By-products from the integrated gas combined cycle in IGCC systems

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14.1 Introduction

Coal gasification is a process which occurs when coal or char reacts with an oxidizer to produce a gaseous fuel-rich product. Integrated Gasification Combined Cycle (IGCC) technology is an efficient and environmentally clean technology for the generation of power from fuel. It is a thermo-chemical process in which coal is converted into a synthesis gas by means of a partial oxidation with air/oxygen and/or steam with low oxygen levels (Font, 2007). IGCC achieves higher efficiencies and lower emissions than other coal-fired power generation technologies (Ilyushechkin et al., 2012). Furthermore, the discharge of solid by-products and waste waters is reduced roughly by 50% versus other coal-fed plants, and the by-products generated (mainly slag and sulfur) are environmentally benign and can be sold (Ratafia-Brown et al., 2002a).

Fig. 14.1 shows an IGCC system indicating “residue” generation. Feed (usually coal, and sometimes biomass, petcoke, other organic wastes, etc.) is introduced in the gasifier (after preparation) which converts carbonaceous feedstock into gaseous components by applying heat and pressure in the presence of steam and oxygen in a reducing atmosphere. The product is called crude synthesis gas (syngas). It consists principally of hydrogen (H_2), carbon monoxide (CO) and nitrogen from air (N_2), carbon dioxide (CO_2), hydrogen sulfide (H_2S), ammonia (NH_3), steam, and methane (CH_4), and traces of some other components.

Minerals contained in the feedstock are separated and leave the gasifier by its bottom as an inert slag in high-temperature operation conditions or ash in relatively low-temperature operation conditions such as in the Kemper IGCC plant. Only a small fraction of the ash becomes entrained in the syngas and requires removal downstream (fly ash) (ELCOGAS IGCC Puertollano, 2001). Gasification at very high temperatures usually ensures the destruction of hydrocarbons, tars, oils, phenols, and other aromatic compounds (Baker et al., 1989). Most of these materials are vaporized in entrained- or fluidized-bed gasifiers, where reaction rates are much faster, and so

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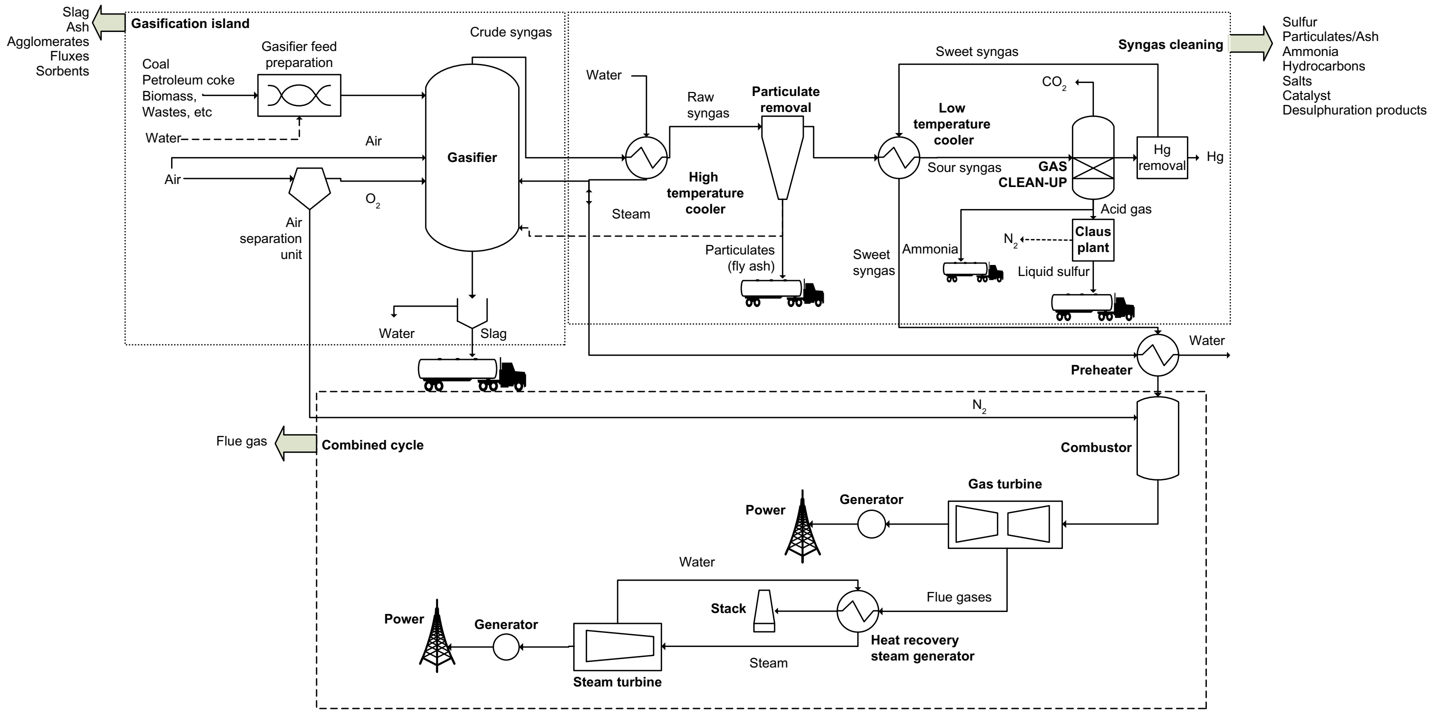

Figure 14.1 Schematic IGCC system.

these systems produce negligible quantities of these substances. However, sometimes wet cleanup systems must be used to remove them from the raw gas and separated organics are typically recycled back to the gasifier for destruction (Selover et al., 1988, as cited by Clarke, 1991). When gasifiers operate at low temperatures, the volatile matter in coal can appear in the gas as tars, oil, naphtha, phenols, cresols, and other compounds. Sulfur is converted mainly to H_2S, but the gas will also contain carbonyl sulfide (COS), CS_2, mercaptans, and thiophene. The nitrogen in coal emerges in the gas as NH_3, HCN, and sulphocyanide compounds. Halogens are converted to their hydrogen halides (Adams, 2004).

Crude syngas has to be cleaned of impurities that can cause corrosion and deposition in the gas turbine. The first step consists of wet scrubbing (sometimes preceded by a filter) for particulates removal. The scrubbers remove some ammonia, chlorides, and other trace components from the syngas.

The second step is gas cleaning through chemical or physical solvents, to extract halides and other nitrogen and sulfur compounds, which are separated afterwards and destroyed in the furnace of the Claus plant. The sulfur in elemental form or sulfuric acid, is recovered from the Claus plant (Abad Secades, 2003). Gas nitrogen compounds react, producing elemental nitrogen using a catalyst.

The syngas is combusted in a gas turbine to produce power. The gas turbine drives an electric generator and in some plants provides some pressurized air to the air separation unit that supplies oxygen to the gasifier. The hot gas from the combustion turbine is sent to a heat recovery steam generator, which produces steam for the steam turbine. Flue gas is emitted to the atmosphere through a stack.

This combined use of combustion and steam turbines boosts the overall thermal efficiency of power generation significantly compared with single-cycle operation.

14.2 Generation of residues in IGCC

In terms of quantities of waste material and toxicity, IGCC power generation has minimal environmental impact (EPRI, 2003). IGCC residues are related to the impurities of the syngas. They consist of ash and/or slag particles, unburned carbon, and other compounds from the coal, sorbents, and fluxes added to the coal, desulfurization products, and process waters (Clarke and Smith, 1991).

The main source of residues in an IGCC system is the gasification island (Fig. 14.1). Those residues are mainly slag or agglomerated ash, except in fluidized-bed gasifiers in which there is no ash fusion and the residues are ash or partially bound agglomerated ash. Those kind of residues are related to the ash in the feedstock (Sloss, 1996).

Particulate material is contained in the crude syngas leaving the gasifier. These fine particles (fly ash) carry partially unburnt carbon and coal dust.

Estimates of daily residue output from various IGCC systems are shown in Table 14.1 (data of conventional pulverized coal combustion (PCC) plants has been included for comparison reasons).

Table 14.1 Daily input and output values from various IGCC plants

IGCC plants	Coal (t)	Slag (t)	Particulates (t)	Sulfur (t)
Wabash River[a]	2400	**323**	–	**52**
ELCOGAS[b]	2600 (50% Coal/50% Petcoke)	583	29	74
TAMPA Electric[c]	2200	181	–	No data
Conventional PCF plant with FGD[d]	**Coal (t)**	**Limestone (t)**	**Ash (t)**	**Gypsum (t)**
	6050	225	605	325

"t" represents the "metric ton" (2200 lb) in Elcogas and PCF plants and the short ton (2000 lb) in Wabash and Tampa plants.
[a]DOE (2002a).
[b]WWW.ELCOGAS.ES.
[c]DOE (2002b).
[d]Schellberg & Ullrich as cited by Clarke (1991).

When the utilization of residues is not possible, those materials have to be disposed of suitably. The US Environmental Protection Agency (EPA) has conducted an interesting study report on residues disposal from the combustion of fossil fuels (EPA, 1999).

14.2.1 Slag generation

In terms of the residues production, gasifiers can be divided into two groups (Adams, 2004):

- Slagging gasifiers, in which the mineral matter in the coal is melted and extracted as molten slag, usually at temperatures above 1350°C (Clarke, 1991). Fixed-bed gasification, if the temperature at the bottom is sufficient for the ash to melt, e.g., British-Gas Lurgi, and entrained-flow gasification. Examples are: Siemens, Pressurised Entrained Flow (PRENFLO), Shell, GE Energy (formerly Chevron Texaco), EAGLE, ECUST, HCERI, MCSG, MHI, TPRI, CB&I E-Gas™ and Tsinghua OSEF gasifiers.
- Non-slagging gasifiers: fluidized-bed gasifiers, in which the temperature is kept below the ash fusion temperature to avoid clinker formation and possible de-fluidization of the bed. The residues of these processes are similar to conventional coal-use residues or to other atmospheric fluidized-bed combustion (AFBF) residues. Examples are: KBR Transport, High Temperature Winkler (HTW), Southern TRIG gasifier (transport gasifier), Kellogg-Brown-Root (KBR), Great Point Energy, or GTI (U-Gas). This group also includes fixed-bed gasification if the temperature at the bottom of the bed is kept below the ash fusion point (e.g., Lurgi dry-ash gasifier) (Ilyushechkin et al., 2012).

According to the EPA (2006), a 500 MW Net capacity IGCC produces 29.5 kg of slag per MWh (for slurry feed gasifier and bituminous coal), 20.4 kg of slag per MWh (for slurry feed gasifier and sub-bituminous coal) and 98.9 kg of slag per MWh (for dry feed gasifier and lignite coal) (Table 14.2). Slag production is a function of the fuel ash content, therefore coal produces much more slag than petroleum coke.

Table 14.2 Slag and sulfur produced in a 500 MW IGCC plant

Gasification technology	Slurry feed gasifier		Dry feed gasifier
Study coal	High sulfur bituminous	Low sulfur sub-bituminous	Lignite
MW net	500	500	500
HHV net efficiency (%)	41.8	40	39.2
Gasifier slag (kg/h)	16.354	11.434	56.29
Sulfur product (kg/h)	3.937	0.474	1.982

Data from US EPA (2006).

14.2.2 Particulates/ashes

The amount of particulate matter in IGCC crude syngas is very low and it is concentrated in a very small gas volume but it can cause blade erosion and turbine corrosion because gas turbines are very sensitive to particle loading (Clarke, 1991).

In many gasification systems the majority of entrained particulate material is first removed using dry cyclone separators. The material delivered from cyclone particulate removal systems, such as those employed in the PRENFLO, Shell, HTW, KBR, or U-gas processes, is recycled to the gasifier as a dry product for the combustion of unburned carbon and removal of mineral matter (Clarke, 1991).

Some IGCC demonstration plants use wet scrubbers, located downstream of the cooling devices, and slurry can be recycled to the gasifier or collected as a filter cake (Clarke, 1991). These scrubbers also remove some ammonia, chlorides, and other trace organic and inorganic components from the syngas (EPA, 2006).

Various devices can be used in hot gas particulates removal such as high-temperature electrostatic precipitators, ceramic filters, etc. Material is collected as a dry dust (fly ash) with similar characteristics to that collected in low-temperature systems. This hot gas cleaning offers the benefits of improving ash handling (because the particulate is removed as a dry solid), reduced heat-exchanger costs and reduced contamination of water (Adams et al., 2004). Chlorides and some other trace components can be removed in dry form with the fly ash.

Candle filters have been the focus of most efforts for final fine particulates removal with large syngas flows. The syngas flows in the filter from the outside through the porous tube walls and flows out of the vessel through the insides of the tubes. Back pulsing dislodges the particulates from the outside walls which are then discharged from the bottom of the vessel. Ceramic candle filters have been employed successfully in both Buggenum and Puertollano IGCC demonstration plants in Europe and Wabash in the US. Most processes remove the entrained particulate matter from the raw gas at higher temperatures before cooling the gas to allow the removal of sulfur compounds. Most of the plants have cyclones upstream which remove most of the particulates before the syngas enters the candle filter vessels, thus greatly reducing the dust loadings on the candles (DOE, 2002a). The bulk of the particulates and char material are recycled to the gasifier (EPRI, 2003).

According to the EPA (2006), a 500 MW Net capacity IGCC plant produces 0.0231–0.0236 kg of particulate matter per MWh (for slurry feed gasifier) and 0.0240 kg of particulates per MWh (for dry feed gasifier).

14.2.3 Sulfur

A second potential large-volume solid stream in IGCC plants is elemental sulfur or sulfuric acid. Sulfur is typically produced as a high-purity liquid, which is a highly marketable by-product. On the contrary, in PCC plants, sulfur is often recovered as gypsum or sludge that must be disposed of (EPRI, 2003).

Under the reducing conditions of fuel gasification, the sulfur in coal is mostly converted to hydrogen sulfide (H_2S) with a small proportion (4–8%) of COS. For IGCC systems without CO_2 capture, depending on the acid gas removal (AGR) technology used and allowable sulfur emissions, hydrolysis can also be accomplished with the AGR unit to get to very low emissions. In systems with CO_2 capture, COS hydrolysis can be accomplished in the water-gas shift reactor. H_2S has to be eliminated from the syngas before its introduction in the gas turbine to avoid corrosion problems in turbine blades and to meet environmental regulations and because recovering saleable sulfur is an important economic benefit for a gasification plant (DOE, 2002a). To illustrate the previous point, in 2011, 8.1 million tons of elemental sulfur were produced, with the majority of this coming from petroleum refining, natural gas processing, and coking plants. Total shipments were valued at $1.6 billion, with the average mine or plant price of $200 per ton, up from $70.48 in 2010. Prices have fluctuated in recent years, but the price of sulfur in 2014 remained well over $150 per ton.

Traditionally, a solvent-based gas cleaning process is used to remove nearly all of the H_2S and some CO_2 from the syngas (adding a second stage to remove the CO_2 from the sulfur free syngas). Cleaned syngas leaves the top of the tower, while solvent with dissolved acid gas leaves the bottom of the tower. The rich solvent is then depressurized, and/or heated to free the acid gas and regenerate the lean solvent. These cleaning processes can use a physical solvent or chemical solvents that react with the acid gas.

Similar to particle collection, eliminating H_2S from gas in gasification processes can be performed at low or high temperatures (Thambimuthu, 1993):

- In all cases, the H_2S elimination is done at low temperatures (40–150°C) (Thambimuthu, 1993). The principal chemical-type solvents are aqueous amines, with methyl diethanol amine (MDEA) being the favorite at the moment for IGCC. The favored physical solvents are methanol and dimethyl ether of polyethylene glycol, as represented by the Rectisol and the Selexol processes, respectively. The mixed chemical/physical processes usually employ mixtures of an amine and a physical solvent in an effort to capture the best characteristics of each solvent. This is the case of Sulfinol, a mixture of sulfolane (tetrahydrothiophene dioxide) and an aqueous solution of an amine, either diisopropanolamine (DIPA) or MDEA (Thambimuthu, 1993).
- The desulfuration at high temperature (250–700°C) is performed by retention onto solid sorbents (metal oxides, ferrites, or zinc titanates) or calcium sorbents (800–1000°C) (Abad Secades, 2003). This kind of technology is currently being tested by RTI at the 50 MWe scale at the Tampa Electric IGCC plant.

Elemental sulfur is usually obtained from the acid gas leaving the H_2S elimination process using the Claus process. Elemental sulfur has much lower transportation costs than sulfuric acid, so when there is a local market for sulfur, it is the preferred form of the sulfur by-product in IGCC plants (EPRI, 2012). However, depending on the local market demand, there are some exceptions: for example, Tampa Electric's Polk Power Station, due to the proximity of a major fertilizer industry that requires large amounts of acid, sells sulfuric acid as a by-product. Another example is Southern's Kemper IGCC, which also produces sulfuric acid.

14.2.3.1 Claus process

The conventional Claus process (Fig. 14.2) involves the partial oxidation of H_2S to elemental sulfur and water.

$$H_2S + 3/2O_2 \rightarrow H_2O + SO_2 \tag{14.1}$$

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S \tag{14.2}$$

The oxidant is usually air, although in some plants oxygen has also been used when the H_2S content is low. The conventional Claus process can approach 98% sulfur recovery efficiency. However, since environmental regulations have become stricter, sulfur recovery unit (SRU) plants are required to recover sulfur with over 99.8% efficiency. To meet these stricter regulations, the Claus process underwent various modifications and add-ons (DOE, 2002a).

One third of the feed gas is burned in the furnace with oxygen from air (Eq. (14.1)) to give sufficient SO_2 to react with the remaining H_2S (Eq. (14.2)). The condensed sulfur is separated and typically discharged to a liquid sulfur pit for subsequent transport and sale.

According to the EPA (2006), a 500 MW Net capacity IGCC produces: 7.87 kg S/MWh (for slurry feed gasifier and bituminous coal), 0.95 kg S/MWh (for slurry feed gasifier and sub-bituminous coal), and 3.96 kg S/MWh (for dry feed gasifier and lignite coal) (Table 14.2).

Some Claus modifications have been reported (DOE, 2002a) such as:

- Oxygen-Blown Claus, based on an oxygen-enrichment; Puertollano in Spain, and the three Italian plants, api Energia, ISAB, and SARLUX use oxygen-enriched Claus units.

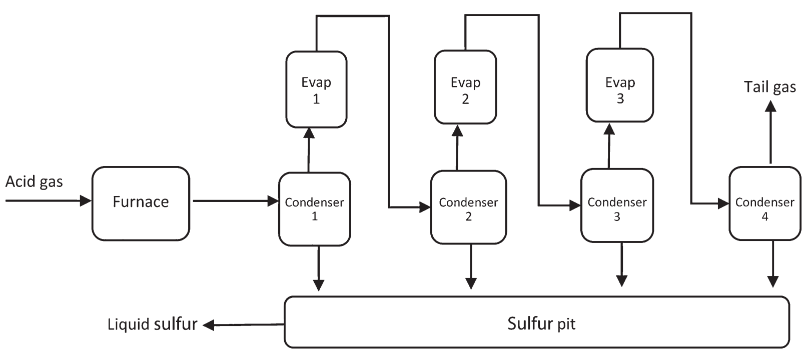

Figure 14.2 Schematic Claus sulfur plant (three stages).

- The Claus Oxygen-based Process Expansion (COPE) process, which needs a specially designed burner with separate feeding of air, oxygen, acid gas, recycled gas, and any fuel gas. It was developed by Air Products and Chemicals and Goar, Allison & Associates (a wholly owned subsidiary of Air Products). The process has been used mainly to retrofit existing Claus plants at refineries to increase their capacity. There are 19 Claus plants that use the COPE Process.
- The Lurgi Oel Gas Chemie GmbH OxyClaus process is based on a burner that is claimed to control temperatures to below the refractory limit. Lurgi has built approximately 22 sulfur-recovery trains based on the OxyClaus process. Most of these were refinery Claus unit revamps. The SARLUX and the ISAB IGCC plants use OxyClaus processes.
- The Sulfur Recovery (SURE) oxygen-blown Claus process was developed by British Oxygen Corp. and Ralph M. Parsons Co. (now Worley Parsons). The SURE process is based on staged combustion. A portion of the oxygen and all of the air, together with all of the acid gas go to a first stage, while the rest of the oxygen is fed to a second combustion stage. Only one burner is used (in the first stage) because the temperature of the gases going to the second stage is sufficiently high to auto-ignite with the rest of the oxygen. For H_2S-rich acid gases, a combination waste heat boiler (WHB) and second stage furnace have been developed by Siirtec Nigi and Parsons for the API Falconara refinery Claus plant revamp.
- Extended Bed Claus processes. There are two major extended bed Claus processes which improve Claus sulfur recovery by either adding, or replacing, the last Claus stage with a catalytic bed. One process operates at above the sulfur dew point (SuperClaus, developed by Comprimo, Gastec, and the University of Utrecht, in the Netherlands), the other below the sulfur dew point (Sulfreen, offered by Lurgi and SNEA).

The Claus plant furnace is often used for disposal of unwanted plant wastes such as gases with NH_3, HCN, H_2S, and hydrocarbons. Most of these wastes can be combusted in the furnace to destruction. However, their combustion results in decreased sulfur recovery efficiency and a tail gas that may contain some unconverted waste materials.

14.2.3.2 Sulfuric acid recovery

As has been mentioned already, sulfuric acid synthesis is an alternative to sulfur recovery when the plant is located close to a sizeable market for sulfuric acid. In this case, H_2S is first burned in a furnace to form SO_2, which is then converted to sulfur trioxide (SO_3), which is in turn scrubbed with water or a recycled weak sulfuric acid stream to yield saleable 98% sulfuric acid. Typically, 99.8% of the H_2S can be recovered in a sulfuric acid plant (DOE, 2002a).

14.2.3.3 Others

Other sulfur-recovery processes are based on catalytic oxidation and wet oxidation. Among the catalytic oxidation processes are the Selectox, BSR/Selectox, and the MODOP processes (DOE, 2002a):

- The Selectox process is based on replacing the Claus first furnace with a catalytic oxidation step that can operate at much lower temperatures. About 16 Selectox plants have been built worldwide, ranging in size from about 0.5 to 30 L/day of sulfur. It appears, from the installed plant inventory, that the process may not be economic for large sulfur plants, particularly for acid gases with a high H_2S content.
- The wet oxidation processes are based on reduction-oxidation reactions to oxidize the H_2S to elemental sulfur in an alkaline solution containing an oxygen carrier: Vanadium

(Stretford process) or iron (LO-CAT and SulFerox process). The optimum application for the wet oxidation processes is for low H_2S content acid gases and small plants, 1–20 L/day of sulfur. Costs are too high for larger plants because of equipment size limitations and plant complexity. Even for small plants, the cost of sulfur recovery exceeds by far the selling price for recovered sulfur. Both processes are capable of up to 99% sulfur recovery.

14.2.4 Nitrogen species

Gasification operates with a deficiency of oxygen, so most of the nitrogen present in the feed coal is converted to N_2 in the gasifier. A small portion is hydrogenated and forms ammonia (NH_3) under the reducing conditions. The amount of NH_3 formed depends mainly on the gasification temperature and also the gasifier design. Higher temperatures usually result in lower NH_3 yields. A small amount of hydrogen cyanide (HCN) may also be formed in the gasifier (Clarke, 1991).

Up to 50% of the NH_3 formed is converted to NO_x in the combustion chamber of a gas turbine. NO_x is a waste product that is not considered a by-product, therefore it is not within the scope of this study. An interesting study in this respect is available at http://www.coalonline.info/flash.

During combustion, NH_3 present in syngas is oxidized to NO_X. NO_x can be reduced by syngas moisturization, nitrogen dilution, or steam injection in the combustor. When NO_X emission has to be polished to meet the emission levels, the expensive selective catalytic reduction (SCR) process can be installed. Thus, removal or decomposition of NH_3 present in syngas prior to combustion results in higher IGCC efficiency and lower costs (Qader et al., 1996). NH_3 can be removed by scrubbing or by thermal decomposition using a catalyst. Nitrogen-containing species are decomposed according to the following reactions:

$$NH_3 \rightarrow 3/2H_2 + 1/2N_2 \tag{14.3}$$

$$HCN + H_2O \rightarrow 3/2H_2 + CO + 1/2N_2 \tag{14.4}$$

If there is a market capability for ammonia, recovered NH_3 can be sold. According to the analysis of Ratafia-Brown et al. (2002b), the amount of ammonia generated in an IGCC plant is 0.0018 kg/MWh. The Kemper IGCC plant is designed to produce ammonia as a by-product for sale.

If the Claus kiln is also equipped with a proper catalyst bed, the nitrogen-containing species from the syngas can be converted to nitrogen in the sulfur recovery processes.

14.2.5 Other potential by-products

When the gasification process generates other residues such as tars, oils, and other organic substances, then wet cleanup systems can be used to remove them from the crude gas. Separated organics are typically recycled back to the gasifier for destruction. Other wastes include spent catalyst, worn refractory lining material from the gasifier, and spent sorbents from Hg and As removal. Some spent catalyst materials are disposed of as hazardous residues due to their high content of metals such as nickel, arsenic, cobalt, or molybdenum. Worn refractories are potentially hazardous due to the high contents of chromium (Adams, 2004). Cleaning systems also generate residues.

Most of these residues are not reused because they are produced in small quantities and the study of their potential for reuse has not been considered of interest. Therefore, they are treated as waste, although they could be considered as by-products in the future.

14.3 Characterization of by-products from IGCC systems

Most of the residues from IGCC systems are produced as slag or ash from the bed, although some is collected as fly ash. High temperatures and pressures of gasification processes have the potential to turn mineral matter within the feedstock into slag instead of the ash that is produced in combustion (NETL, 2015).

The physical and chemical characteristics of gasification by-products depend strongly on feedstock properties and the specific gasification technology used (Ilyushechkin et al., 2012).

Solid by-products in **fixed-bed gasification** appear as dry ash, if the temperature is below the ash fusion point; or as slag, if ash melting occurs.

IGCC by-products of **entrained-flow gasification** include coarse and fine slag, fly ash, spent activated carbon for Hg removal, and spent sorbent from desulfurization process (when RTI process is commercialized), elemental sulfur, or combinations of these streams.

14.3.1 Slag

In slagging systems most of the mineral matter in the coal is converted into molten slag. The slag leaves the gasifier in a liquefied state (temperature above melting point) and flows into water bath, where it is cooled and crushed (Ilyushechkin et al., 2012).

Generally, the chemical composition of the slag depends on the type of fuel used and the amount of flux added to control slag properties, while the physical properties are dependent on the gasification temperatures/melting temperature and the cooling method.

The main components of IGCC slag are SiO_2 and Al_2O_3, followed by CaO and Fe_2O_3; these components typically comprise 90% of the slag. Table 14.3 gives some examples of chemical composition of various slags (Clarke, 1991). Volatile metals, such as mercury, are typically not recovered in the slag, but may be removed from the raw syngas during cleanup.

IGCC slags have similar properties to some coal combustion by-products, specifically boiler slag and bottom ash. Because coal combustion by-products are often used in construction applications, IGCC by-products could be valorized in the same applications.

The chemical composition of IGCC slags varies widely, reflecting the variability of the composition of the coal and other process inputs, which can complicate predictions of waste properties based on averages (Ilyushechkin et al., 2012). A summary of the IGCC by-product leaching characteristics is given in both works of Ilyushechkin et al. (2012) and Ratafia-Brown (2002a).

The morphology and mineralogy of residues from coal gasification are complex and are subject to great variability caused by differences in temperature of formation and slag or ash composition (Clarke, 1991). Water content varies from 5 to 20%, bulk

Table 14.3 Typical chemical compositions of slag from different IGCC gasifiers (Clarke, 1991; Font, 2007)

Maximum and minimum values (%)					
SiO_2	35.8–59.2	Fe_2O_3	0.1–7.4	CaO	4.9–29.5
TiO_2	0.6–1.02	P_2O_5	0.1–1.4	Na_2O	0.5–1.6
Al_2O_3	14.1–28.5	MgO	0.7–5.2	K_2O	0.3–1.84

density is usually in the range 1040–1500 kg/m^3, and size is usually under 2 mm. The particle size of 70–80% of slag is in the range 0.5–4 mm.

Clarke (1991) published a complete report including the characterization of different slags. Ilyushechkin et al. (2014) have reported the characteristics of slag from entrained-flow gasification of Australian coals. Several studies related to the ELCOGAS slag characterization (Acosta et al., 2001, 2002a, 2002b, 2003; Font, 2007) are also available. Aineto et al. (2006) have studied some properties of the same slag.

Gasification slags are generally non-leaching or low-leaching materials according to most of the standard leaching tests applied. Some of the slags obtained from coal-petcoke blends gasification, however, have relatively high leachability and could be an issue for disposal options (Ilyushechkin et al., 2012).

14.3.2 Fly ash

The properties of the fly ash produced in coal gasification plants depend on the gasification technology (fixed-bed, fluidized-bed, or entrained-flow gasifier) and on the feed fuel employed.

The most implemented technology at an industrial scale is the **entrained-flow gasifier**, but studies on fly ash are scarce. Studies on the fly ash produced in the largest IGCC power plant worldwide (Font et al., 2005a, 2006) reported different characteristics for this fly ash than those for conventional PCC fly ash. The IGCC fly ash shows variable and relatively higher LOI (loss on ignition) yields (2.7–10.7%) and BET values (4.3–9.6 g/m^2) (essentially due to the variable content of unburned feed fuel particles), when compared with usual BET values for PCC fly ash (1–4 m^2/g). The density of the IGCC fly ash (1.2–1.3 g/cm^3) is higher (and porosity is lower) when high limestone proportions are added as fluxing agent, instead of fly ash produced with low limestone addition (1.0–1.1 g/cm^3). The most relevant characteristic of the IGCC fly ash is the very fine grain size (median 2.1–5.2 μm) and the high proportion of a made-up amorphous Al–Si glass and unusual reducing and fine crystalline species, mainly galena (PbS), sphalerite wurtzite (ZnS), phyrrhotite (Fe_1-xS), and nickeline (NiAs) as well as other compounds condensed from reducing vapor species in cooling flue gas. Whether the content of trace elements is high in the feed fuel, the high slag/fly ash ratio and the high volatilization-condensation processes of entrained-flow gasifiers give rise to fly ash with extremely high contents (one order of magnitude higher than in PCC fly ash) of a number of trace elements (Pb, Zn, Ge, Ga, Sb, Ni, Cu, As, among others). The high enrichment of IGCC fly ash in the above elements is due to the high slag/fly ash ratio (90:10) of the entrained-flow gasifiers compared with PCC and the subsequent high content of condensing material with respect to the non-volatile Al–Si glass.

Besides the high slag/fly ash ratio and the high volatilisation-condensation processes, feed fuels (coal, pet-coke, and biomass) rich in trace elements also may contribute to an increase in the concentrations of the aforementioned elements in IGCC fly ash. For instance, the metal-rich Puertollano coal contributes to an increase in the concentrations of Pb, Zn, Ge, Ga, Sb, Ni, Cu, and As in fly ash with respect to that of PCC combustion, and pet-coke raises the V and Ni content in fly ashes (Font et al., 2005a,b). The co-gasification of biomass results in increasing the concentrations of K, P, Mg, Na, and Cl while reducing those of the elements supplied by coal (mainly As, Pb, Zn). The most important effect produced by biomass gasification is to increase the volatile proportion of a large number of elements–Hg, S, Cl, P, As, B, Cd, Cu, Pb, Sb, Se, Sn, Tl, Zn, and K. The high occurrence of organic Cl in biomass favours the formation of highly volatile metal chlorides, increasing the volatile fraction of the aforementioned elements and consequently their emissions levels in spite of the significant abatement capacity determined for these elements by the IGCC gas-cleaning systems.

The fine grain size of reduced crystalline phases and the occurrence of water-soluble species of some elements (i.e., hexagonal GeO_2 or GeS_2 and GeS) results in the high water leachable potential of Ge, Ni, As, and Sb boosting the potential valorization of IGCC fly ash by the hydrometallurgical extraction of valuable elements (Ge and Ga), but also the environmental concern of this fly ash.

The aforementioned peculiarities of IGCC fly ash give rise to a number of studies to develop environmentally friendly extraction and recovery methods for valuable elements such as Ge, Ga, and V from Puertollano IGCC fly ash (Font et al., 2005b, Font et al., 2009, Arroyo et al., 2010, Arroyo et al., 2014). Extraction was performed on IGCC fly ash samples produced under different operating conditions using different extractants to cover a wide range of extraction conditions to obtain high and regular Ge and Ga extraction yields. The most promising extraction procedure for Ge included the use of water or weak oxalic acid solution (up to 83% extraction) followed by solvent extraction enrichment process and precipitation by sulfiding the solutions with H_2S, or as an organic complex with CAT/CTAB mixtures and subsequent roasting of the precipitates. Both methods showed high efficiency (>99 %) to precipitate selectively Ge using a single precipitation stage from germanium-bearing solutions (Arroyo et al., 2014).

Gallium yielded up to 70 and 64% extraction after a 24 h leaching period using a weak acid (H_2SO_4) and alkaline solution (NaOH), respectively (Arroyo et al., 2014). An enriched Ga end-product is obtained by an extraction at 25°C and with a weak NaOH solution, followed by a re-circulation of the solution and subsequent precipitation of Ga by two carbonation steps (Font et al., 2009).

Some papers regarding entrained-flow IGCC fly ash properties have been published (Aineto et al., 2006; Ilyushechkin et al., 2014).

Also, some data regarding ashes from **fixed- and fluidized-bed gasifiers**, such as the Sasol–Lurgi fixed-bed dry-bottom gasifier (S–L FBDB), can be found in the literature. The S-L FBDB gasifier treats a feed coal containing c.a. 30% ash-forming minerals, which means that complex mineralogical processes can occur within the reactor (Matjie et al., 2005). To obtain an understanding of the mineral transformations, a quenched commercial-scale S–L FBDB gasifier was sampled and characterized mineralogically. Crystalline phases measured by X-ray powder diffraction (XRD) analyses show that the ash exiting the reactor contains anorthite, quartz, mullite, cristobalite, diopsite, mayenite, anhydrite, muscovite, hematite, and magnetite, with the non-crystalline proportion in the ash c.a. 53%.

14.3.2.1 Characteristics from blended feedstocks

Trace elements in samples of residues generated in the Polk and Puertollano IGCC plant have been determined in several studies (ELCOGAS IGCC Puertollano, 2001; DOE, 2002b; Aineto et al., 2006; Font et al., 2010). In the case of the Puertollano plant, the use of petroleum coke with high V and Ni contents significantly increases the amount of Ni and V in fly ash and slag, compared with the average range of IGCC slag and ash trace element concentrations for gasification of coal alone.

The leaching behavior of by-products obtained from gasification of coal with other feedstock has also been studied (DOE, 2002b; Cousins et al., 2001; Kim, 2009).

14.4 Management of by-products

Residue management options may range from complete disposal to complete and final utilization (in this case, we should not speak of a residue but a by-product).

At first sight, it may appear that disposal and utilization can be distinguished clearly, but the definition of these two activities is one of the key areas of uncertainty. The utilization is a process that brings a financial benefit to the end-product producer, partly or totally negating the cost of removing waste from its site of production to its final end-use, whereas disposal inevitably will involve a net cost to the producer. Difficulties arise over the distinction between the use of materials as a fill and disposal in a landfill. Both are forms of controlled emplacement in the environment and require similar techniques and controls regarding degree of consolidation, prevention of leachate, etc. While use as engineering fill gives an immediate financial benefit, in the longer term the land produced after landfilling can be used for building or other development as engineering fills do (Agüero et al., 1996).

As reported by Ratafia-Brown et al. (2002b), a 300 MWe IGCC power plant using 2500 tons of 10% ash coal per day may generate 250 tons/day of slag or bottom ash, the disposal of which represents a significant operating cost. The commercial application of coal gasification technologies can be enhanced significantly if the solid by-product can be utilized, rather than disposed of in landfill.

Effective management of gasification by-products is a significant factor in determining the environmental acceptability and economics of future gasification technologies. Therefore, some utilization strategies of by-products are analyzed next. The possible use of gasification by-products depends on their physical and chemical properties and the extent to which they might vary. In addition to technical requirements, the following factors also have influence: requirements created by standards or codes of practice; competition from other (traditional) materials; attitudes of potential users; subsidies and incentives; and resource transport and storage.

Many of the IGCC by-products applications have also been studied for other coal-use residues, but as by-products from IGCC power generation have different properties compared with these residues, the relevance of the applications must be examined on a case-by-case basis.

14.4.1 Solid by-products

The main solid by-products of IGCC plants are slag, sulfur, and fly ash. Slag and fly ash come from the mineral matter of the fuel (coal and co-gasification matters) and thus have a similar general composition. As mentioned previously, one important difference between IGCC and conventional PCC systems processing the same fuel is found in the slag/fly ash ratio, which is higher in gasification power plants. The mineral matter partition favours the amount of slag in IGCC plants, whereas fly ash is the main product in PCC plants.

When the literature about possible applications for solid IGCC by-products is consulted one can find that, although slag and fly ash are proposed for the same type of applications, mainly in the construction sector, slag offers many more possibilities than fly ash. This in part may have to do with the larger amount of slag produced as compared to fly ash, but it is also due to compositional differences between the two solids. Thus, the coarser granulometry of slag gives more opportunities for this solid to be used commercially than for the finer fly ash. In addition, although the main components of slag and fly ash are similar, important differences exist in the trace elements often present in both materials and, therefore, in their leachability properties. This implies that, as occurs with other products of the same sort (e.g., MSWI solid residues), the environmental impact of slag is lower than that of fly ash and this could explain the difficulties found in many cases to commercialize IGCC fly ash as compared to IGCC slag.

The advantages of using the IGCC by-product, instead of landfilling, are that it requires a decreased landfill space, conserves natural resources, reduces the cost of energy production, and helps the economic competitiveness of coal (Ratafia-Brown et al., 2002a). In spite of this, the same authors reported that there are still some barriers to IGCC slag utilization. The principal reasons for this are institutional, regulatory, and legal.

In the following, the main IGCC slag applications will be considered, although details will also be given on those cases in which fly ash can be used instead of slag.

14.4.1.1 Roads construction and related applications

Roads consist of two parts: the pavement (surface course, base course, sub-base) and the subgrade (Agüero et al., 1996). IGCC by-products have the strength and resistance requirements to be used as road bases but generally are too fine, so coarser aggregates have to be added to reduce the fineness (Sloss, 1999).

Mixtures of cement and slag may be utilized as road bases (Choudhry et al., 1986). The use of slag in road construction was studied by Choudhry and Hadley (2009), mixing asphalt with slag. By itself, the slag was not found to be suitable for surface pavement applications due to the lack of coarse particles and the tendency to degrade when abraded. However, its use as a sub-base and base material in road construction is quite feasible.

Asphalt is a mixture of aggregates with petroleum asphalt as a binder. Asphalt is commonly used as the surface course for road and pavement construction and IGCC by-products can be added as aggregates to achieve the correct particle size distribution (Agüero et al., 1996). Slag from the Shell gasifier has been used as an aggregate in asphalt (Salter et al., as cited by Clarke, 1991).

Gasifier slags can be used as a substitute in asphalt-treated road bases and asphalt road surfaces when they have high resistance to wear, a low porosity, and a high affinity for asphalt (Choudhry et al., 1986).

GE slags are not suitable for use in hot-mix asphalt concrete because of poor cohesion but they are used more commonly in cold-mix asphalt mixtures, where gradation requirements and durability are not as critical as in hot-mix surface mixtures (EPRI, 2003).

Amick and Dowd (2001) provide an analysis for slag produced at the Wabash River plant. They report marketing for asphalt, construction backfill, and landfill cover applications.

14.4.1.2 Engineered structural fills

IGCC fly ash is similar to PCC fly ash in its applicability to structural fill and sometimes it shows self-hardening properties, which would be beneficial in many applications (Sloss, 1996). Fly ash without pozzolanic activity can be used to replace earthen fills. The American Society for Testing and Materials standard ASTM E 1861 was issued in 1997 in the US for guidance on the use of coal conversion by-products in fills.

Controlled emplacement as a lightweight fill material is one of the most widespread uses of fly ash. One important limitation is the costs of transport and handling (Agüero et al., 1996).

14.4.1.3 Cement additives or replacement (concrete)

Gasification residues can be used in the production of Portland cement. There are two possible methods of utilization (Choudhry et al., 1986): as a raw material in the production of cement clinker or as a replacement for cement in the production of Portland cement (Clarke, 1991). Potter and Baker (1990) describe a process for the treatment of slag from the gasification of coal, which includes mixing the slag with a cementitious material. Majumdar and Singh (1991) describe a silica fume, gasifier slag, fly ash, or other pozzolanic or latently hydraulic material mixing, which preserves the advantages of high-alumina cement.

Slag with pozzolanic properties can be mixed directly with cement clinker. The use of a slag/lime mixture as a partial replacement in Portland cement was studied by Ninomiya et al. (1992). The pozzolanic reactivity of the slag improved with CaO content and decreasing the condensation of silicate ion in the glass phase. The main technical barrier for using IGCC slag in applications such as cement production is excessive carbon content, but technical solutions have already been found. For example, in the Polk IGCC plant, the unconverted carbon is separated and recycled back to process (EPRI, 2003).

The University of Kentucky has conducted a project investigating the potential applications of coal gasification by-products (CAER, 2008a). Samples of slags from Tampa Polk station and Eastman Chemicals were characterized to be used as pozzolanic material or concrete aggregate.

Fly ash is often described as a pozzolanic material. The use of fly ash as a cement additive has two options: fly ash is blended with ground cement clinker to produce a homogeneous mixed fly ash cement or pozzolanic cement (Sloss, 1999), or direct replacement of cement with fly ash at the point of use, usually in concrete. IGCC fly ash can also be used at up to 20% replacement in cements with excellent strength development (Sloss, 1996).

14.4.1.4 Concrete, aggregates, and mortars

Solid IGCC by-products can be used in concrete as a replacement for sand or fine aggregate (Choudhry et al., 1986). Alpert et al. (1992) describe a low-density aggregate product using coal IGCC ash and slag. The US patent 7670425 relates to an ultra-high strength fiber-reinforced cement composition containing cement, silica fume, coal gasification fly ash, gypsum, and metal fiber (Watanabe et al., 2010).

Boiler slag and blast furnace slags have been used successfully as aggregate substitutes in concrete (EPRI, 1984). Slags from ELCOGAS IGCC plant, Shell, CRIEPI, and BGL processes are suitable to be used as concrete additive as several authors have reported (Garstang, 1990; Clarke, 1991; Iglesias et al., 2013).

14.4.1.5 Synthetic lightweight aggregates

Lightweight aggregates (LWA) are defined as construction materials that have a bulk density lower than that of common construction aggregates (Choudhry and Hadley, 2009). It is possible to manufacture LWA and ultra LWA from gasification slag and fly ash, according to Choudhry and Hadley (2009) and Sloss (1996). Laboratory tests carried out by Choudhry and Hadley (2009) show that lightweight aggregate-based concretes manufactured using IGCC by-products exceed ASTM requirements for compressive strength.

Aggregates can also be made from fly ash with or without the addition of other waste materials by pelletizing and sintering in an oven. Such pellets can be made to the required size and can be used to prepare lightweight concrete with a high compressive strength (Sivakumar & Gomathi, 2012). Kockal and Ozturan (2011) have reported the characteristics of lightweight fly ash aggregates.

Fly ash and slags generated in the ELCOGAS power plant (Puertollano IGCC) have been demonstrated to be suitable for recycling as LWA (Aineto et al., 2005). The Electric Power Research Institute (EPRI) and the Illinois Clean Coal Institute have conducted a US Department of Energy-funded project, along with considerable industry involvement. The project has demonstrated the technical and economic feasibility of commercial production and use of lightweight and ultra-lightweight aggregates (Choudhry and Hadley, 2009; Ilyushechkin et al., 2012).

14.4.1.6 Ceramic materials

Both ash and slag residues from IGCC processes have chemical and mineralogical characteristics suitable for use as raw materials in the production of ceramic substances (Manz, 1984). Iglesias Martín et al. (2013) have reported the benefits of using IGCC slag as degreasers in ceramics because slag reduces the plasticity and the linear shrinkage of both raw and dry paste in the same way as other degreasing materials, such as quartz and carbonate sands.

Several authors have reported the utilization of the Puertollano IGCC by-products as grog material in mud bricks (Acosta et al., 2002a,b), in building ceramics (Aineto et al., 2006, 2004), and in the manufacture of bricks (Fernandez-Pereira et al., 2011).

14.4.1.7 Abrasives, sandblasting, and ice control

IGCC slag may provide several advantages compared with sand, gravel, or salt as it is inert, absorbs heat, and does not leach. The economic value of slag utilized in this way is low, but the potential market is large (several million tons in the United States alone). Where slag is available close to areas where grit is required, substantial savings may be possible compared with disposal costs (Clarke, 1991).

IGCC slag has the potential to replace sand and gravel, and provide a partial replacement for salt (Choudhry et al., 1986). In the United States, boiler slags have been used effectively for sandblasting buildings, blasting grit, and as roofing granules (EPRI, 1984).

De-icing grit provides an important market for the use of boiler slag and bottom ash in some parts of the US (EPRI, 1984). Crushed slags from coal-fired utility boilers and smelter slags are commonly used for abrasive blasting (Ilyushechvin et al., 2012).

14.4.1.8 Mineral wool

Mineral wool is a fibrous material used in building insulation. Various gasification slags and ashes have been tested as a substitute for steel mill slag in the mineral wool process, producing similar results, and resulting in a potentially attractive raw material (Manz and Laudal, 1986; Choudhry and Hadley, 2009).

14.4.1.9 Structural fills and soil stabilization

Soil stabilization is defined as chemical or physical treatments which increase or maintain the stability of a soil or improve its engineering properties. The addition of IGCC residues to a soil may provide a construction sub-base, improves soil strength and durability, controls soil volume changes, and provides a temporary wearing surface (Choudhry et al., 1986; Agüero et al., 1996).

Slag size gradation, shear strength, permeability, and compaction make gasification by-products more suitable than heavier conventional materials for these kinds of applications (Choudhry et al., 1986).

14.4.1.10 Agriculture (uses in soil and agriculture)

Few studies have been carried out on the use of gasification ash for soil/mine spoil reclamation in combination with lime, sludge, etc. (Mbakwe et al., 2013; Ram and Masto, 2010). This is particularly important since potentially toxic elements and minerals may become concentrated in vegetation (Francis et al., 1985). The potential markets of IGCC slag and fly ash as soil conditioners are large but will vary locally.

Choudhry and Hadley (2009) reported the use of gasification slag as a lime substitute to loosen clay-rich soils. The addition of slag, with a relatively low bulk density (Clarke, 1991), would also decrease the bulk density of the soil (Choudhry et al., 1986). The alkalinity of gasification ashes (particularly those from fluidized-bed IGCC systems with added sorbents) suggests that they could be used to amend acidic soils, or reclaim acid-damaged soils (Clarke, 1991).

IGCC slag can also be used as a low-grade fertilizer (Choudhry and Hadley, 2009). Major element analyses of the slags indicate moderately higher potassium and phosphorus contents compared with typical soils. The leachability of slag is generally low, but may be sufficient to provide a slow release of useful elements.

IGCC slag can even be used as a carrier for fertilizers or insecticides (Choudhry et al., 1986; Clarke, 1991).

14.4.1.11 Materials recovery

Metals are generally present in the slags or ashes at sub-economic concentrations and recovery will only be viable if substantial enrichments are economically possible or the residues are found to contain strategic metals. Recoverability depends on the mineralogy of the residue. Gasifier slags typically contain Al_2O_3 (Table 14.3) which can be extracted by acid leaching (EPRI, 1984). Garstang (1990) reports that the economics of the aluminum recovering from the BGL gasifier slag process compares well with those of the Bayer process for bauxite.

Most gasification slags or ashes contain Fe_2O_3 (Table 14.3). A portion of this iron is suitable for extraction by simple dry magnetic separation (EPRI, 1987). Some slags contains metallic iron-rich nodules, which are strongly ferromagnetic and economically extractable by conventional magnetic separation equipment (Garstang, 1990).

Several studies carried out on the Puertollano IGCC fly ash have focused on a general characterization and the speciation of major and trace elements (Font, 2007; Font et al., 2010). The recovery of valuable elements such as Ge, Ga, or V has been studied by Font et al. (2006), Arroyo et al. (2009, 2014), Arroyo and Fernandez-Pereira (2008, 2011), Hernandez et al. (2006) and Marco-Lozar et al. (2007). Titanium, cobalt, chromium, manganese, and strontium can all be enriched in solid residues, although additional steps are required to separate these metals (EPRI, 1984). Ashworth et al. (1986) has presented an integrated method for the recovery of carbon, magnetite, alumina, ferric oxide, and iron chloride from coal by-products.

14.4.1.12 Industrial fillers

IGCC residues may be suitable for use as industrial fillers or extenders for plastics, rubber, and other elastomers (Choudhry et al., 1986). The properties required by a filler depend on the special requirements for each application. In order to meet the requirements of a filler or extender, gasifier slags and ashes may require size screening and/or grinding (Clarke, 1991).

14.4.1.13 Others

The results of a study performed by the University of Kentucky (CAER, 2008b) indicated that the carbon-rich gasification by-products of gasification can be used as an Hg adsorbent from combustion flue gas; employing a material cheaper than activated carbon. Several studies on the Puertollano IGCC fly ash focused on zeolites synthesis (Querol et al., 2002; Moreno, 2002).

14.4.2 Ammonia

By far the most widely and extensively used intermediate for making nitrogen fertilizers is ammonia, with over 80% of worldwide ammonia production going towards the synthesis of fertilizers such as urea (NETL, 2015).

A high portion of ammonia is applied directly to farm fields as anhydrous ammonia. Most of the remaining ammonia is converted into other types of nitrogen fertilizers (or precursors), which include ammonium nitrate, urea-ammonium nitrate, ammonium sulfate, nitric acid, and urea (Czuppon et al., 1992).

Ammonia can also be used as a transportation fuel, either by burning it in an internal combustion engine, or by feeding it to a fuel cell. Ammonia has several desirable characteristics that make it potentially attractive as a medium to store hydrogen: it can be liquefied under mild conditions, it has a large weight fraction of hydrogen, and it has a volumetric hydrogen density about 45% higher than that of liquid hydrogen. Ammonia can be decomposed over a catalyst to produce hydrogen and nitrogen (Lipman and Shah, 2007).

Like most fuels, ammonia is flammable. Ammonia is also toxic at high concentrations, primarily due to its alkaline nature (NETL, 2015). Ammonia is recovered as anhydrous ammonia which can then be used in selective catalytic reduction (SCR), or sold for fertilizer or other chemical markets.

14.4.3 Sulfur

Currently, sulfur is a saleable product, although it is important to be aware that were a large part of the power industry to switch to gasification-based processes and sulfur production continues to increase from oil refineries, the sulfur market would become oversaturated. Nonetheless, even in this case the amounts of sulfur would be substantially smaller than with gypsum (Higman and van der Burgt, 2008).

A part of the elemental sulfur from IGCC plants is converted to sulfuric acid (H_2SO_4). Sulfuric acid is a basic chemical with a wide range of uses. The phosphate fertilizer uses 34% of the sulfuric acid consumed each year. In addition, for chemical fertilizers, sulfur is a secondary nutrient. Elemental sulfur produced at the Cool Water IGCC plant in California, US is typically 99.67 % with small quantities of ash, chlorine, and fluorine. This product is of saleable quality, as occurs with sulfur from most operating plants. However, if the market for raw sulfur became saturated then it might be necessary to store the sulfur for long periods of time or dispose of it as a waste.

14.5 Examples

There are two very interesting sections in the articles of Ilyushechvin et al. (2012) and Ratafia-Brown et al. (2002b) with particular data from the largest IGCC plants related to by-products management and utilization. A summary of the IGCC by-products usage shown in examples taken from both papers is presented in the following paragraphs.

The **Polk power station in Tampa**, Florida, US was built and is operated by the Tampa Electric Company (TECO). Solid wastes from the Polk facility consist primarily of gasifier slag and entrained particulates in the syngas. Dewatered slag is loaded into trucks for offsite use or temporary onsite storage (up to five years). Particulate removal from the syngas occurs in a conventional cold gas cleanup unit.

A by-product handling issue reported at the Polk plant is related to the ash/char recycle stream. The Polk GE gasifier generates char that is mixed with a very fine glassy frit, which requires separation prior to re-injection. The separated frit must be washed with clean water before it can be disposed of economically or used commercially.

TECO provides the slag to a cement manufacture company. Slag not used by the cement industry is subject to disposal. Although the slag is classified as non-hazardous, local regulations require disposal in a different class of landfill: Polk must use a Class I landfill that is double-lined with leachate extraction/control, which is more expensive ($20/ton) than conventional landfill.

Puertollano power station uses a coal blend based on sub-bituminous coal and petroleum coke with a normal weight proportion of 50:50. The amounts of by-products generated during a 10-month period in 2000 are shown in Table 14.4 (DMSEMS, 2010).

Recently, the slag has been valued as a by-product to be used in the manufacture of ceramic products, and the company has agreed to sell the slag to a local ceramic workshop (Aineto et al., 2005). Fly ash has also been valued as a by-product to be used as an additive for concrete and is being used by local cement and concrete industries as a component in the manufacture of concrete.

Nakoso IGCC power station uses an air-blown, dry-feed, entrained-flow gasifier. Coal slag discharged from the gasifier is considered as an inert waste and is suitable for use in land reclamation. This slag can also be used as a substitute material for clay in the cement industry and as a fine aggregate for concrete production (Araki and Hanai, 1996).

Solid by-products from the gasification process at the **Wabash River IGCC** facility consist primarily of gasifier slag, fly ash, and sulfur. The slag from the gasifier is removed as a slurry and directed to a dewatering system. The dewatered slag is loaded

Table 14.4 By-products of ELCOGAS IGCC plant

By-product	Amount (metric ton)	% w
Fly ash	7135	10.5
Slag	52,226	76.5
Filter cake	4690	6.9
Sulfur (exit)	4185	6.1

into a truck or railcar for transport to market or to a storage site. The entrained particulates are collected from the cooled syngas and recycled to the gasifier. They generally contain 3–10% unconverted carbon and are marketed for asphalt, construction backfill, and landfill cover applications. Slag production is proportional to ash and fluxes in feedstock (Ratafia-Brown et al., 2002b). The plant also produces 99.99% pure elemental sulfur that leaves the plant in railcars. It is sold for agricultural applications.

Before its closing, the slag produced in **Buggenum** was recycled as a raw material in cement clinker production. The cement industry located near Maastricht and Liege enabled the use of 150,000–300,000 tons of slag/year.

14.6 Future Trends

The future trends in IGCC technology development are related to the improvement in thermal performance and environmental signature (focus on CO_2 removal and gas cleanup technologies (Zhu and Frey, 2012). All these trends can affect the nature and quantity of the by-products obtained, thus modifying the scenario already shown in previous sections.

Many specialists recognize that IGCC with carbon dioxide (CO_2) capture and storage (CCS) is a promising technology to satisfy the market needs in a carbon-constrained environment (Coal-Gen Europe, 2009), although there are many obstacles ahead. IGCC plants with CO_2 capture gained interest in recent years. However, until recently, there have been no applications of CO_2 capture in an electric power plant at a large scale and no IGCC in operation with CO_2 capture (Wu & Wang, 2012). The biggest obstacle for large-scale application of CCS in IGCC plants is the loss in electric efficiency, which typically amounts to 5–15% (Rubin et al., 2007). Therefore, the application of the CCS in IGCC plants forms a challenge in pursuit of commercial application of CO_2 capture and storage (Carbo, 2009).

Most of the studies related to IGCC with CCS are referred to pre-combustion systems. In those systems, feed is gasified to produce syngas, and the carbon monoxide produced in this process is converted to carbon dioxide by the water-gas shift reaction. CO_2 is then separated from the syngas before syngas combustion. Other pollutant gases can also be removed before combustion, resulting in a minimum emission of pollutants. The resulting hydrogen-rich syngas is subsequently used in a combined cycle power plant with high thermodynamic efficiency.

Among the biggest and more advanced projects related to IGCC plants with CCS are the ZeroGen Project, the GreenGen Project, and the Kemper County Project. The ZeroGen Project might have been the world's first commercial-scale IGCC power plant to incorporate CCS capability. Mitshubishi Engineering would serve as the exclusive manufacturer, supplier, and builder of the IGCC facility, including CCS systems. The 530 MW plant was scheduled to enter operation in 2015. However, it has since been canceled as a large-scale integrated project and is now considered a storage-only initiative (Garnett et al., 2014).

According to the ZeroGen project promoters, the IGCC facility was designed to take advantage of opportunities to produce by-products with the potential for direct sale into existing markets, or which have the opportunity for beneficial reuse. The technology selected for the ZeroGen IGCC facility was the physical solvent–based Selexol™ process.

The mentioned ZeroGen study also contemplated an important modification affecting the solid by-products produced. Thus, the power plant would convert nearly all the ash in the coal feed into a non-leachable, extremely low carbon, environmentally inert glassy and granular slag. ZeroGen investigated the use of the slag in a number of beneficial use applications. One potential application is to use the slag as fill material in an adjacent coal mine, as it is environmentally inert and a structurally strong material. Another application for the slag is as an aggregate–type material in road bitumen surfacing materials, thereby reducing the amount of aggregate. As it was already presented in section 4.1, IGCC slag has already been used successfully in similar applications for many years.

GreenGen Project, initiated by China Huaneng Group (CHNG) in 2004, aimed to research, develop, and demonstrate a coal-based power generation system without pollutants and CO_2 emissions. GreenGen Project is similar in key technologies, development process, objectives, tasks, etc. to some other plants or projects in the world, such as ZeroGen in Australia.

GreenGen is being carried out in three phases. In Phase I, a 250 MW IGCC demonstration power station with proprietary technologies was constructed. In Phase II (currently underway), the key technologies involved in GreenGen will be further researched, developed, and demonstrated. Examples of key technologies include hydrogen production from coal gasification, the separation of H_2 and CO_2 (i.e., pre-combustion CO_2 capture), fuel cell power generation, and carbon capture, utilization, and storage. In Phase III, the plan is to build a 400 MW GreenGen demonstration project that will include full integration of key technologies, realizing high-efficiency coal utilization with near-zero emissions (Shisen, 2014).

GreenGen officially started to construct the Tianjin IGCC Demonstration Power Plant in July 2009 and was completed by September 2012. In November 2014, the plant successfully passed the standard test of 72 hours of continuous operation with another 24 hours of operation at full load.

In order to develop carbon capture, CHNG is developing a pilot-scale system that will draw about 7% of the syngas from the GreenGen IGCC demonstration power station, shift CO and H_2O to CO_2 and H_2, and then separate the CO_2 from the H_2 after desulfurization (Shisen, 2014).

With regard to the process by-products, the GreenGen flow sheet describes the production of two types of marketable products: ash and slag, and sulfur. The project contemplates the use of cyclones and ceramic filters to remove the dust, MDEA process for CO_2 capture, and LO-CAT technology (the LO-CAT process is a patented, wet scrubbing, liquid redox system that uses a chelated-iron solution to convert H_2S to elemental sulfur) to reduce SO_2 emission to 1.4 mg/Nm^3 and recover 23 tons of sulfur per year (Zheng, 2009).

The IGCC power project in Kemper County (582 MW: 3.0 Mt of CO_2 captured annually) uses Transport Reactor Integrated Gasification (TRIG) technology, which was developed by the Department of Energy, Southern Company and KBR at the

Power Systems Development Facility (PSDF) in Wilsonville, Alabama. TRIG technology is designed to work efficiently with lower-rank coals, such as Mississippi lignite. The Kemper County IGCC Project is a scale-up of a test plant already in operation at the Power Systems Development Facility (PSDF). The TRIG process was developed at the PSDF, a flexible test center sponsored by the US Department of Energy and operated by Southern Company Services. The gasification process features the transport gasifier, a dry-feed, non-slagging fluidized-bed gasifier, which operates at lower temperatures than other commercially available coal gasifiers.

The test unit at the PSDF proved easy to operate and control, achieving more than 15,600 hours of gasification. The gasifier successfully gasified high-moisture Mississippi lignite for more than 2300 hours of operation. On lignite, the transport gasifier operated smoothly over a range of conditions, confirming the gasifier design for Kemper County. Once operational, the Kemper Project will be a first-of-a-kind electricity plant to employ gasification and carbon capture technologies at this scale. The Kemper power station is scheduled to operate in IGCC mode in the end of half of 2016.

The Kemper County plant is designed for 65% capture of the CO_2 produced using the Selexol process that can operate selectively to recover H_2S and CO_2 as separate streams, so that the H_2S can be sent to a wet sulfuric acid unit for conversion to sulfuric acid (Haldor Topsoe's wet sulfuric acid) while, at the same time, the CO_2 can be prepared for carbon storage. This capture rate will result in emissions equivalent to 360 kg CO_2/MWh. The captured CO_2 will be used for enhanced oil recovery (around 3,400,000 tonnes per year).

Some data may be found regarding other Kemper County IGCC expected by-products as sulfuric acid (135,000–150,000 tonnes per year) and ammonia (19,000–22,000 tonnes/year).

As previously mentioned, when a comparison is made between conventional IGCC and IGCC with CCS, some differences can be expected in the nature and quantity of the by-products obtained. One can find in the literature many simulation techno-economic studies regarding different IGCC with CCS systems. The comparisons are usually established in terms of plant efficiencies and electricity generation costs associated with both technologies. Some of the studies give information on the residues produced, but most do not (Majoumerd et al., 2012; Huang et al., 2008). Among those comparative studies giving some data on the solids produced, the work from Mondol et al. (2009) can be mentioned. In this study, the techno-economic analysis of four near-zero emissions novel IGCC processes proposed for low-rank brown coal have been presented. The performance of the proposed plants was compared with two conventional IGCC plants with and without CO_2 capture. The aims of the proposed IGCC plants was to upgrade low-rank coals into three useful products: (a) hydrogen-rich fuel gas; (b) a highly concentrated CO_2 purge gas stream, ready for transportation to sequestration or chemical fixation; and (c) a pre-calcinated feed for a cement kiln consisting of CaO, coal ash and other required additional minerals. According to the authors, in the four new IGCC processes more ash is produced than in the two conventional IGCC systems. Moreover, the study shows that the IGCC + CCS plant produces a higher ash quantity than the IGCC plant without CCS.

Polygeneration is an option also explored by different authors for future IGCC developments (Cormos, 2012). But the case studies give no information related to by-products obtained. In general, the polygeneration simulations described in the literature tend not to consider this problem.

14.7 Summary

IGCC is a clean technology for power generation. The amount and toxicity of by-products produced by IGCC are expected to be much lower than those from conventional power plants. IGCC residues are related to the impurities of the syngas. The most abundant by-products are slag and sulfur, and to a lesser extent ash and ammonia. According to the US EPA (2006), a 500 MW net capacity IGCC plant produces 20.4–29.5 kg of slag per MWh and 98.9 kg of slag per MWh. Slag production is a function of fuel ash content; therefore coal produces much more slag than petroleum coke.

In many cases, gasification plants are able to make the by-products reusable as a raw material in other industries, depending on the plant's ability to market and sell them, as well as local regulations. When utilization of the by-products is not possible, they must be dealt with as waste materials and disposed of properly.

Slag is discharged from the bottom of the gasifier, and is formed when the mineral content of coal is melted. The main components of IGCC slag are SiO_2 and Al_2O_3 followed by CaO and Fe_2O_3 but the chemical composition varies widely, reflecting the variability of the composition of the feedstock. Slag is a non-leachable residue and it is typically marketable for asphaltic applications, roads construction, or aggregate.

Fly ash is recovered in the particulate removal system and is either recycled to the gasifier or landfilled. The ash has a very fine grain size and contains a high proportion of an amorphous Al–Si glass and unusual reducing and fine crystalline species condensed from reducing vapor species in the cooling flue gas. Most of the fly ash is used in various structural applications: use in cement and concrete production, followed by structural fills and waste stabilization.

After the acid gas cleaning stage, IGCC plants have a sulfur recovery plant. Depending on the gas cleanup system used, sulfur or sulfuric acid is produced from the hydrogen sulfide produced in the syngas cleaning stage. Both are valuable by-products.

In addition, in some IGCC plants, ammonia can be recovered, to be used basically in fertilizer production. The principle technical barriers for IGCC by-products utilization include specifications and materials characterization, product demonstration and commercialization, user-related factors, institutional and legal barriers, and rigid regulations.

Effective management of gasification by-products is a significant factor in determining the environmental acceptability and economics of future gasification technologies. In many cases, gasification plants are able to market the by-products reusable.

14.8 Sources and further information

American Coal Ash Association (ACAA), available in www.acaa-usa.org

Basel Convention, available in www.basel.int

Cluster for Clean Coal Technologies (CCT) and Carbon Capture and Storage (CCS) Technologies for the Indian Thermal Power Sector, available in http://carbon-cap-cleantech.com

Coal Combustion Byproducts Recycling Consortium (CBRC), available in www.wvcoal.com/

Coal Online, available in www.coalonline.org

Electric Power Research Institute, available in www.epri.com

H_2-IGCC website, available in http://www.h2-igcc.eu

IEA Clean Coal Centre (CCC), available in www.iea-coal.org.uk

Office of Fossil Energy's National Energy Technology Laboratory (NETL), available in http://www.netl.doe.gov

Power magazine, available in www.powermag.com

SFA Pacific Inc., available in www.sfapacific.com

The Gasification Technologies council, available in http://www.gasification.org

University of Kentucky Center for Applied Energy Research, available in www.caer.uky.edu/

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