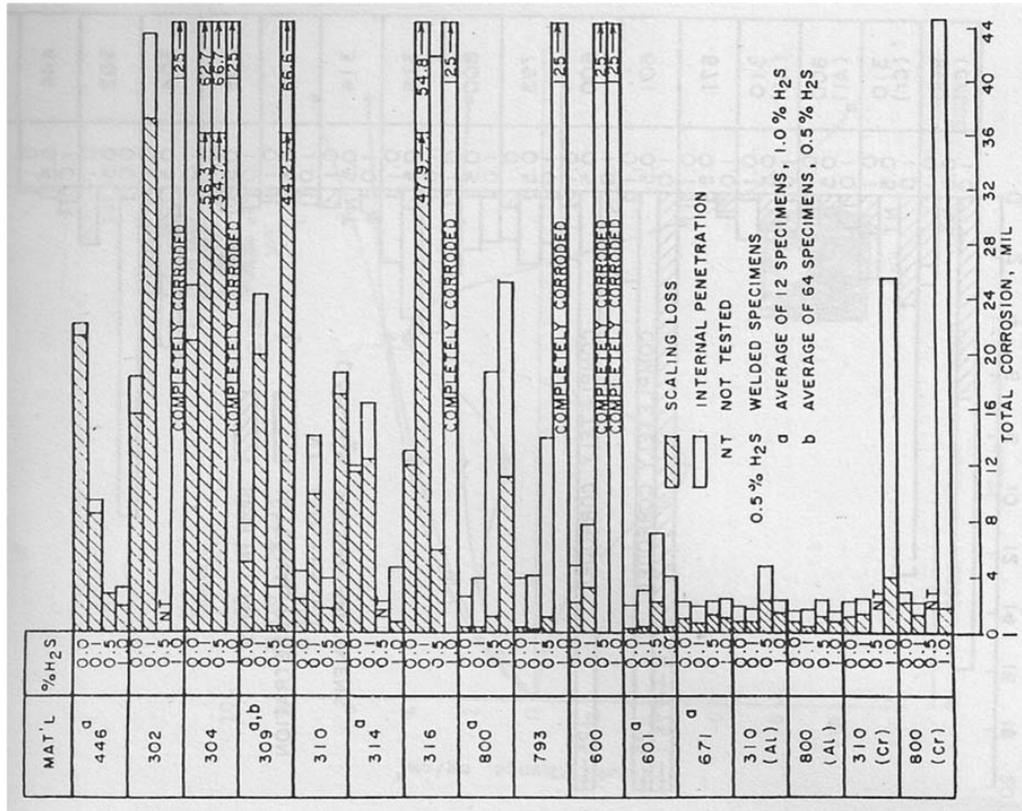
North American coals intended for gasifiers contained sulphur, the range being 1–4%. Hence, the perception was that the biggest danger, in terms of corrosion, was attack by H₂S, as gasifier environments are far more reducing than normal combustion products. Despite this, the hope was that the high steam content of raw syngas would

enable stainless alloys to form the usual protective chromia scales. For example, syngas with a steam to hydrogen ratio of about 1.5:1 has a $p\text{O}_2$ value of $\sim 10^{-16}$ atm at 800°C, several orders of magnitude more than is needed to ensure the stability of chromia. In theory, some commercial alloys would be viable. Accordingly a large corrosion programme, based on conventional stainless steels and other high temperature alloys, was organised by the Materials Property Council (MPC), the focus being on the long term behaviour between 1650 and 1800°F (900 and 980°C). Materials would be deemed acceptable if corrosion rate was less than 20 mils ($\sim 0.5 \text{ mm}$) per annum. Experience from the oil refining sector indicated that above this level, scales formed on pipework or heat exchangers tend to break off and block downstream equipment.

The results of the MPC and associated tests were disappointing, especially at H₂S levels in excess of 0.5%, which is what would be expected from North American coals. The better alloys would work well for a few hundred hours, but then went into breakaway corrosion. Chromia scales would often form, inadvertently perhaps, during start-up of test autoclaves, giving some initial protection. The first signs of breakaway would be the formation of what must have been semimolten globules of nickel and iron rich sulphides at edges and corners of specimens, which then spread across the specimens. In some manner, H₂S was breaking through the chromia scale and reacting with the underlying metal. Blough *et al.*¹² stated that all the commercial alloys, even when given chromised or aluminised coatings, had poor performance.

Results of 1000 h tests at 982°C are shown in Fig. 3. It can be seen that the standard type 300 steels and Incoloy type alloys, commonly used for high temperature equipment, were quite inadequate. This programme continued for some time, reaching test durations of 10⁴ h. The best alloys appeared to be either cobalt containing alloys (RV18, RV19 and N 155) or nickel based alloys with high amounts of chromium (In 671 and In 657) which did well even at 982°C. Unfortunately, cobalt alloys would have been too expensive and the Ni–Cr alloys could not be used for heat exchanger tubing or other structural parts. Some iron and nickel based materials appeared promising, although it is difficult, even now, to explain why they did well, as their compositions were not dissimilar to other alloys that went into breakaway. One possibility is that inadvertent pre-oxidation was causing these differences. Howes¹³ showed that, at 482°C, most materials were fine, apart from Type 316. An operating temperature of 650°C was also a possibility for some materials such as Incoloy 800 and RA333.¹³

In explaining how materials go into breakaway, oxidation theory indicates that the oxygen potential at the base of a chromic oxide scale should fall to a very low value, typically a $p\text{O}_2$ of 10^{-25} atm, at gasifier temperatures. At this $p\text{O}_2$, it would be impossible for iron or nickel to form oxides, and it is only just possible for chromium to react with oxygen. However, these elements are free to react with any other species that get through the scale, providing the thermodynamics are favourable. Chromic oxide is likely to contain microchannels or microcracks through which other gases will migrate. Since these gases do not react with the oxide, as



3 Results of 1000 h tests¹² in 'medium Btu' gas at 982°C at H₂S levels of 0.0, 0.1, 0.5 and 1.0%

they travel through it, the sulphur potential, given by the H₂/H₂S ratio, would be unaffected. If pS_2 is greater than $\sim 10^{-7}$ atm, H₂S will react with the iron, nickel and chromium at the interface.

If the chromic oxide is reasonably thin and intact, but is still growing, one can envisage that any microcracks that form will have some tendency to heal. Hence, the ability of H₂S to channel down to the interface will initially be limited. Later on, as the oxide thickens, growth becomes slower and the risks of H₂S getting down to the interface increase. Eventually, the attack at the interface is severe enough for nodules of metal sulphides to form. The chromic oxide scale will then crack, on what might be termed the visible level. Sulphides, which are quasi-molten, then extrude up on to the surface, as explained by Stott *et al.*¹⁴ The gettering principle is that when H₂S comes into contact with the interface, it preferentially reacts with elements that form protective metal sulphides, which then stifle the sulphidation attack, just as chromia stifles attack by oxygen. It will be apparent, however, that a good oxide scale is needed to slow down the arrival of H₂S at the interface; otherwise, the gettering elements will be overwhelmed.

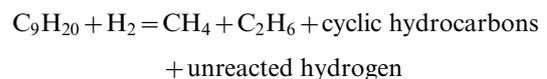
In theory, once in contact with the bulk gas environment, the oxygen potential should be high enough to oxidise the sulphides. However, Natesan¹⁵ has recently pointed out that 'the rate of transport of cations and sulphur are so much higher than through the oxide scale, the sulphidation attack continues in an accelerated manner'. It is worth pointing out that there was an extremely bad tendency to refer to the oxidising and sulphiding characteristics of syngas in terms of pO_2 and pS_2 . At constant H₂/H₂O and H₂/H₂S ratios, pO_2 and pS_2 values increase rapidly with temperature, making it seem that the gases become thermodynamically more aggressive

when the syngas is very hot. This is not necessarily the case, since oxides and sulphides become less stable as temperature increases.

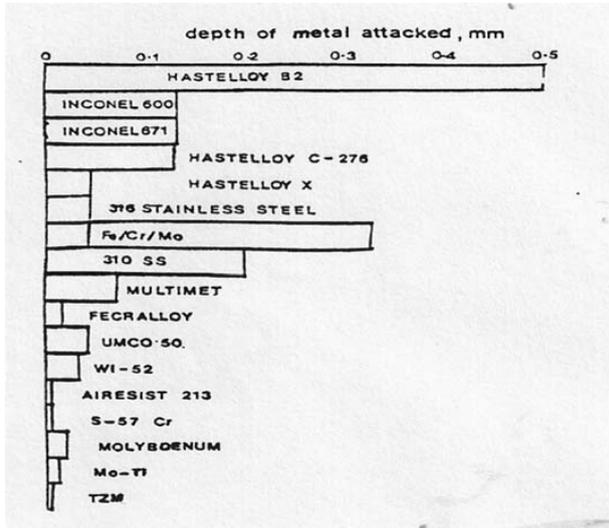
British Gas activities and the UK university based programme

British Gas was developing two completely different processes. The slagging gasifier, now known as the BGL gasifier, was a straightforward development of the German Lurgi gasifier, which dates from 1936. All the significant work on the slagging gasifier was carried out at Westfield in Scotland, where an existing Lurgi gasifier was modified, in which the dry ash grate was replaced by a watercooled slag tap. The most important feature of the Westfield programme was a nine month run. There were no materials issues with the 'slagger', since it was possible to use water cooling at all critical points. The BGL gasifier will be described in more detail below.

The main focus of materials work within British Gas R&D was on hydrogenation processes, in which the metallurgical challenges increased as British Gas 'went down the barrel', the bottom of the barrel being coal. Assuming the feedstock was heavy naphtha, of which one of the main components is nonane, the basic reaction was of the type



The programme began with the hydrogenation of light naphtha, an easily vaporisable, petrol-like fuel, the process being used commercially in the gas recycle hydrogenator. Since the sulphur content was below 100 ppm, the pS_2 was below the level at which gross sulphidation corrosion



4 Extent of corrosion attack on selected alloys after 72 h in fluidised bed hydrogenator test gas of composition $54\cdot2\text{H}_2\text{-}38\cdot0\text{CH}_4\text{-}1\cdot3\text{CO}_2\text{-}0\cdot7\text{CO-}0\cdot8\text{C}_6\text{H}_6\text{-}0\cdot5\text{H}_2\text{S}$ (after Ref. 17)

could occur. However, this level of sulphur was actually required to suppress metal dusting (the sulphur ‘poisoned’ metal surfaces, preventing them from being catalytically active and promoting metal dusting reactions). But as the plant got older, it was apparent that stainless steel heat exchangers were becoming carburised.

During the 1970s, a fluidised bed process was developed using heavier oils, which contained significant amounts of sulphur. Although the hydrogen stream did contain a few percent of CO, CO₂ and steam, $p\text{O}_2$ was much lower than that in the US gasification processes. The view was that since the refinery industry had shown that stainless steels could not be used at temperatures much higher than 500°C (as well summarised by Sorrell *et al.*¹⁶), it was necessary to look elsewhere. This led to some new insights into how materials might be designed to resist high temperature corrosion.

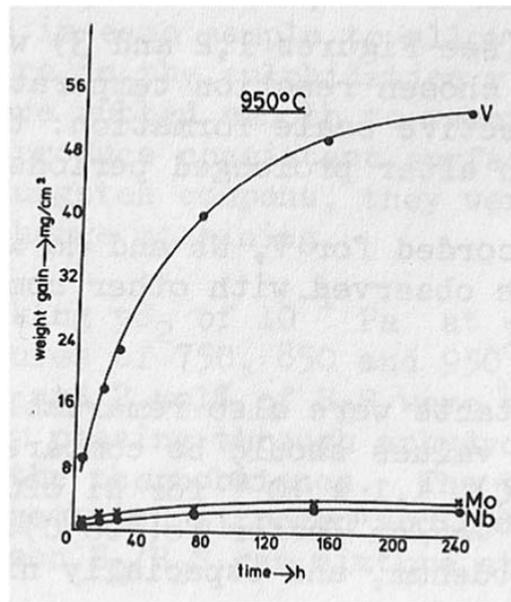
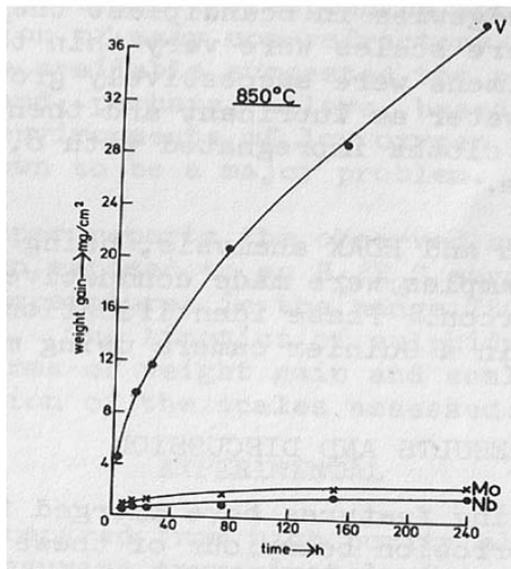
Two possibilities were explored, one to utilise refractory metals, some of which have inherently good resistance to

sulphidation, but are normally discounted for high temperature use, since in air the corrosion rate is unacceptable. In the hydrogenator, the hope was that the conditions would be so reducing that oxidation would be suppressed. Instead, protective metal sulphides would form. Tests on molybdenum suggested this might be true (Fig. 4).¹⁷

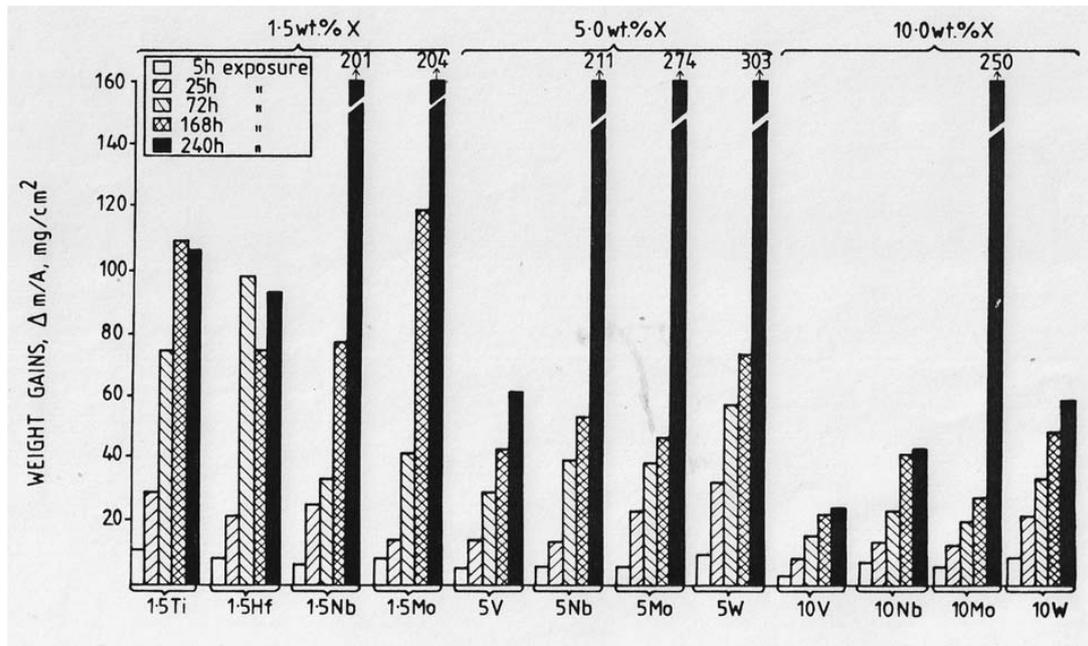
Subsequently, the good behaviour of other refractory elements, including Mo, Nb, Ta, W and V, was confirmed by Strafford and colleagues.^{18,19} Results for vanadium, molybdenum and niobium at 850 and 950°C in a water free H₂/H₂S atmosphere are shown in Fig. 5. Both tests were conducted at a $p\text{S}_2$ of 10^{-6} atm, at the corresponding H₂S levels of 4.2 and 2%. The attack rates for Mo and Nb are extremely low, comparable to the oxidation rates of stainless steel in air. The corrosion of vanadium is initially quite high, but after 240 h, the rate was beginning to flatten out. Similar behaviour was found at 750°C, but the H₂S level in this case was 10%, as required to give $p\text{S}_2=10^{-6}$ atm at this temperature. This emphasises the point made above about the dangers of using $p\text{O}_2$, $p\text{S}_2$, etc. in discussion of experimental work.

Another approach conceived by Strafford was to design an alloy in which refractory gettering elements, e.g. niobium and molybdenum, were incorporated into the formulation. As described above, the idea was that thermodynamic stability of the sulphides of the gettering elements would be higher than those of Fe, Ni, Co and Cr. Accordingly, if any H₂S did penetrate the oxide scale on one of these experimental alloys, it would be gettered by, for example, niobium, instead of reacting with cobalt or iron.

To enhance behaviour further, especially given the very low oxygen potential in hydrogenation type gasifiers, the alloy was to be an alumina rather than a chromia former. Furthermore, in the first series of tests it was agreed that the base element was to be cobalt rather than iron or nickel, since the stability of the cobalt sulphides was suspected to be relatively low. This would give more chance for the gettering element to ‘grab’ the sulphur. Coming from a slightly different direction, one of the present authors had previously



5 Corrosion of V, Mo and Nb in water free H₂/H₂S atmospheres at 850 and 950°C (after Refs. 18 and 19)



6 Effect of gettering elements on sulphidation attack in model cobalt base alloys¹⁹

identified a cobalt based alloy, AiResist 213b (Co–20Cr–3.5Al–6.5Ta–4.5W–0.1C–0.1Zr–0.5Fe–0.5Ni), as one in which the tantalum and tungsten content might contribute to good resistance to sulphidation. This did well, along with molybdenum in the short term tests, mentioned above.¹⁷ This type of composition, in which the aluminium content was quite low, was used as the basis for all of the early experimental alloys at Newcastle Polytechnic.^{18,19}

In the initial tests on the cobalt based alloys^{18,19} the H₂S content of the test gas was very high (10%), to give a p_{S_2} value of 10^{-6} atm at 750°C. The water content of the gas was 3%, giving a p_{O_2} value of 10^{-18} atm. Furthermore, there was no attempt to pre-oxidise the specimens. Not surprisingly, the rates of attack were very high, the results being shown in Fig. 6. However, a three layer scale developed, in which the outer scale was a cobalt sulphide, the intermediate scale, was a chromium rich sulphide, and the inner scale was mainly a sulphide of the gettering element. In the case of the alloys containing 10% vanadium and niobium, the attack rate slowed with time, suggesting that the inner scale was becoming protective. In retrospect, one would comment that the H₂S level should have been nearer 1 than 10%, which should have suppressed the formation of cobalt sulphide.

Because of the cost of cobalt, the last part of the programme was on iron based alloys containing high levels of gettering elements. Owing to the increased stability of iron sulphides, only the more reactive gettering elements worked in this set of experimental alloys. The aluminium content was raised to 8.0% and to prevent too much loss of ductility, chromium content was dropped to 12%. This was done since earlier tests had shown that 3.5% aluminium was marginal in promoting a protective alumina scale. It was also shown that unless these alloys were pre-oxidised, the H₂S would immediately react with the alloys on exposure to the gasifier environment. The pre-oxidation involved – suggested by Stott following work on Fecralloy type

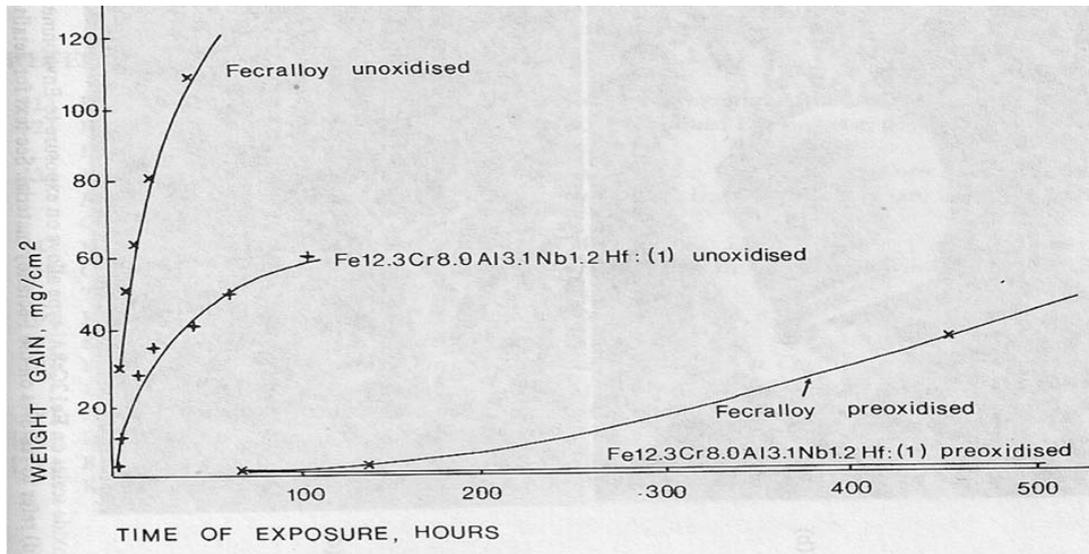
alloys – exposure to a hydrogen–steam atmosphere, the idea being to promote the growth of an alumina scale and suppress chromia formation. Pre-oxidation was a practical option for gasifier operation since during the start-up period a hydrogen–steam mixture could be circulated to assist in heating up the reactors.

The importance of combining the gettering element with pre-oxidation is clearly shown in Fig. 7. Fecralloy, even when preoxidised, does quite badly, and the ‘gettered’ alloy containing 3%Nb, without pre-oxidation, also corrodes at an unacceptable rate.²⁰

For completeness, it is worth mentioning work at Leeds University on binary Fe–Mo alloys. Since over 90%Mo was needed before the material was resistant, this work did not lead to any practically applicable alloys, but did highlight the fact that the refractory metal sulphide must have a much greater stability than the base metal to produce effective protection. A good piece of work by Tomkings as part of his PhD research showed that in some cases, once a material had begun to sulphidise, deep carburisation would occur, undermining mechanical properties. Unfortunately, none of the Leeds work reached the wider literature, and there seems to be little awareness that carburisation might be involved in break-away phenomenon or occur at quite low temperatures.

In work on aluminising, Stott and colleagues at UMIST showed that unless the substrate contained significant quantities of nickel, back-diffusion of aluminium led to the coating being attacked. The results suggested that aluminising would be effective up to at least 750°C. The technical issue with aluminising is that when the process is performed commercially, tubes slump and bend in the process boxes, because of the temperature and difficulty of supporting them. The straightening procedure tends to crack the coatings, and this may account for the mixed results in practice.

As a result of this work, it is possible to lay out some general requirements for a gettering element (built largely on Strafford’s original insights):



7 Effect of pre-oxidation treatment on performance during exposure to mixed oxidising gas (2.8% H_2S , 4.7% H_2O , balance H_2) at 900°C (Ref. 20)

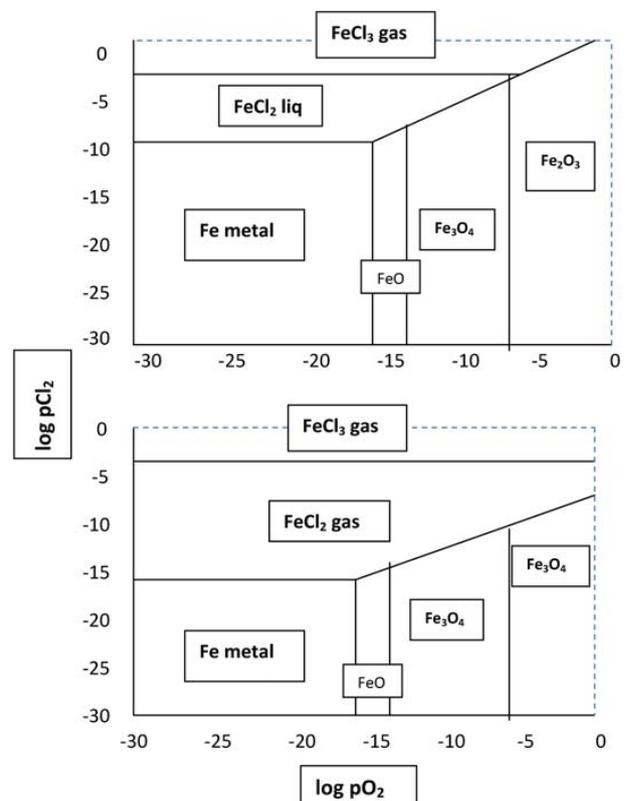
- (i) the stability of the gettering element sulphide should be significantly higher than that of the base alloy, the difference being at least 20 kJ when the element is reacted with one mole of sulphur
- (ii) the rate of growth of the gettering element sulphide should be slow: $k_p < 10^{-10} g^2 cm^{-4} s^{-1}$
- (iii) the concentration of the gettering element in the alloy should be >4 at-%
- (iv) the diffusion rate of the gettering element should be high
- (v) if the gettering element forms intermetallics with other constituents (especially chromium or aluminium), these should be relatively unstable at temperature.

These rules seem also to apply to oxidation resistant alloys containing silicon, where this forms a sublayer beneath a chromia scale.

At this point in the programme, in which the results were very encouraging, British Gas moved to hydrogenation of coal. The main difference in the environment was the presence of HCl since UK coals contain $\sim 0.5\%$ chlorine. Because p_{Cl_2} is affected by the square of the partial pressure of HCl, it is difficult to do realistic tests at ambient pressure and high pressure autoclave tests are essential. These autoclave tests were extremely difficult to do, mainly because of the problem of getting HCl into a gas at 70 bar pressure. The results showed that iron based alloys would not survive and a number of the refractory alloys were badly attacked by HCl.

Discussions with the National Physical Laboratory (NPL), which produced thermochemical stability maps for metal-oxygen-chlorine systems, based on its MTDATA programme, revealed that the thermodynamic stability of metal chloride vapours is higher than that of solid chlorides. This effect, shown in Fig. 8, can be demonstrated in the two thermochemical stability diagrams for iron-oxygen-chlorine phases at about 1000°C, which are simplified versions of those provided by the NPL. The top diagram is one of a conventional type in which the only 'condensed phases' (solid or molten liquid) are considered. For the purposes of calculation the activity of the gaseous phases is taken to

be unity. The diagram shows that the p_{Cl_2} has to be in excess of about 10^{-9} atm before $FeCl_2$ would form (as a liquid phase). This results in the iron area (Fe solid) of the diagram being quite wide, indicating that the iron is unlikely to be attacked. However, if we consider $FeCl_2$ as a gaseous phase, in which its partial pressure is 10^{-8} bar, as in the lower diagram, the iron area shrinks. Attack on iron then becomes thermodynamically possible, when the p_{Cl_2} is above 10^{-16} atm. It should be noted that the stability areas of iron oxides also shrink when the calculations involve $FeCl_2$ vapour. The



8 Stability of iron and iron oxides as influenced by formation of iron chlorides at low vapour pressures

pCl_2 figure of 10^{-8} atm, used in the calculations, was advised by the NPL since they had found that at vapour pressures above this, volatilisation effects from compounds such as CrO_3 become noticeable.

Accordingly, pCl_2 levels that might have been deemed safe could result in the formation of chloride vapour at the temperatures of concern. As noted above, high pressures tend to enhance pCl_2 levels, increasing the risk of attack. Several vapour phase corrosion mechanisms become possible, including direct attack on the alloy, attack at the interface resulting in oxide spalling, and intergranular corrosion in which alloying elements are selectively attacked.

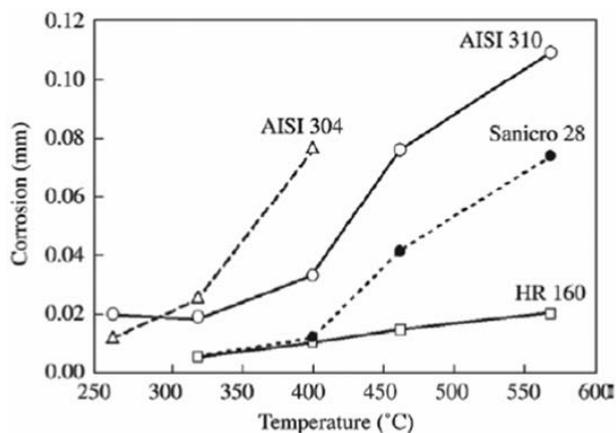
Superheater materials for IGCC systems

Alongside the work on materials for processes to produce a substitute natural gas ran another materials programme biased to IGCC requirements, aimed at gasifiers that produced a stream of hot syngas (for use in a gas turbine) whose heat that could be used to produce superheated steam. This would be integrated with superheated steam from the CCGT section of the IGCC. Accordingly steam temperatures in the 450–500°C range were desirable, implying metal temperatures between 550 and 600°C.

Although the metal temperatures were lower than that required for gasification process equipment, tests in gasifier pilot plant and large scale ‘demonstration’ IGCC facilities suggested that the corrosion rates would be unacceptable.^{21,22} It was an unpleasant surprise, since the MPC autoclave tests had suggested that many materials would survive if the temperature was dropped to below 750°C. However, most of the early work in America and Europe seems not to have taken into account the fact that many coals contain significant amounts of chlorine. The difficulty of performing autoclave tests with HCl at high pressure may have been another reason for its absence from test programmes.

An idea of H_2S and HCl levels can be obtained from the DOE/NETL process flow simulations for the GE/Texaco and Shell gasifiers, as mentioned above.² These were based on the use of Illinois no. 6 coal (composition, after drying: 71.72% carbon, 5.06% hydrogen, 1.41% nitrogen, 0.33% chlorine, 2.82% sulphur, 7.75% oxygen and 10.91% ash). It is apparent from Table 2 that syngas from the Shell gasifier should be considered to be more aggressive as it contains less steam and CO_2 , and the HCl and H_2S levels are slightly higher.

Bakker focused on the chlorine issue, partly in an attempt to explain why the performance of materials in pilot plants was so poor compared to the autoclave tests of the 1980s. Bakker points out that HCl could affect the corrosion rate directly by migrating down cracks in scales consisting of various Fe, Ni and Cr sulphides, which are themselves not very protective, then forming a layer of $FeCl_2$ at the interface.²¹



9 Corrosion rates after 2000 h in Prenflo gasifier²²

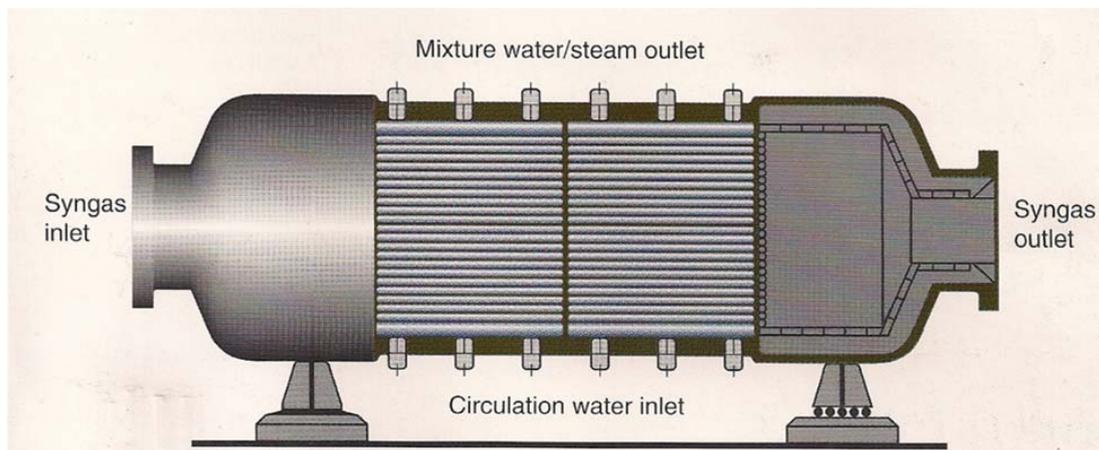
As in waste incineration plants, Bakker considered that there was some potential for a reflux mechanism to build up the levels $FeCl_2$ in the scale. If liquid or vapour chloride migrates back outwards through the scale, steam could react with $FeCl_2$, thereby increasing the local concentration of HCl and increasing the rate of attack. Bakker points out that with some materials higher levels of sulphur seem to inhibit attack, which again is similar to what happens in waste incineration (although given the absence of SO_2 , the mechanism of attack suppression must be different). As with waste incineration, during downtime periods, when everything is wet, HCl and hygroscopic chlorides will cause acidic aqueous corrosion of the underlying metal, disrupting protective scales.

Bakker’s work was largely backed up by tests in the Prenflo gasifier,²² which suggest that Sanicro 28 has good resistance up to ~400°C. The results in Fig. 9 indicate that the alloy may be on the borderline for use in superheaters, and perhaps boilers, where the pressure is in excess of 100 bar and local temperatures may be over 350°C.

In this respect, tube and shell type boilers may have some advantages for syngas as the straight-through design is easy to clean and does not trap particulates in difficulty to clean spaces. Tube and shell designs are also referred to as ‘fire tube boilers’ since the hot gases pass through the tubes surrounded by the boiler water but the weak point of the design is the risk of high temperatures on the tube plate at the syngas inlet end. Temperatures can be kept down in this region by using parallel flow heat transfer, whereby the incoming cooler water is fed into the syngas inlet end and the heated water, at the boiling point, is taken off at the exit. This will result in a bigger boiler than normal. The compromise cross-flow arrangement in Fig. 10 was suggested by Sandvik for use with Sanicro 30 clad boiler tubes. Here, water whose temperature is already close to boiling, enters through a

Table 2 Syngas compositions, temperatures and pressures for GE–Texaco and Shell gasifiers according to DOE/NETL simulations²

	Composition/%										Temperature/°C	Pressure/bar
	CH ₄	CO	CO ₂	COS	H ₂	H ₂ O	HCl	H ₂ S	N ₂	NH ₃		
GE–Texaco	0.12	35.2	13.7	0.02	34.2	13.6	0.08	0.73	0.80	0.21	677°	56.2
Shell	0.06	58.0	1.4	0.07	30.1	2.5	0.09	0.81	5.67	0.36	1079°	42.4



10 Schematic diagram of Sandvik cross-flow fire tube boiler²³

set of inlets at the bottom of the boiler shell and flows upwards and across the tubes. Heated water, with some steam, exits through a similar set of outlets on the top.²³

It has been suggested that Inco 625 may be better than Sanicro 28, but there are a few points worth making about this alloy. Bakker's results show that Inco 625 only halves the corrosion rate, which given the usual 'rule of thumb' for predicting the effect of temperature on corrosion, would still limit metal temperatures to below 500°C.

Coal aspects of gasification

Collot has provided a good overview of coal suitability for all types of gasifier, and Droughy has reviewed methods of reducing the intrinsic moisture of coals and lignites.^{24,25} This is distinct from any external water from rain or water washing, which must also be disposed of, since in entrained and fluidised bed gasifiers the presence of water adds to oxygen demand and reduces gasifier efficiency. Drying of lignites in steam plants is becoming a standard process, since moisture contents are very high.

All commercial and near-commercial gasifiers, using hard coals, reject ash in the form of a slag. Hence, coals whose ashes have a low melting point are best suited for these types of gasifier. It is easier to dispose of a slag than to remove an ash. All the slagging gasifiers incorporate an arrangement where the molten slag drains down into a pool of water, where it breaks up into a glassy frit. The water and frit 'mixture' is then carefully drained off through a series of lock hoppers, until the frit and water emerged at atmospheric pressure to be separated out for disposal.

Ash melting points and slagging characteristics are in complete contrast to the needs of conventional steam plant and oxy-fuel processes, where a low melting point ash will lead to serious fouling of evaporators and superheaters. In gasifiers the slag needs to be quite mobile, to allow it to drain off easily. Limestone may have to be added to bring down melting points, since the alternative is to fire the gasifier at higher temperatures, to reduce slag viscosity. High temperature operation results in more (costly) oxygen being consumed, with syngas being of lower quality because of the reduced amount of H₂ and CO, and higher proportion of CO₂. Accordingly, Cormos *et al.* showed that running gasifiers on 'crappy coals' (by normal power plant

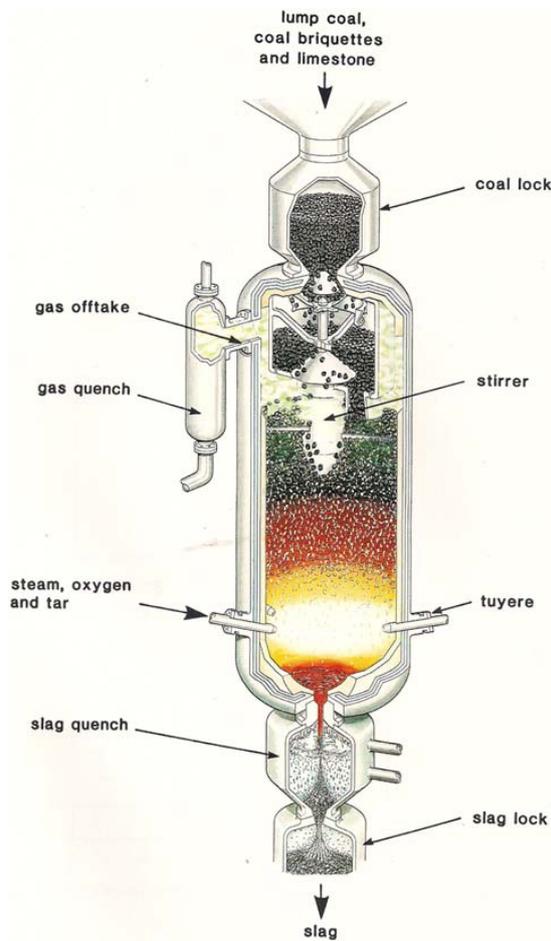
standards) would result in increased output.²⁶ This is usually overlooked when comparing the operating costs of IGCCs with pulverised fuel steam plant.

As is well known, in conventional power stations the sodium and potassium silicates in coals can result in serious fireside attack of superheaters, a problem that becomes more serious as steam temperatures increase. But coals of this type may also present problems in certain types of gasifier, since the combination of high temperatures and reducing conditions may liberate alkali metals as a fume. In blast furnaces, where the conditions in the hearth zone are not dissimilar to gasifiers, liberation of alkali compounds is a serious issue, since there is a gradual build-up in the mid temperature region of the furnace as the alkali condenses and is recycled down to the hearth.²⁷ It might be thought that similar problems could occur in moving bed gasifiers. However, the blast furnace problem is exacerbated by the need to use a slag of very high basicity, which cannot absorb much potassium or sodium. In entrained flow gasifiers, build-up will not occur, of course, as the fumes will be swept out of the gasifier. Where the syngas is quenched with a water spray most of this material is likely to be washed out, but it seems possible that in other cases deposition of 'fume' could lead to fouling of heat exchangers and particle filtration systems.

As noted, the sulphur and chlorine, are the principal reason why it is difficult to produce high temperature steam in gasifiers. H₂S has to be eliminated before the syngas or hydrogen can be burnt in the CCGT, using various types of acid gas removal processes. The HCl will be washed into any black or grey water, either as an acid or as alkaline or ammonium salt. High sulphur levels, by reacting with hydrogen, have an impact on the output of the gas turbine, but some of this energy can be recovered from the heat generated by burning the H₂S in a Claus kiln.

Gasifier options for IGCC

Almost all the SNG oriented gasifier concepts promoted during the 1970s and 1980s have disappeared. This is especially true of fluidised bed systems, in which the gasifier temperature has to be kept below the slag melting point, making it difficult to gasify hard coals. Usually, an ancillary process is needed to burn unreacted char. Dust carry over and tar are also issues.



11 Schematic depiction of BGL gasifier

Slagging gasifiers

Although most accounts of commercial systems start with entrained flow gasifiers, it is worth pointing out that, during the 1970s and 1980s, the British Gas–Lurgi slagging gasifier (Fig. 11) converted over 100 000 t coal. Since then, the gasifier has been used at Schwarz Pumpe in Germany, to dispose of a ‘lake’ of unwanted tar, which was mixed with lignite and waste plastics to form briquettes. The gasifier is of the moving bed type (also, confusingly, called the fixed bed) in which a bed of coal moves down the inside of the gasifier vessel towards the hearth zone. Here, it meets steam and oxygen, which are injected into the hearth zone via tuyeres.

Coal is periodically added to the top of the bed using a lock hopper. The reaction temperature in the hearth zone is over 1500°C and the coal, which at this point is basically a coke, is completely converted to a mixture of CO, H₂ and CO₂. The DTI report on the work at Westfield^{28,29} indicated that some of the coals used contained up to 2.64%S and 0.42%Cl. Operating pressures are currently 32 bar, but pressures up to 70 bar are feasible.

The slag from the molten ash drains down into a water cooled tundish, and thence, periodically, down into the quench chamber containing a water bath. A thin layer of solidified slag forms on the surface of the tundish preventing any attack on the metal. A ring burner running at a slightly higher pressure than the gasifier is situated below the hole in the tundish. The jet of flame from the burner channels up through the

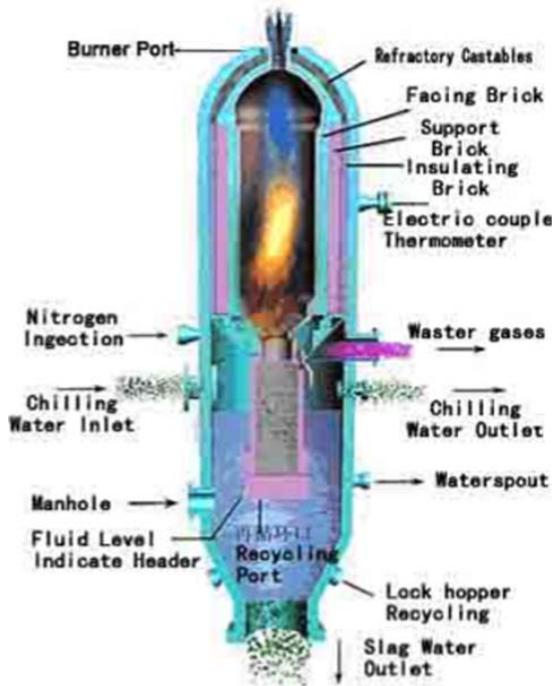
drainhole in the tundish, holding back the slag pool and at the same time preventing the slag from solidifying. Periodically the pressure in the quench chamber is reduced slightly allowing slag to pour through the drainhole into the water bath.³⁰ The slag is collected as a frit of glassy slag which is periodically lock hopped out as a ‘suspension’ in the water. Limestone may have to be added to the coal to reduce slag melting, as described above. In the BGL the target slag viscosity is up to 200 P at 1500°C, which is somewhat more viscous than the 50 P/1425°C figure used in cyclone boilers on steam plant where the ash is drained off as a slag.³¹

The mixture of CO, H₂ and steam from the hearth zone percolates up through the bed of coal, heating it up. At an intermediate level in the bed, the gases pyrolyse the ‘organic’ constituents in the coal, producing methane, tars and phenols. Nearer the top of the bed, the gases are still hot enough to dry the coal. This is an important advantage over other gasification processes, whereby the moisture in the coal has to be removed to a low level, as it increases oxygen consumption and effectively wastes coal. This is not necessary in the BGL gasifier.

Because the gases lose so much heat in drying the coal, the exit temperature from the gasifier is ~600°C, unlike many entrained flow systems where the temperature immediately after gasification is >1300°C. It follows that only a relatively small proportion of the energy in the coal is in the form of heat. The exit gases, which contain ~5% methane, as well as hydrogen and carbon monoxide, contain ~90% of the energy in a chemical or burnable form. The exit gases are given a limited quench, which condenses out tars and phenols, after which the temperature is brought down to ~200°C.

The pressure vessel is of a double skinned form, as developed by Lurgi. Boiler water at the same pressure as the gasifier circulates between the inner and outer wall of the vessel. Somewhat confusingly, this is referred to as a jacketed type of pressure vessel, even though the ‘jacket’ cannot be removed. Since the water in the jacket is just at the point of boiling, its temperature is always high enough to prevent condensation occurring on the gasifier side of the inner wall. For example, if the gasifier is operating at 32 bar, the boiling point of the jacket water at this pressure is 237°C. However, supposing that syngas contains 25% steam, the steam could not condense on the walls of gasifier, since its partial pressure is only 8 bar, giving a dewpoint of 170°C. Avoiding condensation eliminates aqueous corrosion, which can be an issue in other designs where the pressure vessel is of the normal type. Not much heat is lost to the water: heat transfer to the jacket water is only ~3% of the energy input.

This arrangement can be regarded as a more sophisticated form of the cooling plates used on blast furnaces, which intersperse the refractory on the inside of the shell. Although the refractory is the first line of defence, as the slag eats into the refractory, it encounters colder regions, and becomes more viscous and less aggressive, until attack stops when the slag solidifies. These cooling arrangements are critical in the hearth region of the blast furnace where there are tens of square metres of refractory exposed to molten iron and slag. The coolers use water at ambient temperature, which rules them out for protecting the refractory in entrained



12 Schematic depiction of GE-TEXACO gasifier

flow systems, because of the extreme risk of inducing acid corrosion of the pressure vessel shell.

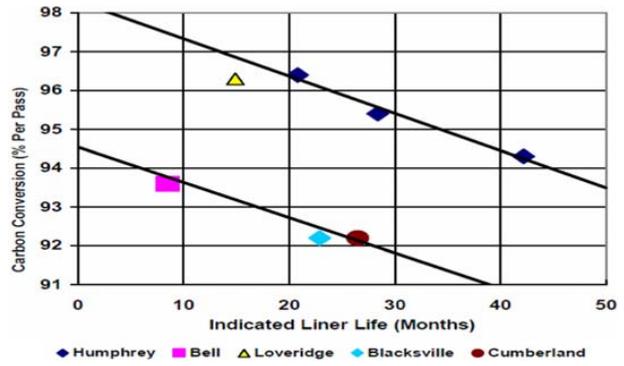
There are no significant high temperature metallurgical issues associated with the slagging gasifier. Critical parts are protected by refractory bricks. The only really high temperature zone is in the hearth region. Here, local water cooling helps prevent slag attack; although there may be some attack by the slag on the refractory, it soon comes to a halt as the slag solidifies as soon as it begins to penetrate the cooler regions.

Slurry fed entrained flow gasifiers

Entrained flow gasifiers are tolerant of the coal characteristics and on these grounds to have been favoured by proponents of IGCC. Coal is dispersed as particles in a high temperature ‘flame’ so there is high burnout of the fuel. There is no tendency for the coal to agglomerate into a sticky mass of pyrolysed coal and tar, which can be a problem in moving bed gasifiers. The only coals that might present difficulties are very high ash types, where the need to melt the ash results in increased coal and oxygen consumption. Indian coals are of this type, with ash contents up to 40%, and ash melting points around 1600°C. For such coals the dry ash Lurgi has been advocated.³⁰

Because of the problems in handling pulverised coal at high pressure, the designers of the Texaco gasifier (Fig. 12), now marketed by General Electric Inc., chose to use a water based slurry to feed coal into the top of the gasifier, which has the form of a tall refractory lined vertical shaft. The slurry meets a stream of oxygen, reacting at temperatures between 1300 and 1500°C to produce a mixture of CO, H₂ and CO plus excess steam.³¹

Temperatures are high enough to melt the ash, and the mixture of hot gases travels downwards. There is no pressure limitation with slurry fed gasifiers since a liquid is being pumped into the gasifier. The ability to work at high pressure is a real advantage when capturing CO₂, as it reduces the energy demands when the CO₂ is



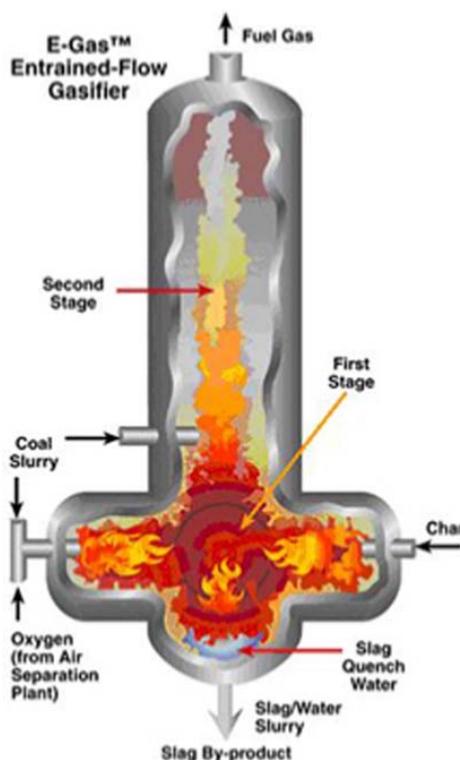
13 Effect of carbon conversion rate and coal type on refractory liner life:³² operational data for GE/TEXACO Gasifier at Tampa Electric Polk Power Station

pumped up into pipelines for dispatch to the sequestration site. The drawback of slurry feeding is that heat is required to evaporate the water and raise the steam to reaction temperatures. In consequence, as with the high ash coal issue, the syngas has a high CO₂ content and a high oxygen demand. Accordingly the efficiency is less than with dry feed systems. When capturing CO₂ there is still an efficiency penalty but it is not so marked.

The heat in the gases and in the molten slag is recovered using either a syngas cooler or a water cooled quench. The syngas cooler is a heat exchanger of the water-wall boiler type situated within the internal circumference of the lower sections of the gasifier vessel. Within a very short time the tubes rapidly become covered with a layer of slag, protecting the tubes from both intense radiative and convective heat transfer. Metal temperatures are fairly low since no superheating occurs. Nevertheless, the saturated steam can be incorporated in the HRSG section of the plant. Hence, the syngas cooler arrangement is favoured in IGCC plants which are not intended to capture carbon.

The IGCC efficiency of the other technique, water quench, is less good. Here, the hot gases and slag are cooled down to ~250°C by directing them, via a dip tube, into a quench bath, as shown in Fig. 12. The raw syngas, which emerges on the outside of the dip tube, is sent on to a shift converter, and is saturated with wet steam. Here, after heating the syngas to dry out droplets of water, the now superheated steam in the syngas is used in ‘converting’ carbon monoxide to hydrogen. The reaction of carbon monoxide with steam also produces carbon dioxide, which can be captured for storage. Water quenching also removes much of the particulates and HCl in the gas stream. However, in both methods of cooling the syngas, the droplets of slag fall into a water bath where they can be locked off, periodically. Obviously, it is possible to combine the two methods of cooling, which has the merit of helping to maintain efficiency while simplifying the gas clean up equipment.

The upper section of the Texaco gasifier is refractory lined. Good resistance to slag attack is needed, and clearly, the lower the operating temperature, the more viscous will be the slag, and the less the attack on the refractory. However, low operating temperatures reduce the rate of carbon conversion. The upper line in Fig. 13 shows how attempts to increase the conversion rate of Humphrey coal affected refractory life during runs at Tampa Power Station where a gasifier was being



14 Schematic depiction of E-Gas gasifier

evaluated.³⁴ The other points and the lower line on the graph indicate that other coals are less amenable to carbon conversion and, presumably, because of this have to be gasified at a higher temperature, resulting in reduced refractory life.

The ConocoPhillips E-Gas gasifier (Fig. 14) uses a slurry fed process in which gasification is accomplished in two stages. The intention is to utilise the very high temperature of the syngas produced in the first stage of the process to gasify a coal slurry mixture in the second stage. Accordingly two opposite-facing slurry–oxygen burners, each housed in a large tee-connection, near the base of the gasifier shaft, are used to gasify about 80% of the coal. At this point the temperature is so high (nominally 1425°C) that the ash is molten and most of it hits the sides of the refractory lined shaft and drains down into a slag pool. Further up the shaft the remaining 20% of the coal is injected, also as a water based slurry. Here it meets the up-flowing syngas. The temperature is such that the remaining coal is gasified. There is a significant drop in temperatures, since the reaction is endothermic and also because of the heat needed to evaporate the water. Accordingly, the ash from this portion of the coal remains as a solid.³³

The nominal exit temperature at this point is 1035°C and the syngas is cool enough to be passed to the syngas boiler. But, it appears that the 1000°C plus temperatures before the boiler are too high for a cyclone to be considered. Hence, the dust and slag particles are not removed until the syngas exits the boiler, when candle filters are used. Depending on the coal, the syngas will contain HCl and this is only removed at quite late stage in the process, using a water wash.

An issue with this type of gasifier is the slagging characteristics of the ash, which seem to be fairly critical. Too high a slag melting point will cause difficulties in tapping off the slag. But too low a viscosity could result

in semimolten slag being carried downstream (a water spray downstream of the gasifier to bring temperatures below 900°C would eliminate this problem). Difficulties have occurred at the Wabash site, where E-Gas was being evaluated, because of iron rich material accumulating on the syngas boiler (iron rich slags tend to have low melting points). In addition, lumps of solidified slag, which broke off the downstream gasifier section, have been carried forward where they blocked the boiler. A boiler screen was needed to prevent this.³⁵

Dry feed entrained flow gasifiers

Pulverised coal is blown into dry feed gasifiers using a stream of pressurised nitrogen, to react with oxygen. Reaction temperatures appear to be >1600°C, indicating that some means of recovering or utilising the heat is essential if IGCC is to be efficient.

The most straight-forward approach is used in the Siemens gasifier, in which a refractory lined water wall is used in conjunction with a quench system. Here, the burner is directed down the shaft, where towards the bottom, it meets the quench spray.³⁶ As noted above, at some cost to efficiency, the quench system greatly simplifies the downstream equipment requirements, since HCl is washed out along with the dust and slag particles.³⁴

Others have chosen to use a more sophisticated approach. The Shell type of design has a number of side wall burners located towards the base of the gasifier. Partly through the buoyancy of the hot gases, the combustion products move up the shaft of the gasifier, then exit at the side. Most of the ash particles melt and are either large enough to drop downwards into a water bath, at the base of the gasifier shaft, or hit the sides of the gasifier, which is of the water wall type.³⁷ Figure 15 shows a schematic diagram of the Shell gasifier and a picture of the water wall boiler, as fabricated, and ready for installation in the gasifier pressure vessel. A solidified layer of slag sticks to the tubes, but the outer layers of slag are molten and slowly drain into the quench bath. The slag layer effectively protects and insulates the tubes. To give the tubes protection the coal has to contain a minimum of 7% ash. If this is not possible some of the slag frit needs to be recycled.

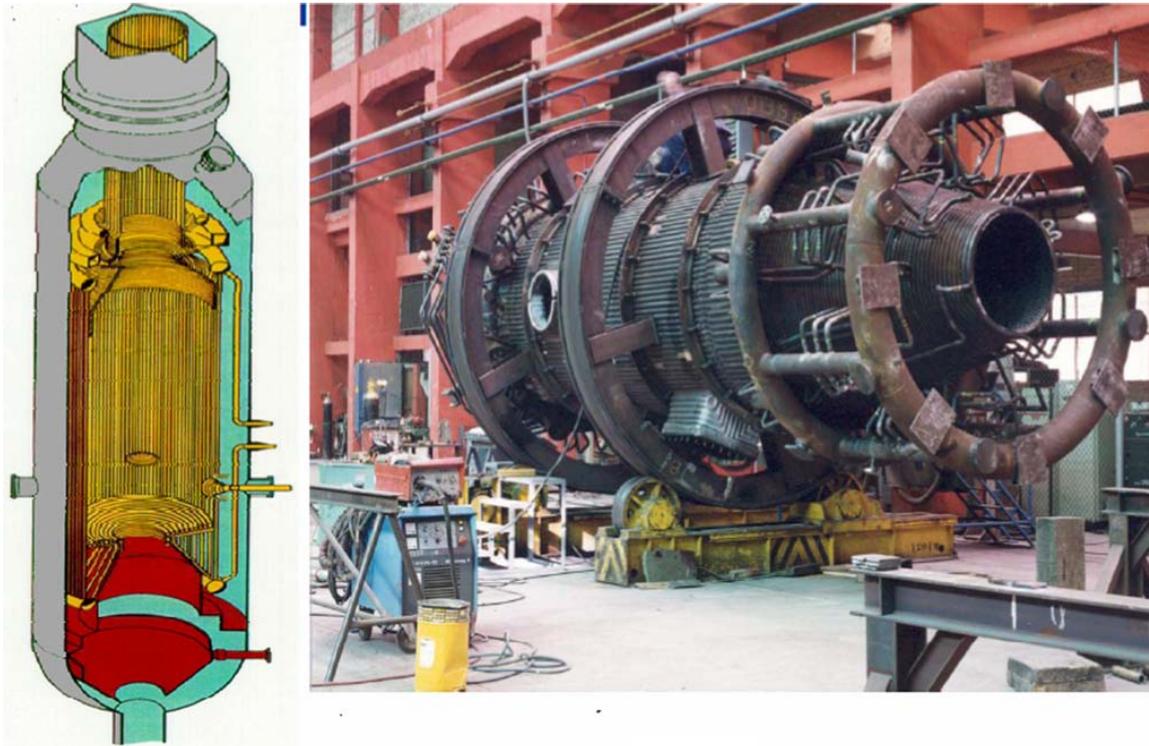
The syngas from the top of the Shell gasifier is at >1300°C and contains fine ash and fume. The syngas is brought down to ~700°C by injecting a stream of 'cold' syngas from the downstream section of the plant. Any fume or entrained slag is solidified and is carried forward by the raw syngas into the syngas boiler. After exiting the boiler, the temperature is low enough, below 300°C, for any particulates to be trapped on candle filters.³⁸

More recently, Shell has considered using a water spray quench instead of the gas quench at the syngas exit of the gasifier. This eliminates many of the problems with fouling, and the need for filters.³⁹

Syngas treatment

Non-carbon capture IGCC

If there is no need to capture carbon, CO₂ is left in the syngas, since a gas at pressure is able to carry out work when expanding through the gas turbine of the CCGT. In consequence, the acid gas treatment process needs to leave as much CO₂ in the syngas as possible. One reason why methyldiethanolamine (MDEA) has been favoured as a solvent for non-carbon capture IGCCs is its



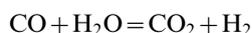
15 Schematic depiction of Shell gasifier and illustration of water-wall boiler

selectivity.⁴⁰ Mackenzie *et al.*, in the context of an MDEA plant for cleaning up a 'sour' natural gas, give a clear account of the chemical engineering required.⁴¹ The potassium bicarbonate process of Benfield, widely used by the UK gas industry in the manufacture of gas from oil and coal, is not favoured because of the risk of potassium salts being carried over into the gas turbine. Raw syngas usually contains some COS, which will not be absorbed by MDEA. Accordingly, after removal of particulates and HCl, the syngas is put through a reactor at 175–209°C to convert the COS to H₂S.

Carbon capture IGCC

Integrated gasification combined cycle systems are ideal for capturing CO₂ as the syngas is at high pressure, facilitating its removal. The CO₂ removal can be combined with the process for removing H₂S by adding another stage onto the AGR process. The CO₂ purity for capture and storage needs to be very high and in particular the loss of hydrogen into the 'capture stream' should be kept to less than 0.2% of the total hydrogen generated. A variety of solvents can be used but a scheme designed by Cormos *et al.* using Selexol (dimethyl ethers of polyethylene glycol), which is a physical solvent,²⁶ is typical. An advantage of physical solvents is that some CO₂ can be released from the solvent at pressure, minimising CO₂ compression costs. Furthermore, steam requirements for solvent regeneration are minimised.

Before H₂S and CO₂ are removed, the syngas is 'shifted', that is the carbon monoxide is reacted with dry steam in the gas to produce hydrogen and carbon dioxide



The catalytic reaction is carried out in two stages, since the reaction is exothermic and higher temperatures push the reaction to the left. The first stage is at ~350°C and

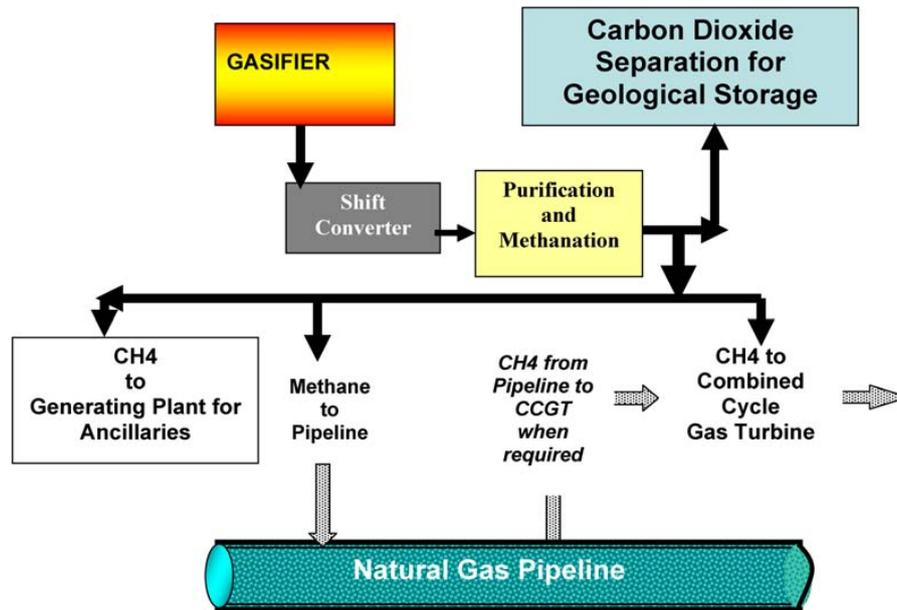
the second stage, in which only about 2–5% of CO is left in the gas, is carried out at ~200°C. The heat generated by these reactions is used for medium and low pressure steam production. The shift reaction converts any COS to H₂S.

Quench water systems, such as those of Texaco and Siemens, have the advantage that the raw syngas contains a high level of steam, which is needed for the shift reaction. With dry feed systems it is necessary to bring in a superheated steam line from the HRSG, resulting in some loss in the electrical power. It follows that whereas dry feed gasifiers are definitely better in simple non-carbon plants, since the gasifier efficiency is high, the difference is not so marked when carbon capture is required.

It is not generally recognised that, because hydrogen is the main constituent of the fuel gas, there is a marked drop in IGCC output in a CCS plant. A minor effect comes from the fact that the mass flow of combustion products through the gas turbine is less than when synthesis gas is used. More important is the huge loss of energy that occurs when the latent heat in the water vapour, which results from the combustion of hydrogen, passes out of the HRSG up the stack. Such a loss occurs whenever coal, oil or natural gas is used in a power station. But, because the proportion of hydrogen in these fuels is much less than in hydrogen itself, the latent heat loss is much less devastating. The Americans recognise this issue and insist on efficiencies being quoted in terms of the HHV of the input fuel. In Europe, this effect is disguised by using the lower heating calorific value.

Gasification for electricity plus substitute natural gas

An IGCC could produce substitute natural gas from coal as well as electricity. The advantage of such a plant is that it fits present day requirement to stop generating power at night, when demand falls, and also to meet the



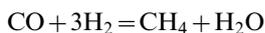
16 Schematic depiction of IGCC plant modified to produce SNG for subsequent transmission by pipeline or use on-site in integrated CCGT

increasing challenge of compensating for the variation in wind energy.

In this concept, the gasifier and gas treatment units on the plant would produce SNG all the time. During the day, the SNG would be used for electricity generation in the CCGT part of the plant. At night, when the need for electricity falls, the SNG would go into the existing natural gas pipelines.

The technology for producing SNG from syngas has long been commercialised, with numerous plants, which used light naphtha as the feedstock, being built in the USA. In the UK, which developed the technology, conversion of existing towns gas plants were made at Plymouth, Croydon, Edinburgh and Portsmouth.

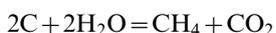
The simplest process involves first giving the purified syngas a partial shift and removing some CO₂ to give the correct ratio of carbon monoxide to hydrogen for the 'methanation reaction'



The catalyst used in the methanation reactor is not tolerant even of traces of H₂S. This can be removed using the Rectisol process, which uses refrigerated methanol as an absorbent. Some CO₂ can also be removed at this stage, which is obviously beneficial since ~30% more methane is produced when methanating CO than CO₂.

The reaction is strongly exothermic and increases gas temperature to over 400°C; this may require a special reactor containing an *in situ* boiler to extract the heat and control temperature. The gas coming from the reactor contains over 90% methane and is essential a synthetic or substitute natural gas.

The main argument against such a process is that only 50% of the carbon in the coal is removed. The overall reaction to produce SNG can be written as



Because of the increasing price of natural gas and the declining reserves in Europe and elsewhere, Williams has

looked at producing SNG from coal. A key finding is that, using the BGL gasifier, the coal to SNG efficiency can be as high as 72% on the HHV basis.⁴² If such plant were integrated with an advanced gas turbine of the 'H' type then, using the European LHV approach, efficiencies in the 45–47% range would be anticipated. The removal of CO₂ from the gas stream is an integral part of the SNG production. Unlike other capture systems, it does not require extra energy. In fact, the shift and methanation reactions can be used to generate steam that can be utilised in the HRSG, giving prospects for additional improvement.

How such a plant would be arranged is shown schematically in Fig. 16. Note that by connecting it to the natural gas pipeline network, gas would be exported at night or at times when there is a high output from wind farms. In the UK, the current plans for 33 GW wind capacity could lead to all fossil and nuclear plant being shut down during moderately windy periods.⁴³ There are other advantages. The connection of the plant to gas pipelines enables it to generate electricity when gasifiers are off for maintenance. Because of the variation in air temperature, gas turbine output can vary significantly from summer to winter, requiring the gasifier to run at different outputs. Hence, the ability to take or send methane from a pipeline would be helpful. But, perhaps one of the most important features of this proposal is that, unlike conventional IGCC, which produces syngas as a fuel, there is a wide choice of gas turbines.

The economics of such a combined electricity and SNG plant are likely to be very good. A similar IGCC scheme, based on hydrogen rather than SNG, was investigated by Starr and Tzimas. It was concluded that the very high effective availability of the plant, and operation of the gasifier at 100% of design led to extremely competitive costs of both hydrogen and electricity.⁴⁴

Increasing efficiency of IGCC plants

The coal requirement and electrical output of an IGCC plant is basically determined by the size of the gas

turbine, which is always a modified version of a natural gas fired industrial machine. The size and cost of all other equipment stems from this fact.^{45,46} Many simulations are based on the GE Frame 7001F and 9001F gas turbines, which are available for operating on syngas.⁴⁷ Zheng and Furinsky⁴⁸ based their simulations, using a Canadian coal, on a near constant gas turbine output of 190 MW. Their results for three gasifiers are summarised in Table 3; although the efficiencies are similar, plant outputs vary widely. The low output from the BGL gasifier is because the coal, which contains 19% moisture, is transferred direct into the gasifier from a locked hopper, whereas with the entrained flow gasifiers the coal was completely dried before being injected in the gasifier as a slurry or using a stream of nitrogen.

Given the limitations with heat exchanger alloys, only marginal improvements appear to be in prospect for the gasification section of the IGCC. There is good reason, however, to expect continuing progress with gas turbine technology. Susta and Greth⁴⁷ consider that CCGT efficiencies of over 62% should be attainable by 2015, with the possibility of reaching 75% in the longer term. It is this development which should enable the IGCC to surpass the best that coal fired steam plant can offer.

At the present time industrial gas turbines offer efficiencies of just under 40% for simple cycle machines. These are near relations of aircraft gas turbines. Straight aeroderived gas turbines actually offer efficiencies about 5% higher than the industrials, but this is at the expense of low turbine outlet temperatures, which are <450°C. In consequence, steam conditions in the HRSG are quite poor and excess air levels are high. If industrial gas turbines are to improve, it cannot be by copying aeroderived technology, which, in concert with the increases in turbine inlet temperature and better air cooling, has achieved efficiency gains by increasing pressure ratios. For example, the Rolls-Royce Trent 1000, intended for the Boeing 787, has a 'top of climb' pressure ratio of 52:1.

Fortunately, there are signs that the industrial gas turbine is now starting to use techniques that would be difficult, if not impossible, to apply to an aircraft engine. For example, Alstom is using reheat, or interstage combustion with the GT 24 and 26. Higher than normal pressure ratios need to be used with reheat to optimise efficiency, but despite the high pressure ratio, the turbine outlet temperature is 640°C, giving very good steam conditions in the HRSG. The GE LMS 100 uses interstage cooling in conjunction with a turbine inlet temperature of 1380°C, giving an efficiency of 46%, without the help from steam turbines. A feature of the LMS 100 is that the compressor is divided into two spools, each of which is driven by a separate turbine. The intercooler is positioned between the two spools and each spool runs at an optimum speed. This is beneficial when designing gas turbines to run at very high pressure ratios and operate over a range of outputs. Also, a

separate power turbine is used in the LMS 100, similar to current aeroderived machines, which frees the compressors from having to rotate at a speed corresponding to grid frequency, that is 3000 rev min⁻¹ in Europe and 3600 rev min⁻¹ in the USA.

Intercooling and reheating are modifications to the Brayton cycle, whereby compressor work is minimised and turbine work is maximised. Pressure ratios, when utilising these techniques, have to be increased to ensure adequate expansion through the turbine. The other approach is to improve compressor and turbine performance. Given the high pressure ratios that are now being required, it seems unlikely that more than a percentage point or so can be got from reducing the aerodynamic losses of compressors. And if air cooling of turbines is retained, it will be a similar story, of fast diminishing returns for the R&D effort. The big improvement will come from eliminating air cooling of the turbine and other hot components.

Air cooling is very detrimental, since air has to be abstracted from the compressor. Although some of the cooling air does pass out through the stator and rotor blades, it does not produce as much power as the gases coming from the combustors. The rest of the cooling air, which is used for disc and bearing cooling, is more than just wasted; it reduces the entry temperature into the HRSG.

Air cooling comes with other disadvantages. It disrupts blade aerodynamics as the air exits the blades, and less power is obtained. Steam cooling, which is being pioneered by GE, eliminates this. In the latest Frame 9001H, the steam for blade cooling is taken from the exit of the combined cycle high pressure steam turbine, and is at medium pressure when it enters the gas turbine blading. After picking up heat from the blade, and keeping the metal temperature within limits, the steam is hot enough to rejoin the reheat steam circuit and carry out useful work driving the IP turbine. Since more of the air can go through the combustor, temperatures can be held down, reducing NO levels.

Some work on what happens if intercooling, reheating, and steam cooled blading are applied to a gas turbine has been carried out on a hydrogen fuelled turbine by the present authors. It was envisaged that the development of steam cooling, plus thermal barrier coatings, will permit turbine inlet temperatures in the 1500°C range. The hydrogen could come from electrolytic sources, or from a carbon capture IGCC plant.

A major issue with hydrogen is that high NO_x levels result when combusted in conventional burners, as a slightly air rich mixture is what is actually burnt, giving flame temperatures in excess of 2000°C. The problem can be mitigated to some extent by using nitrogen dilution and by deliberately setting turbine inlet temperatures lower than in natural gas fired machines. Hydrogen also gives concern with existing burners because of 'light back' at reduced outputs as a result of its high flame speed. Most of the air going through a normal combustion system bypasses the flame. It is used to 'dilute the temperature' and has no part in the combustion process proper.

It is therefore proposed that all the air from the compressor should be mixed with hydrogen before being burnt in a catalytic combustor. Hydrogen is well suited to this technique, since it has a very wide flammability

Table 3 Efficiency of IGCC processes⁴⁸

Gasifier	GE-Texaco	Shell	BGL
Gas turbine output/MW	191.5	192.1	191.9
Coal throughput/t h ⁻¹	267.3	227.5	271.0
IGCC efficiency/%	41.97	42.37	42.47
IGCC total Output/MW	342	293	284

range of 4–75% hydrogen in air. To give inlet temperatures of $\sim 1500^{\circ}\text{C}$, the air to hydrogen ratio would correspond to a hydrogen content of $\sim 14\%$, indicating that there would be no problems in getting the hydrogen to ignite. The most important advantage of catalytic combustion is that temperatures will be below that at which NO_x begins to form.

Obviously a staged catalyst will be needed, in which the reactivity will be very high at the inlet, to induce ignition, but once this occurs, a catalyst which is less prone to sintering, but less reactive, will be used in later sections of the combustor. The design of the combustor requires some consideration, and the silo form of combustor is worth consideration, as this is the normal way of containing catalysts at pressure. If this were chosen ducting of hot steam laden combustion products at 1500°C would require some thought.

Our calculations suggest that the efficiency of the gas turbine with catalytically combustors was 54% on a net basis. This is eight percentage points better than the LMS 100 mentioned above. But, unlike the GE machine, which has quite a low exhaust temperature, the proposed turbine would have an outlet temperature is 598°C . Heat recovery steam generator steam conditions will be good, allowing three pressure operation with reheat. At the time of writing, work has yet to begin on optimising the HRSG section, but one can make a reasonably good prediction of what would be the overall efficiency of the CCGT. Typically the steam turbine section of a CCGT will turn about one-third of the heat energy in the exhaust gases from the gas turbine into electrical power. On this basis, the steam turbine will increase efficiency by $(100-54)/3$, namely 15%. Overall efficiency for the CCGT will then be 69%. With optimisation, efficiencies in the low seventies should be possible.

To achieve such a figure, the overall pressure ratio of the gas turbine is 119. This seems high but it is achieved in two stages. The pressure ratio is about 10:1 in the first stage of compression, and about 12:1 in the second. The turbine inlet temperatures for the first and reheat combustors are 1526 and 1515°C respectively. Other salient figures are that 70% of the hydrogen goes to the first combustor and 30% to the second, and that the intercooler outlet temperature is 150°C . The cooling water from this will be $\sim 140^{\circ}\text{C}$, which will be utilised for steam raising in the HRSG.

In terms of materials technology, the turbine appears to offer only design and development issues rather than ‘challenges’. The exit temperature from the final stage of compression is 619°C , which implies precipitation hardened nickel based alloys for the blades and long life martensitics for the discs. If normal combustor cans are used to hold the catalyst, these will have to be in the form internally of a steam cooled insulated chamber (or chambers). Although a complex arrangement, because of the need for steam cooling, it avoids the long transfer ducts needed by the silo design.

The requirements for the cans and ducting point to 12% martensitic or modern austenitic steels, with the internal insulation having to withstand surface temperatures up to $\sim 1350^{\circ}\text{C}$. Good resistance to thermal shock and erosion would be needed, possibly pointing to a modified thermal barrier coating. The big difference is that the substrate temperatures would be 600 rather than

1000°C . Thermal barrier coatings will be needed on the gas turbine blades and will have to resist sintering from the superheated water vapour, which results from the combustion of hydrogen. At the inlet to the high pressure turbine, the partial pressure of the water vapour would be 8 bar.

If this type of turbine was to run on natural gas, CCGT efficiencies would also be in the 70% range. It is a little difficult to estimate how such a turbine would enhance the performance of an IGCC plant, but we do know that the two IGCCs in Europe at Buggenum and Puertollano were achieving efficiencies of $\sim 41\%$. The gas turbines used in these plants, the Siemens V94-2 and V94-3, enabled CCGTs to reach efficiencies in the 50–55% range.

Pruscheck⁵⁰ suggests that if the Puertollano IGCC switched to Pittsburgh coal rather than the present mix of coal plus high sulphur petroleum coke, the GT temperature was raised from 1120 to 1250°C , and the stack gas temperature was lowered to 60°C , plus various other improvements, an efficiency of 49.2% is attainable. On this basis, using an advanced turbine we could expect *IGCC efficiencies* in the mid fifties or even higher. When modified for 90% carbon capture, with zero NO_x and SO_x emissions, a coal to electricity efficiency of 50% is a strong possibility. It should be kept in mind that as the basic plant efficiency rises, less energy is wasted in capturing CO_2 . Conversely, the ‘capture penalty’ for CO_2 in the UK’s old subcritical plants, if we were stupid enough to convert them, would be very high. And taking an extreme case, a plant with an efficiency of $\sim 20\%$ would spend all of its energy capturing carbon dioxide!

Discussion and conclusions

Gasifier aspects

Of the numerous efforts to develop new concepts in gasification during the 1970s and 1980s, the only ones which have reached commercial status have been based on well proven earlier systems. Systems now in operation include the BGL fixed bed gasifier, the slurry fed Texaco and E-Gas entrained flow gasifier, and the Shell dry fed entrained flow gasifier.

These are systems which have designed out, to a very large extent, critical metallurgical issues. When entrained flow gasifiers are modified for carbon capture, the need for high temperature heat recovery virtually disappears. The final point worth emphasising is that IGCCs with carbon capture can be built now, unlike pulverised fuel steam plant and oxyfuel plant.

High temperature corrosion and alloy design

Despite the optimism which comes through in some papers, no one seems to have had the courage to build a system which relied on *off-the-shelf stainless alloys* being able to resist long term corrosion at temperatures much higher than 550°C in gasifier environments. The main cause of attack is H_2S , which results in breakaway corrosion, when chromium and aluminium oxides cease to give protection. Designers will be aware that although medium term tests, in the 1000 h range, might appear promising, unless the time to breakaway can be predicted with some certainty, it would be impossible to guarantee the life of high temperature equipment.

It became clear to many active in the field that, given the shortcomings of tube materials, novel coatings would be needed. This review has focused on work at, and sponsored by, British Gas, which realised at a very early stage that, given the almost complete lack of oxidising species in oil and coal hydrogenator environments, any reliance on conventional alloys should be ruled out immediately. The work at Newcastle Polytechnic using refractory metals as 'gettering' elements, especially when applied to cobalt based alloys, plus pre-oxidation^{18–20} showed good prospects of success. From this work, some simple rules of thumb for the choice and amount of gettering element have been developed. These rules may apply to other oxide resistant alloys, and there should be an effort made to put these rules on a quantitative basis.

It took some time for researchers to recognise, however, that the presence of chlorine in coal was adding to the effects of sulphur, which helps to explain the poor performance of alloys in gasifier pilot plant. The conclusion of the present review is that the combination of HCl and H₂S lowers the maximum safe use temperature of heat exchanger materials to <500°C. Because of the tendency of metals to form volatile chlorides, the development of resistant alloys for gasifiers is proving as intractable as those for waste incineration plants. Aluminised coatings may be a solution, but tests need to be carried out in plant and in high pressure autoclaves to explore this possibility.

Efficiency improvement in IGCC plants and carbon capture

Because of the high temperature corrosion issue, it is unrealistic to expect significant improvements to be made in the ability to turn coal into syngas at much higher efficiencies than are now being realised. The BGL moving bed gasifier, is claimed by its supporter to offer coal to syngas efficiencies of over 90%. Entrained flow gasifiers are not so efficient, but they do produce significant amounts of steam. In practice, there is little to choose between them in an IGCC, especially when the plant is modified to capture CO₂.

The BGL gasifier may, in theory, be less flexible in having a preference for lump coal rather than coal in pulverised form, but its ability to dispense with the drying step that entrained flow and fluidised bed gasifiers require cannot be discounted. Here, it is worth pointing out that gasifiers are better suited to coals with low ash melting points, and although high sulphur will have some impact on efficiency, as operations at Puertollano show, the effects are not too adverse. This again is something which tends to be overlooked when comparing IGCC with supercritical power plants.

Given these high 'cold gas efficiencies' of 80–90% it is unrealistic to expect major advances, even if good heat exchanger alloys were available. The main gains in IGCC performance will come from improvements to the CCGT section of the plant. Quite small changes can be of surprising benefit. The major losses in output on an IGCC come from the plant ancillaries, in particular the oxygen plant and acid gas removal units. These losses are fixed, so a relatively small development with the CCGT can be very useful.

Steady improvements are being made to industrial gas turbines, with some manufacturers purportedly offering

turbine inlet temperatures just above 1400°C, which in simple cycle mode give efficiencies of under 40%. It has been demonstrated above that by applying intercooling, reheating and catalytic combustion, to the gas turbine, a hydrogen fired CCGT could be built with an efficiency of 69%. If the same technology were applied to an IGCC with carbon capture, a coal to power efficiency of over 50% is possible.

Such advanced gas turbines will require developments with high temperature alloys and coatings. Much of the technology currently being used for low supercritical plants can be directly applied. There are also opportunities for European silo combustor technology, which is well suited for this advanced gas turbine.

Building for European energy scene

Europe, and especially the UK, is heavily reliant on natural gas. In the UK about 35% of electricity comes from CCGTs, which makes power generation a significant user of gas. However, this market is dwarfed by the use of gas for space heating and in light industry. For this reason, the fact that an IGCC can be easily modified to produce substitute natural gas, rather than syngas, has been emphasised above.

The SNG could be used to supplement Europe's fast diminishing reserves of natural gas and burnt in a standard CCGT to produce electricity. Since the gasifier, which is the expensive section part of the plant, is run at full output all the time, the simple economics are very good. More importantly, the plant is able to vary the demand for electricity, selling power into the high price daytime market, but at night dispatching SNG into the European pipeline network. Flexibility in power production will be needed as wind power capacity grows. In our view, this combined IGCC–SNG–partial CCS is the only feasible way of meeting Europe's energy needs in an economic, secure and environmentally friendly manner.

Acknowledgement

The views and opinions expressed in this paper are an honest attempt by the authors to make an objective critique of the R&D carried out on gasifier materials over the past 40 years, and to assess various aspects of gasifier design from an engineering viewpoint. As such, no statement made in this paper carries any legal or technical force. As such, neither the authors, nor the Claverton Energy Group, nor ETD Ltd, nor Babes-Bolyai University, Romania are responsible for any actions taken on the basis of this paper. This paper is a modified version of a presentation made to the 8th International Charles Parsons Turbine Conference organised by the Institute of Materials, Minerals and Mining at Portsmouth, UK on 5–8 September 2011.

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Owing to an error during correction and revision, the version of this paper originally posted contained several errors in the Introduction section on p. 428. In addition, on pp. 435 and 436 the negative signs in the exponents of chlorine partial pressures were omitted in four places. These errors have been corrected in the present version of the paper.