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Chapter 8

# Emissions of Inorganic Trace Pollutants from Coal Power Generation

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Additional information is available at the end of the chapter

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**Abstract**

Coal-fired power plants are a major source of emissions for a number of air pollutants including $SO_2$, NOx, particulate matter (PM), HCl, HF, Hg, and so on. Hazardous air pollutants such as As, Be, Cd, Cr, Pb, Mn, Ni, Se, and other metals are integral components of fine PM that are also emitted directly from coal-fired power plants. The potential problem of coal-fired power plants associated to the emissions of air pollutants can be treated by flue gas desulphurisation (FGDs), as the sulphur (S) will be retained in the FGD-gypsum ($CaSO_4.2H_2O$), and eventually be disposed. Further, FGD chemistry (alkaline sorbent) allows the capture of many pollutants other than sulphur, such as F, As, B, Cl, Se or Hg, in a gaseous form and/or as PM. In this chapter, the current position of coal power generation and the generation of inorganic trace pollutants derived from it are presented and discussed. The partitioning, speciation, and fate of inorganic trace pollutants during pulverised coal combustion (PCC)-FGD are also reviewed.

**Keywords:** particulate matter, hazardous air pollutants, flue gas desulphurisation systems (FGD), partitioning, speciation

## 1. Introduction

Coal plays an essential role in our global energy scheme for power generation as most of the world's coal production is consumed mainly to generate electricity. However, coal is currently a target especially for Europe, where political and social opposition to coal is mounting as efforts intensify to limit $CO_2$ emissions. In the United States, coal industry also declined in 2017, and its trend toward long-term structural decline is all but sure to persist in 2018 [1] while in China concerns about their air quality and related health issues caused demand

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for coal to fall from 2014 to 2016 [2]. As coal consumption declines in most of developed countries, including those in Europe and the US, the future of coal is increasingly dependent on developing countries.

Most European power generation producers have ruled out the construction of new coal plants, and utilisation at existing coal-fired power plants in Europe is decreasing as renewable energy sources expand [2]. The demand for coal in China, on the other hand, the primary driver of coal since the 2000s, has just about peaked and is probably to begin declining in the early 2020s [2]. Instead, Chinese government is promoting a shift from coal to less polluting sources, including renewables, in order to address the country's air quality. However, under this entire scenario, coal demand will either continue to grow modestly or remain stable as coal is the world's most abundant energy resource. There are 1,139,331 million tonnes of proven coal reserves worldwide, sufficient to meet 153 years of global production. In comparison, proven oil and natural gas reserves are equivalent to around 50 and 53 years, respectively, at 2016 production levels [3]. Therefore, despite the decline in coal production and consumption, coal is and will be a reliable source for power generation.

Coal-fired power plants are a major source of emissions for a number of air pollutants including $SO_2$, NOx, particulate matter (PM), HCl, HF, and Hg among and solid residues, mostly ashes [4]. The potential problem of coal-fired power plants associated to the emissions of air pollutants can be treated by flue gas desulphurisation (FGDs), as the S will be retained in the $CaSO_4.2H_2O$, and eventually be disposed. Further, FGD chemistry (alkaline sorbent) allows the capture of many pollutants other than sulphur, such as F, As, B, Cl, Se or Hg [4–6], in a gaseous form and/or as PM [4].

Commercial power generation wet FGD system uses calcite ($CaCO_3$) from limestone, slaked lime ($Ca(OH)_2$), or a mixture of $Ca(OH)_2$ and alkaline FA sorbents, which react with $SO_2$ to form a Ca-S compound [7]. Although the wet limestone based process is by far the most widely FGD employed because of its high desulphurisation performance, reliability, and efficiency [7], the use of slaked lime has also been proposed since lime shows over limestone higher pH values and better reactivity defined as capacity to provide alkalinity.

In this chapter, we explore the current position of coal power generation as a source of inorganic trace pollutants emissions. Firstly, the current situation of coal combustion for energy production and the generation of inorganic trace pollutants are presented and discussed. Secondly, the classification of trace elements according to their affinities in coal and their partitioning and behaviour during combustion is evaluated. Thirdly, the partitioning, speciation, and fate of inorganic during PCC-FGD are reviewed.

## 2. Power generation from coal

### 2.1. Coal

Coal is defined by the American Society for Testing and Materials [8] as 'brown to black combustible sedimentary rock composed principally of consolidated and chemically altered plant'. Over 90% of the coal consumed in Europe, the US, and other countries is used to

generate electricity. Coal power is also used as a basic industry source for making steel, cement and paper, among other industries.

Coal-fired power plants currently fuel 40% of global electricity, and, in some countries, coal fuels a higher percentage of electricity [9]. Owing to the Paris climate agreement, in Europe, the use of coal for power generation retreated for the fifth successive year in 2017. The European Power Sector 2017 reported that coal's share of Europe's total power generation fell to 20% last year, while the share from renewables increased to 30%. Nevertheless, Europe's progress in reducing the use of carbon-intensive power is gradual and uneven.

In 2017, coal production in the US was higher than in 2016, which was attributed in part to the bankruptcy-caused restructuring of several major coal producers, which resulted in lower production costs [10]. China produced 3.45 billion tonnes of raw coal in 2017, a year-on-year rise of 3.2%, showed data released by the National Bureau of Statistics on January 18 [11].

However, the role of coal in power generation is set to continue. Coal currently fuels 40% of the world's electricity and is forecast to continue to supply a strategic share over the next three decades [12]. There are 1,139,331 million tonnes of proven coal reserves worldwide, sufficient to meet 153 years of global production (**Table 1**). Total proven coal reserves are shown for anthracite and bituminous (including brown coal) and sub-bituminous and lignite. In comparison, proven oil and natural gas reserves are equivalent to around 50 and 53 years, respectively, at end 2016 production levels [3].

| Million tonnes | Anthracite and bituminous | Sub-bituminous and lignite | Total | Share of total | R/P ratio |
|---|---|---|---|---|---|
| Total North America | 226,906 | 32,469 | 259,375 | 23% | 356 |
| Total S. & Cent. America | 8943 | 5073 | 14,016 | 1.2% | 138 |
| Total Europe & Eurasia | 153,283 | 168,841 | 322,124 | 28% | 284 |
| Total Middle East & Africa | 14,354 | 66 | 14,420 | 1.3% | 54 |
| Total Asia Pacific | 412,728 | 116,668 | 529,396 | 46% | 102 |
| Total World | 816,214 | 323,117 | 1,139,331 | 100% | 153 |

**Table 1.** Proven coal reserves worldwide.

## 2.2. Coal combustion

Pulverised coal combustion (PCC) is the most widely technology to produce energy from coal. In this process, coal is pulverised by coal mills in order to be ground to fineness (such that 70–80%). The oxidant, an air stream, is injected into the coal mills to form an air-coal mixture, which is carried by conveyors to feed individually each burner in the boiler. The secondary/extra air necessary for the combustion process is injected into the burners via secondary and tertiary air nozzles to initiate combustion, depending on the coal rank, at temperatures from 1300 to 1700°C [13]. The generated heat from the combustion process is handed to water tubes placed in the boiler walls, so as the water in it turns into a steam (34–44 bars and 540°C). This

steam powers a high vapour pressure turbine (38–51 bars and 3000 rpm) and later is recirculated and expanded to power medium and low vapour pressure turbines. After the recirculation, the steam is delivered in a condenser where it is cooled and sent to the boiler to heat it again. Finally, the combustion gases are used to overheat the water from the economiser and the air used in combustion (**Figure 1**).

Coal combustion by-products (CCBs) are the materials produced from the combustion of coal for the production of electricity. CCBs primarily include: bottom ash (BA) and/or boiler slag (BS), fly ash (FA), and flue gas desulphurisation (FGD)-gypsum. The coarse fraction of ashes, BA or BS, is generally removed from the bottom of the boiler while the smallest fraction of these, FAs, can either be captured, depending on the depuration train technology, in an electrostatic precipitator (ESP) or fabric filter (FF) [5, 6]. ESPs and FFs operate with a very high efficiency (>99%); however, a small fraction of FAs may escape from the control and reach the FGD system (4) where S will be retained in the $CaSO_4.2H_2O$, and eventually be disposed. Further, FGD chemistry (alkaline sorbent) allows the capture of many pollutants other than S, such as F, As, B, Cl, Se or Hg [4–6], in a gaseous form and/or as PM (**Figure 1**).

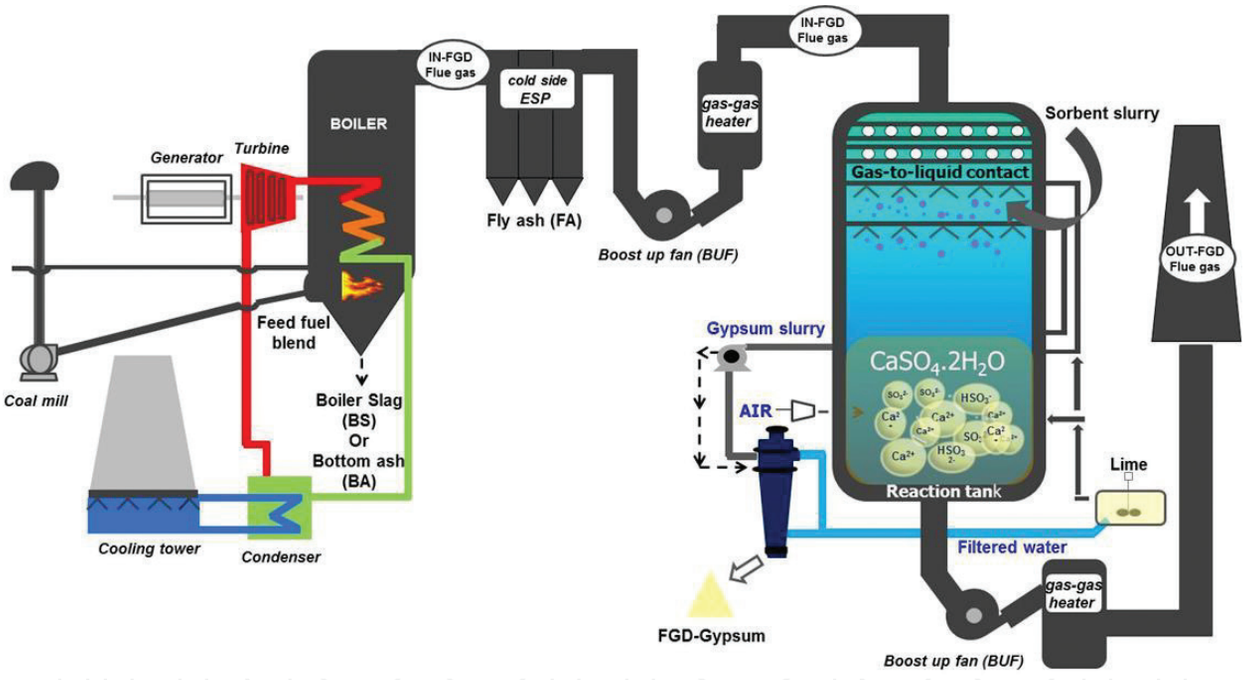



**Figure 1.** Configuration of a PCC plant equipped with an FGD system.

There are alternatives other than PCC for coal power generation. Fluidised bed combustion (FBC) is a technology in which, coal or any solid fuel is suspended on jets of air during the combustion process, which allows for a more efficient mixing of gas and solids and results in more efficient heat transfer. One primary advantage of FBC technology is that the combustion reaction can take place at lower temperatures, which reduces the formation of toxic nitrous oxide ($N_2O$). In addition, $SO_2$ can be more cheaply and easily removed during combustion than using FGD technology. Lastly, FBC can support the addition of other solid fuels such as biomass into the reaction mixture along with coal [14]. Currently, three different types of FBC are available, the circulating FBC (CFBC), the bubbling FBC (BFBC), and pressurised FBC [7] (**Table 2**).

| | Principle | Fluidisation | $SO_2$ retention | NOx emissions |
|---|---|---|---|---|
| Circulating FBC | Addition of limestone during combustion to react with $SO_2$ | 3–9 m/s | 98% | 120 mg/Nm$^3$ |
| Bubbling FBC | Addition of limestone during combustion to react with $SO_2$ | 1–3 m/s | | 200–300 mg/Nm$^3$ |
| Pressurised FBC | Air is pressurised using a gas turbine compressor | | SOx level of approximately 5 ppm through in-bed desulphurisation | NOx level of approximately 100 ppm |

FBC: fluidised bed combustion.

**Table 2.** FBC technologies.

## 2.3. Co-combustion

Co-combustion means simultaneous combustion of two or more fuels in the same plant for energy production. The current and future energy policy aims at increasing the share of renewable energy in worlds energy supply. One possibility to enhance energy production by renewable sources within a short term is co-combustion [15].

Co-combustion can be carried out in different ways according to the operating conditions of the existing power plant. Accordingly, co-combustion can be carried out by using (1) a small amount (a few percent of total fuel power) of co-combustion matter fired together with coal in a boiler, originally designed for coal; (2) a small amount of fuel with a high heating value fired together with a fuel having a low heating value such as sewage sludge that needs thermal support to attain a desired combustion temperature; and by (3) spontaneous use of co-combustion with fuels in any ratio, depending on price, availability and local supply conditions [16].

The most common co-combustion matters fired together with coal can be petroleum coke, sewage sludge, and biomass. Petroleum coke is a carbon-rich solid that emerges as a by-product of crude oil refining and other 'cracking' processes, in which complex organic molecules such as heavy hydrocarbons are broken down into simpler and more valuable lighter petroleum products. Depending on the process of production, there are three types of petroleum coke: delayed coking (93% of world production), fluid coke (6% of pet-coke production), and flexicoking (1% of pet-coke production) [17]. These three types of pet-coke have higher calorific values than coal and contain less volatile matter and ash (less than 1–2%); qualities that make petroleum coke an attractive alternative for power producers.

Sewage sludge, a type of bio-solid, is a by-product of wastewater treatment. In the context of new energy policies and legislation, the use of sewage sludge for power generation is promoted, not only by environmental considerations (sewage sludge is burned with zero net $CO_2$ emissions), but also by economic considerations due to the gain of reducing disposal charges [18].

Biomass represents a lot of various materials, either waste materials or special energetic plants. Fuels based on wood biomass (sawdust, shavings, chips, tree-bark) can also be used for the production of high-quality biofuels, such as wooden briquettes and pellets, or can be co-combusted with coal [19]. Although biomass co-firing is one of the most effective means of

reducing Green House Gas (GHG) emissions in PCC power plants [16], the chemical properties of biomass have implications for combustion quality and/or impacts on equipment when it is fed as co-matter [20].

### 2.4. Oxy-combustion

Oxyfuel combustion is one of the leading technologies considered for capturing $CO_2$ from power plants with carbon capture and storage (CCS) [21]. This involves the process of burning the fuel with nearly pure oxygen instead of air, which results in higher flame temperatures. For this reason, the mixture is diluted with a portion of the resulting flue gas composed primarily of $CO_2$.

The oxygen for oxy-fuel combustion is provided by two oxidiser streams: primary and secondary stream (**Figure 2**). The primary oxidiser stream supplies part of the oxygen necessary for combustion by carrying the pulverised coal into the wall firing burners placed in the oxy-boiler while the secondary oxidiser streams consists of oxygen that comes from the air separation unit (ASU) mixed with a portion of the recycled flue gas (FGR) to moderate flame temperatures and obtain a boiler heat transfer profile similar to that of air-firing in the case of retrofit. Depending on oxy-fuel combustion configuration, the secondary stream will constitute the equivalent to the secondary, tertiary, and overfire (if necessary) air flows (OFA) when oxygen has been added. Several options exist for the position where the secondary recycle stream is taken. As an example, at the largest oxy-PCC demonstration plant [22], the $CO_2$-rich FGR is divided into three oxidant streams: CB1, CB2, and CB3 (**Figure 2**), and it can also operate with an OFA system as part of an overall NOx reduction strategy by staging the combustion process. The OFA system normally reduces the oxygen availability early in the oxy-combustion process by reintroducing it later through ports located above the combustion zone (**Figure 2**).

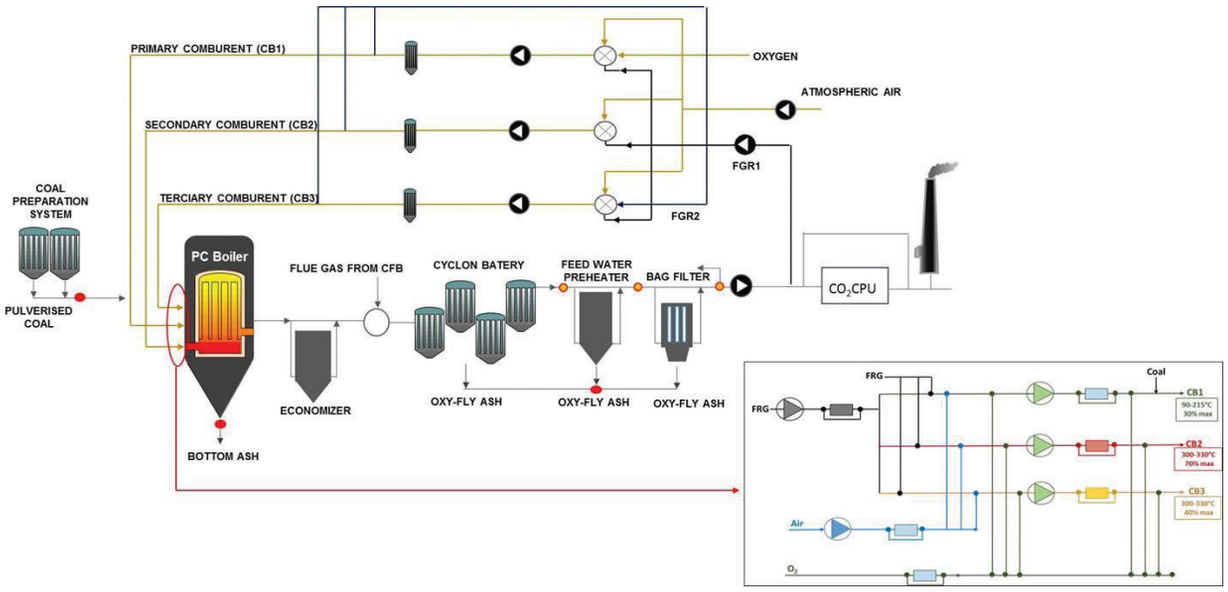



**Figure 2.** Configuration of the largest oxy-fuel demonstration plant [13].

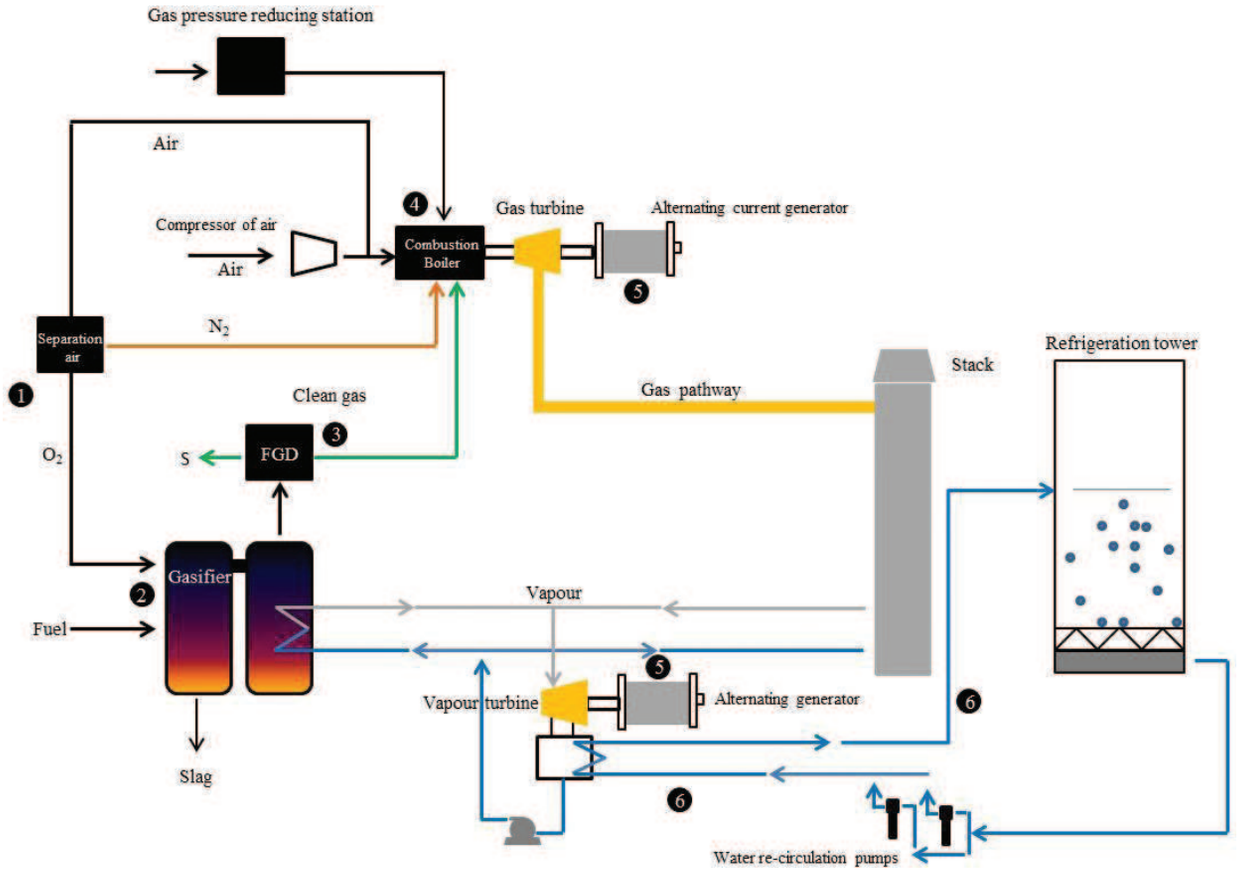



**Figure 3.** Configuration of a integrated gasification combined cycle (IGCC) power plant [3].

## 2.5. Gasification of coal

While the goal of coal combustion is to produce the maximum amount of heat possible by oxidising all the combustible material, coal gasification is a thermochemical process in which coal is converted into CO, $H_2$ and $CH_4$ synthesis gas (syngas) by means of the partial combustion with air or water vapour and low levels of $O_2$ [23]. Different technologies of coal gasification that are currently available are shown in **Table 3** [23]:

| | Principle | Temperature (°C) | Pressure (bar) |
|---|---|---|---|
| Fixed bed gasifier | Coal moves in counter current to the gas flow | 400–1100 | 10–100 |
| Fluidised bed gasifier | Gaseous agents are blown through a flow of solid particles to keep these in a state of suspension | 800–1050 | 10–25 |
| Entrained bed gasifier | Coal and gasifier agents flow in the same direction with velocities higher than the rest of gasifier | 1200–1600 | 25–40 |
| Integrated gasification in combined cycle (IGCC) | Use of the CO-and $H_2$-rich gaseous in a gaseous turbine and the use of the leftover heat in a vapour turbine | ~1500 | 25 |

**Table 3.** Coal gasification technologies.

Among the current technologies of coal gasification, integrated gasification combined cycle (IGCC) is the most common (**Figure 3**). The IGCC is characterised by the use of the CO-and $H_2$-rich gaseous stream resulting from the gasification, usually of coal and/or petroleum coke, in a gaseous turbine and the use of the leftover heat in a vapour turbine (**Figure 3**). The IGCC entails an initial fractionation of air (1) in the ASU. In this unit, cryogenic distillation separates $O_2$ from air by liquefying air at very low temperatures (−300°F). Ambient air is compressed in multiple stages with inter-stage cooling then further cooled with chilled water. Residual water vapour, carbon dioxide and atmospheric contaminants are removed in molecular sieve adsorbers. In the gasifier, (2) coal reacts with the $O_2$ and $H_2O$ stream to generate a syngas at high temperature (~1500°C, 25 bar) [24]. Heat in the gasifier liquefies the coal ashes and subsequently the molten ash is quenched and crushed at the bottom of the gasifiers before being dewatered for disposal. The syngas stream passes to the flue gas depuration train (3) in which $SO_2$ and other gaseous pollutants are removed from the gaseous stream. The cleaned gas is then burned in a combined cycle power generation unit (4). In this unit, the gaseous stream is expanded in a gaseous turbine, whereas the leftover heat is expanded in the vapour turbine both connected to generators of electric energy (5). The water vapour condensates as a consequence of the heat exchange with water from the refrigeration tower (6).

The formation of NOx in the combustion chamber of the gas turbine is suppressed by saturation of the fuel gas with steam prior to combustion and by dilution with $N_2$ from the air separation unit.

## 3. Behaviour of trace elements during coal combustion

Trace elements are introduced in PCC from coal or co-combustion material. According to their different contents, these elements can be divided into (1) major elements (C, H, O, N, S) whose content is >1000 ppm; (2) minor elements which include coal mineral matters (Si, Al, Ca, Mg, K, Na, Fe, Mn, Ti) and halogens (F, Cl, Br, I), with concentrations between 100 and 1000 ppm; and (3) trace elements with concentration < 100 ppm. It is generally accepted that trace elements combination and contents differ from one coal to another due to the different coalification processes [25–27]. The correlation between the organic content or the different mineral phases in coal with the content of major, minor, and trace elements allows the establishment of trace elements affinities in coal as follows [28]:

**1.** Elements with inorganic affinity:

- ***Clays and feldspars*** (Al, K, Mg, Na, P, Ti, Li, Cr, Ni, Cu, Ga, Rb, V, Sr., Y, Sn, Cs, Ba, Ta, Pb, Bi, Th, U, Zr, and REEs).
- ***Sulphide minerals*** (S, Fe, Ni, Co, Cu, Zn, As, Se, Mo, Cd, Sb, Hg, W, Pb, and Tl).
- ***Carbonate minerals*** (C, Ca, Mn, and Co).
- ***Sulphate species*** (S, Ca, Fe, Ba).

- ***Heavy minerals*** (B, Ti, Th, and Zr).
- ***Several mineral phases*** (Co and W) in carbonates and sulphides; Ni, Cu, and Pb (clays and sulphides).

**2.** Elements with total or partial organic affinity (C, N, S, Be, B, Ge, V, and W).

Studies on the fate of trace elements during combustion have shown that their volatility depends on their affinities and on the physical changes and chemical reactions of these elements with S or other volatile elements during combustion [29–31]. **Figure 4** shows the behaviour and fate of elements in accordance with their volatile behaviour at the boiler and at the ESP, respectively, during combustion according to Córdoba et al. [32, 33]. This classification of the volatile behaviour of trace elements during combustion is in agreement with most of the literature [34–36], except for some specific elements, where elements are classified into three groups (**Figure 4**).

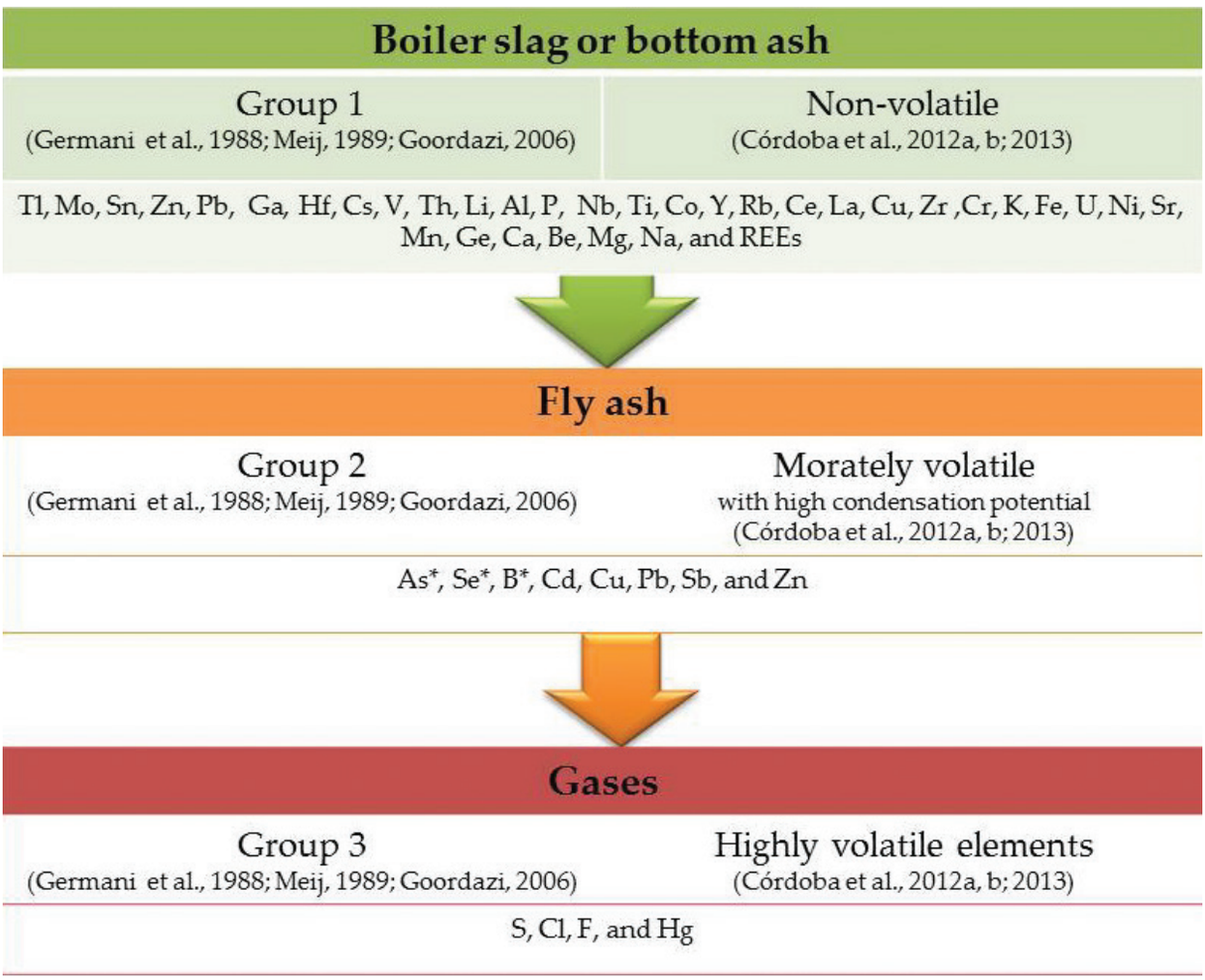



**Figure 4.** Behaviour of trace elements during coal combustion.

Elements classified as non-volatile and moderately volatile with condensation potential, respectively, from Córdoba et al. [32, 33] are in line with Group 1 and 2 elements from the abovementioned literature. However, elements such as As, Se and especially B can also be classified as highly volatile, which would correspond to Group 3.

The partitioning and fate of trace elements during combustion, discussed above, may be different by the use of secondary fuels. As discussed in Section 2.2, the use of co-matters such as petroleum coke, sewage sludge and/or biomass may have implications for combustion quality and/or modify the chemical environment of gaseous pollutants. Co-firing petroleum coke, for instance, may modify the chemical environment of Cl and S because of the resultant high concentrations of HCl and SOx, respectively, in the flue gas. An increase in the HCl concentration favours the formation of gaseous species, whereas increasing concentration of $SO_2$ in the gas composition enhances the formation of sulphate condensed species [37]. In addition, the heavy metals contents of the ash are generally high with Vanadium (V) and Nickel (Ni) contents ranging from 500 to 3000 ppm, although pet-cokes with >10,000 ppm V can also be found [38]. Molybdenum (Mo) can also be present in relatively high concentrations in petroleum cokes. The organic affinity of Mo, V and Ni in petroleum coke favours their volatility during pulverised coal combustion (PCC) and later condensation on the finest particles of FAs.

The main drawback of the sewage sludge combustion, on the other hand, is mostly related to high NOx emissions. The level of some toxic heavy metals and Cl in the raw material may also increase the emissions of hazardous pollutants (metals and dioxins).

### 3.1. Elements concentrated in coal combustion solid residues

There are some elements that either tend to get concentrated on the coarse residues BS or BA, partition equally between BS or BA and FA particulates, or to get enriched on the fine-grained particles, PM, which may escape particulate control systems.

BA is a granular material removed from the bottom of dry boilers, which is much coarser than FA though also formed during the combustion of coal. BS, on the other hand, is a vitreous grained material deriving from coal combustion in boilers at temperatures of 1500–1700°C, followed by wet ash removal of wet bottom furnaces [39].

FA is a fine powder made up of spherical high vitreous particles with Fe-oxides and Al-Si species, and irregular unburned coal and ash particles. The contents of principal oxides are usually in a descending order: $SiO_2 > Al_2O_3 > Fe_2O_3 > CaO > MgO > K_2O$. Fly ash also contains many trace elements, some of which are of environmental concern. Commonly, elements such as Cr, Pb, Ni, Ba, Sr., V and Zn are present in significant quantities. Coal aluminous-silicate impurities, mainly clays, with much lower proportion of feldspars, melt during combustion and rapidly shape themselves into spherical droplets [40]. The chemical composition of FAs may differ depending on the technology of combustion but especially on the characteristics of the feed coal. While coal combustion FA is constituted by an aluminous-silicate glass, with Ca, Fe, Na, K, Ti, and Mn impurities, and variable amounts of quartz, mullite, lime, haematite, magnetite, gypsum and feldspars, IGCC FA is characterised by a predominant Al-Si glass

matrix and variety of fine crystalline reduced species (mostly metal sulphides) as a consequence of the low $pO_2$ at which fuel is burned [41].

### 3.2. Elements emitted in the flue gas

As aforementioned, most of the trace metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Sb, Tl, V, and Zn) may be released during combustion, emitted with a different form of occurrence (e.g. from sulphide in coal to oxides and chlorides in flue gas), and/or condense onto the surface of smaller particles in flue-gas streams. Therefore, most of trace metals are retained in particulate control devices and only specific high volatile metals may escape from ESP and reach FGD systems in a gaseous mode of occurrence. In this regard, FGD chemistry also allows the capture of many pollutants other than S, such as F, As, B, Cl, Se or Hg [41–46] both in a gaseous form and/or as PM. Thus, importantly, FGD systems can also be considered as a measure for the PM abatement emissions.

The abatement of NOx (NO, $NO_2$, and $N_2O$) emissions is based on the De-nitrification (DeNOx) process that aims at reducing NOx into $N_2$ and $H_2O$. The emission control systems that are in use to carry out the DeNOx process are: selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR).

## 4. Chemistry, partitioning and fate of inorganic trace pollutants during PCC-FGD

According to the foregoing discussion, trace elements during combustion may get concentrated on the coarse residues BS or BA, partition equally between BS or BA and FA particulates, emitted with a different form of occurrence (e.g. from sulphide in coal to oxides and chlorides in flue gas), and/or condense onto the surface of smaller particles in flue-gas streams. Either way, most of trace metals are retained in particulate control devices and only specific high volatile metals may escape from ESP and reach FGD systems in a gaseous mode of occurrence.

In the FGD systems, under operational conditions of water re-circulation, inorganic trace pollutants in FGD waters may reach equilibrium and a subsequent saturation in the water stream after a number of water re-circulations in the scrubber. The gradual increase in the concentration of inorganic trace pollutants from the sub-saturation to equilibrium and/or saturation because of continuous water re-circulation in the scrubber, accounts for enriched inorganic trace pollutants in the re-circulated water. Other elements retained in high proportions by gypsum sludge and/or FGD-gypsum do not pose this problem because they are extracted from the system by the gypsum by-product that is used for different applications or for landfilling [4]. The general trends of the inorganic trace pollutants in through the PCC to FGD are reported below.

*Arsenic* is present as As-sulphides species in raw coals and it is mostly released as $As_2O_{3\,(g)}$ [47] during PCC. In the boiler, gaseous $As_2O_3$ can be chemisorbed on the FA surface and/or remain in the gas phase. The chemisorption of $As_2O_3$ on FAs, which will depend on the

temperature and gas composition, may occur via reaction with CaO to form $Ca_3AsO_4$. The small fraction of FAs in the flue gas that escapes from the control would be the main route by which $Ca_3AsO_4$-FA would enter the FGD. Accordingly, $Ca_3AsO_4$-FA would pass through the sprayers and dissolve to $AsO_4^{3-}$ in the aqueous phase of the sorbent slurry. If $As_2O_3$ remains in the gas phase during the post-combustion atmosphere, a proportion of gaseous $As_2O_3$ could enter the FGD either by reacting with moisture in the flue gas to form $H_3AsO_4$ and condense in the scrubber as the flue gas undergoes a rapid quench (50–60°C), or by diffusing through the gas to the aqueous phase of the sorbent slurry where $As_2O_3$ would get hydrated to $H_3AsO_4$. Depending on the operating FGD conditions, As partitioning and fate may differ. Generally, As is mostly partitioned in the FGD-gypsum with values comprised in the range 90–99%.

*Boron* is largely organically associated in coals although a fraction can also be associated to aluminium silicates. Boron is generally released as $H_3BO_3$ and $HBO_2$ [48] during PCC. Since the chemisorption mechanism of $H_3BO_3$ and $HBO_2$ on FAs has not been documented, the main route by which $H_3BO_3$ can reach the FGD is with the incoming FGD flue gas. In the FGD gas-to-liquid contact zone, $H_3BO_3$ may diffuse through the gas to the aqueous phase of the sorbent slurry when flue gas passes through the sprayers and remain in the FGD reaction tank. Depending on the operating FGD conditions, B partitioning and fate may differ but in general, B is removed in the aqueous effluent (filtered water) and only a fraction of B may remain in the flue gases. However, since B concentration in FAs is relatively high and largely leachable, we can assume that FA containing B species such as $CaHBO_3$ can also contribute to increase B content in the in the FGD-gypsum [49].

*Selenium* casually present as selenide in coal is volatilised as elemental $Se^0$ and $SeO_2$. In the boiler, gaseous $SeO_2$ can be chemisorbed on the FA surface to form the stable $CaSeO_3$. The main route by which Se would reach the FGD is the small fraction of FAs escapes from the control and reaches the FGD. In such a case, Se chemisorbed in FAs could dissolve in the aqueous phase of the lime slurry to form an array of aqueous Se-complexes such as selenosulphate ($SeSO_3^{2-}$), selenotrithionate ($Se(SO_3)_2^{2-}$) and selenopentathionate ($Se(S_2O_3)_2^{2-}$) by reaction with polyoxysulphur donors [50]. Selenium can either be removed in the aqueous effluent (filtered water) or partitioned in the FGD-gypsum. However, a small fraction of Se can remain in the flue gases and be emitted into the atmosphere.

*Mercury* occurs in coals in mineral sulphide impurities, although other forms of occurrence, such as Hg-Se species, have been described [51]. During combustion, Hg is released as elemental Hg ($Hg^0$). During post-combustion, and with decreasing temperature, $Hg^0_{(g)}$ may remain as a monatomic species or may oxidise to $Hg_2^{2+}$ and $Hg^{2+}$ compounds. The reaction of $Hg^0_{(g)}$ with $HCl_{(g)}$ or $Cl_{2(g)}$ to form $HgCl_{2(g)}$ is generally considered to be the dominant Hg transformation mechanism in coal combustion flue gas [51]. The main route by which gaseous Hg can reach the FGD is with the incoming FGD flue gas. Gaseous compounds of $Hg^{2+}$ are generally water-soluble and can dissolve in the aqueous phase of the sorbent slurry of wet FGD systems [52]. However, gaseous $Hg^0$ is insoluble in water and therefore does not dissolve. It is speculated that some of the absorbed Hg ($HgCl_2$) can be converted back to $Hg^0$ and re-emitted, S (IV) being the main precursor of $Hg^0$ re-emission [53–55].

Coal *chlorine* is released primarily as HCl during combustion in the high temperature zone of a boiler [56]; as the combustion gases cool (430–475°C), a proportion of HCl can partially be oxidised to $Cl_2$. The main route by which HCl can reach the FGD is with the incoming FGD flue gas. In the FGD gas-to-liquid contact zone, HCl may diffuse through the gas to the aqueous phase of the sorbent slurry when flue gas passes through the sprayers and react with cations such as $Ca^{2+}$, $Na^{+}$, $Mg^{2+}$, etc. to form highly soluble salts. Generally, Cl in FGD systems is removed in the aqueous effluent (filtered water) and only a fraction may remain in the flue gases.

*Fluorine* is released as HF during combustion. The main route by which gaseous HF can reach the FGD is with the incoming FGD flue gas. Depending on the operating FGD conditions, F partitioning and fate may differ. HF contained in the flue gas may be dissolved in the aqueous phase of the sprayed droplets of limestone slurry, if a limestone-based FGD, giving rise to the formation of $CaF_2$. However, in the presence of aluminium compounds, HF may also react with limestone to form Al-F compounds, typically represented by $CaAlF_3(OH)_2$-$CaF_2$ [57]. These compounds can coat the surfaces of the limestone particles and consequently cause a decrease the reactivity of limestone [58, 59]. In addition, if F is partitioned in the FGD-gypsum, it can play a crucial role in the leaching potential of the FGD gypsum end-product as a consequence of the precipitation of F solid species on FGD-gypsum surface. In order to avoid this, the use of additives has been proposed as measure for the optimisation of the $SO_2$ removal efficiency and for reducing the precipitation of F solid species, respectively.

*Heavy metals such Zn, Cu, Cr, Ni, Mn and U* tend to form highly soluble aqueous complexes with $SO_4^{2-}$. Depending on the operating FGD conditions, their partitioning and fate may differ. Acidic conditions, for example, contribute to the stabilisation of metals in solution, therefore, in the aqueous effluent. As a result, very low amounts of heavy metals are found in the leachates of the FGD-gypsum. Alkaline conditions, however, contribute to the precipitation of these elements in the FGD-gypsum.

## 5. Conclusions

Coal is currently a target to accomplish with the Paris climate agreement for both countries and companies. As a consequence, in 2016, world coal production fell by 6.2%, the largest decline on record. However, coal is the world's most abundant energy resource, meaning that despite the decline in coal production and consumption, coal is and will be a reliable source for power generation. The most negative consequence of coal combustion is the emissions of a number of air pollutants including $SO_2$, NOx, PM, HCl, HF, Hg and As, Be, Cd, Cr, Pb, Mn, Ni, and Se, integral components of fine PM. A number of studies have shown that FGD chemistry allows also the capture of many pollutants other than S, such as F, As, B, Cl, Se or Hg both in a gaseous form and/or as PM. Most of specialised literature reports that most of trace elements in FGD systems are removed in the aqueous effluent (filtered water) and only a fraction of a few remain in the flue gases (such as B, Hg, and Se). According to these studies, it can be concluded that wet limestone FGD systems reach high retention efficiencies for trace elements (>90%). However, it is also important to note that the retention efficiency

of FGD system for trace elements may be reduced because of the emission of fly dust in evaporate droplets saturated with gypsum. In view of the discussion exposed in the review, we can conclude that the emissions of inorganic trace pollutants from coal power generation depend on each facility including the flue gas depuration train as well as the operating conditions associated to it.

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