

Chapter 19

Risk Assessment and Control of Emissions from Ironmaking

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Abstract Processing of raw materials to valuable products results in the formation of undesired compounds due to feedstock impurities and process inefficiencies. During the iron and steelmaking process, iron ore is converted to iron and steel at high temperatures using carbon energy sources. As the iron ore and carbon sources contain minor and trace element impurities and the combustion of carbon is incomplete, certain undesirable compounds may be formed that can be detrimental if emitted to the environment. These emissions can pose significant risks to humans and to the health of the ecosystem. This chapter outlines the various emissions associated with ironmaking, the risks these emissions pose to the environment and the technologies employed to minimise or eradicate the pollutants.

19.1 Introduction

The iron and steelmaking industry is a highly material and energy-intensive process contributing to pollutant emissions and significantly affecting the air, water and soil quality. For example, in China, the atmospheric emissions of SO₂, NO_x (nitrogen oxides), PM_{2.5} (particulates with size of less than 2.5 μm) and VOCs (volatile organic compounds) from the iron and steelmaking industry were estimated to be approximately 2.2, 0.9 and 0.6 Mt respectively with the total crude steel production of 731, 040 Mt in 2012 (World Steel Association 2015; Wu et al. 2015). Pollutants are mainly formed from the conversion of minor and trace element impurities as well as other contained compounds during the processing of iron ores and other raw materials.

Iron and steel production typically consist of:

1. Ironmaking processes:
 - (a) Integrated ironmaking plants

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Pelletising: agglomeration of fine iron ores to produce pellets using a pellet plant

Sintering: agglomeration of fine iron ores to produce sinter using a sinter plant

Cokemaking: metallurgical coke production using coke ovens

Ironmaking: pig iron production using ironmaking blast furnaces

(b) Direct reduced iron (DRI) plants

2. Steelmaking processes:

(a) Steel production:

Steelmaking using basic oxygen furnaces (BOF) which is typical for integrated plants

Using electric arc furnaces (EAF) which is typical for DRI plants

(b) steel refining, casting and shaping:

Ladle metallurgy furnaces (LMF)

Continuous casters and batch casting in ingot moulds

Shaping the steel in rolling mills

The ironmaking processes account for the majority of pollutant emissions from the entire iron and steelmaking industries. This chapter is thus mainly focused on the pollutant emissions from the main processes of an integrated ironmaking plant, including sintering, pelletising, cokemaking and ironmaking blast furnaces.

These processes emit pollutants of different amounts. For example, in the sintering process, significant amounts of SO_2 are contained in the exhaust gas while in blast furnaces most sulphur partitions to the iron and slag. Sinter plants contribute the largest share of pollutant emissions in the ironmaking plants and are the second largest emitter after municipal solid waste (MSW) incineration (Philip 1999). For example, in China, sinter plant emissions are responsible for around 70 % of the atmospheric emissions of SO_2 and VOCs, 50 % of NO_x , 25 % of $\text{PM}_{2.5}$, 98 % of PCDD/Fs (dioxins and furans) and 10 % of CO_x (carbon oxides) (Gan et al. 2012; Wu et al. 2015).

Pollutant minimisation and recycling are major concerns for retaining the sustainability of industrial operations. The updating and implementing stricter environmental regulations by global governments (e.g. US Environmental Protection Agency and European Commission) are driving technological improvements in the iron and steel industry. For developing countries (e.g. China and India), there is much room for technological improvement and huge investments are required to avoid further lagging behind the developed countries. To comply with legislations, a variety of technologies and facilities have been employed to minimise or even eliminate the pollutant emissions.

This chapter is intended to give an introduction to the types of pollutant emissions, material inputs and outputs (especially the pollutant outputs) of ironmaking plants, and the commonly adopted abatement measures (primary and secondary) of various pollutant emissions. The effects of pollutant emissions on environment and human health as well as the quantitative assessment of the corresponding risks are also presented in the final section of this chapter.

19.2 Pollutant Types and Their Effects

Pollutant emissions can be categorised into several groups based on the affected environmental media: (1) pollutant emissions to atmosphere, (2) pollutant emissions to water and (3) pollutant emissions to soil. These emissions are further subcategorised according to their chemical nature. The majority of research has been devoted to the pollutant emissions to atmosphere which mainly consist of SO_x, NO_x, particulate matter (PM), heavy metals, polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) and dioxins and furans (PCDD/Fs). Among these, SO_x, NO_x, CO, Pb and PM (PM₁₀ and PM_{2.5}) are priority pollutants. PCDD/Fs and PAHs have been of great research interest in recent years. They are air toxics in the category of persistent organic pollutants (POPs) that are resistant to environmental degradation and pose severe effects to human health and environment (Zhang et al. 2012).

Gaseous and particulate pollutants have different negative impacts on the environment and human health. CO₂, CH₄ and N₂O are greenhouse gases (GHG) that can contribute to the radiative forcing of the atmosphere. NO_x and SO₂ are acidic gases contributing to wet and dry acid deposition. CO, CH₄ and NO act as precursors for tropospheric ozone formation through photochemical reactions, which then make the major component of smog.

The atmospheric particulate matter (PM) is one of the most vital indices of ambient air quality. It can result in severe damage to the respiratory and cardiovascular systems of human beings. According to the particle diameter, for regulation purposes, PM emissions are generally defined as PM₁₀ (<10 µm) and PM_{2.5} (<2.5 µm).

VOCs refer to a variety of organic compounds with low boiling points (usually <100 °C), such as benzene and derivatives (e.g. toluene and p-xylene) and formaldehyde. Some of the VOCs will cause the generation of ozone and other photo oxidants, which subsequently cause harm to the environment and human health. Generally, VOCs can cause irritation to the eyes, nose and throat and possibly other long-term health effects and even cancer. The target annual limit of average benzene concentration for VOCs from 2010 was set to be 5 µg/m³ by the European Commission (Ciaparra et al. 2009).

The persistent organic pollutants, PAHs and PCDD/Fs, have also attracted much concern for environmental regulation, specifically for iron and steelmaking. PAHs have been determined to expose high risk of carcinogenicity for which the concentration value of benzo [*a*] pyrene (B[*a*]P) is selected as the indicator. They are also harmful to the skin and respiratory systems of human bodies. In Europe, the B[*a*]P in air was targeted at 10⁻⁹ g/m³ by the end of 2012 (Ciaparra et al. 2009). Among all the iron and steelmaking sectors, cokemaking, sintering and ironmaking blast furnaces are the main sources of PAH emissions.

The formation of PCDD/Fs may take place during any combustion reactions in the presence of C, O and Cl (Demirbas 2008). Dioxins and furans have specific molecular heterocyclic structures with impregnated halogen atoms such as chlorine. PCDD/Fs refer to polychlorinated dibenzo-*p*-dioxins and dibenzofurans, which are highly hazardous and carcinogenic. The total toxicity of PCDD/Fs in gas is commonly expressed as international toxicity equivalents (I-TEQ).

19.3 Material Inputs and Outputs of Iron Industrial Processes

19.3.1 Sintering Process

The sintering process aims to agglomerate fine iron-bearing particles into larger porous clinkers (sinter product) that are suitable for use in blast furnaces. The input materials generally include ferrous materials (e.g. natural iron ores, fine iron ore powder from screening, slag, mill scales and sludge from iron and steelmaking), fluxes (e.g. limestone or dolomite) and 5% solid fuels (e.g. coke breeze or anthracite). The simplified flow diagram of a sinter plant with inputs and emissions is shown in Fig. 19.1.

In a sintering process, the blend of input materials is loaded onto the travelling sinter strand to form a sintering bed, where the sintering reactions take place. At the start point of the sinter strand, the ignition burners ignite the coke breeze in the blend, and the combustion initiates as air is sucked through the bed. Very high bed temperatures ($>1300\text{ }^{\circ}\text{C}$) cause the bed material to melt and agglomerate to form the sinter product. The produced combustion gas is pulled down through the sinter bed height into the wind boxes beneath the strand by suction fans. An entire sintering cycle occurs from the ignition of coke breeze in the sinter mixture to the burn-through point (Lu et al. 2015).

The exhaust gas in the wind boxes is a complex mixture of (1) fine particle matter which comprised of contains heavy metals and organic compounds; (2) low concentrations of CO, NO_x (e.g. 200 ppm) and SO₂ (e.g. <500 ppm); (3) low concentrations of PCDD/Fs; and (4) miscellaneous minor constituents such as HCl, HF and moisture (Chen et al. 2008a; Zhang et al. 2012).

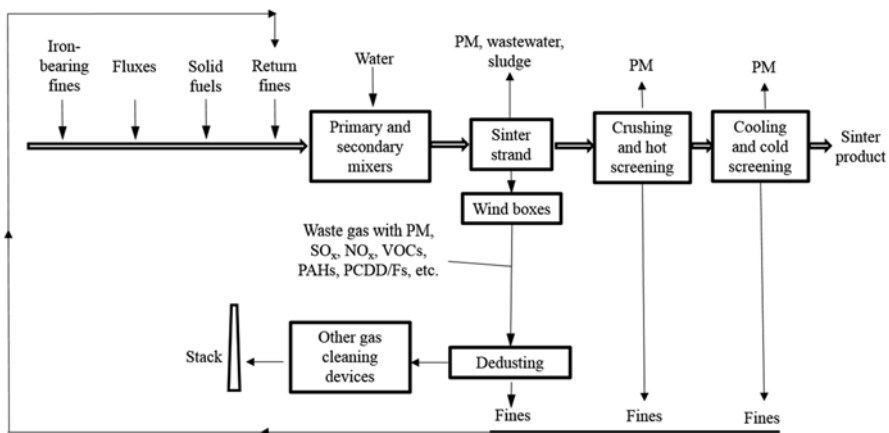


Fig. 19.1 A simplified flow diagram of a sinter plant with inputs and emissions

The exhaust gas also possesses other properties, such as a wide temperature range and fluctuating gas amounts with large flow rates (e.g. $100 \text{ m}^3/(\text{m}^2 \text{ min})$). As shown in Fig. 19.1, particulate matter is emitted along the entire flow of the sintering process. Materials handling, wind box exhaust gas, sinter discharge (crushing and hot screening) and cold screening contribute to the major emissions of particulate matter. Wind boxes experience the most noteworthy concentrations of PM emissions and carry iron and sulphur oxides, carbonaceous materials, heavy metals, metal chlorides, aliphatic hydrocarbons, dioxins and other possible contaminants, e.g. NH_3 (ammonia), As (arsenic), and fluorides. The main components of PM emissions from sinter crushing and hot screening are generally iron oxides and calcium oxides. The particle size of sinter plant dusts mostly ranges below $10 \mu\text{m}$ which is different from the blast furnace particle size distribution which can range up to $1000 \mu\text{m}$ in size (Formoso et al. 2000). The effective removal of fine particulates and aerosols at sinter plants is a difficult technical problem (Menad et al. 2006).

The concentrations of CO_x , NO_x , SO_x , VOCs, HCl and HF depend on the quality of the input raw materials as well as the reaction conditions. CO_2 and NO_x are discharged into the wind boxes throughout the entire sintering cycle. The combustion of fuels contributes more than 90 % of the NO_x emissions with the rest from other components of the sinter mixture. For example, in China the iron and steelmaking industry annually produced NO_x of up to millions of tons, most of which was caused by the sinter plants (Chen et al. 2008b).

The majority of generated SO_2 is firstly detained by the wet zone in the lower sinter bed and then released when the burn-through point approaches (Lu et al. 2015). SO_2 arises from the combustion of sulphur in the charged solid fuels, such as coke breeze or anthracite, and the oxidisation of the sulphur contained in the fluxes and other sulphur-bearing materials (e.g. ferrous fines).

VOCs are also produced mainly due to the evaporation of oils contained in certain materials (e.g. mill scale) and are pulled into the wind boxes before the formation of the sinter (Carmichael and Carson 1998).

PCDD/Fs can be also present in the exhaust gas. Sinter plants are a significant source of PCDD/F emissions. According to the statistical data by the European Environment Agency (EEA), during 1993–1995, sinter plants in Europe emitted flue gases with dioxin content of $1\text{--}10 \times 10^{-9} \text{ g I-TEQ}$ (International Toxic Equivalent) per m^3 (Menad et al. 2006) which accounted for more than 90 % of the total dioxin emitted by the entire iron and steelmaking industry (Babich et al. 2008). In China, PCDD/F emissions from sinter plants are responsible for nearly 60 % of the metallurgical plants or about 26 % of the total national PCDD/F emissions (Yu et al. 2012).

The formation of PCPP/Fs during the sintering process may be due to (1) the combustion of the chlorinated precursors (e.g. chlorinated aromatics) in the sinter bed and/or (2) the de novo synthesis reaction of chlorinated precursors with hot fly ash which is catalysed by Cu and other metals such as Fe (Lu et al. 2015).

Other molecules such as HCl, Cl_2 and gaseous chlorides presented in the exhaust gas should be the result of high-temperature reactions of chlorine-containing compounds such as sodium and potassium chlorides.

19.3.2 Iron Ore Pelletising

19.3.2.1 Iron Ore Pelletising Process

With the depletion of high-grade lump ores and sinter fines, iron ore pelletising has gained popularity during the past 2–3 decades (Cameron et al. 2015). Pellet plants are nowadays confronted with less stress from the increasingly stricter environmental legislations than the sinter plants due to the following three reasons (Poveromo 2006):

- (a) The majority of the global pellet plants were constructed during the past 30–40 years and equipped with relatively more modern pollutant abatement systems than sinter plants.
- (b) Release of lower emissions from pelletising than sintering due to the different nature of the two processes.
- (c) Considerable degradation and mass loss of sinter feed occur during handling and transportation. On the contrary, for pellet feed, the effect is minor. Most pellet plants are located at or close to the remote mining areas contrary to the sinter plant location at iron and steelmaking plants in urban areas with stringent laws.

Pelletising process involves three major steps of:

- (a) Pretreatment: mixture preparation of iron ore concentrate, coal or coke breeze, fluxes (e.g. limestone, dolomite, olivine and quartz), binders (mainly bentonite, hydrated lime and organic binders), moisture and other additives
- (b) Balling: production of green pellets in balling drums or discs followed by screening
- (c) Induration, cooling and final screening: heating of green balls to very high temperature (1250–1400 °C) in induration furnaces to form hard pellets (Carvalho et al. 2015) External fuels are used to supply the required heat, including liquid (e.g. fuel oils), gaseous (e.g. natural gas and coke oven gas) and solid (e.g. coal) fuels. Solid carbonaceous materials (e.g. coal) may be added into the iron ore concentrate in advance. Final pellets of 6–18 mm after screening are ready for use in blast furnaces.

The induration is the core operation of the pelletising and typically consists of four distinct phases: drying, preheating, firing and cooling. Three commercially available induration furnaces are (1) shaft, (2) straight/travelling grate and (3) grate–kiln system wherein the induration of green pellets takes place in the rotary kiln. Other new emerging induration technologies such as circular pelletising are underway (Cameron et al. 2015). The overall inputs and outputs of the pelletising process can be described by Fig. 19.2.

The waste gases from pellet plants mainly include CO₂, CO, CH₄, NO_x and SO₂. Other pollutant emissions such as PM, VOCs, PCDD/Fs, fluorides, heavy metals (lead and mercury) and other trace elements are also commonly present.

Among these, the NO_x emissions are of particular concern. There are three main mechanisms for explaining the formation of NO_x (Dean and Bozzelli 2000).

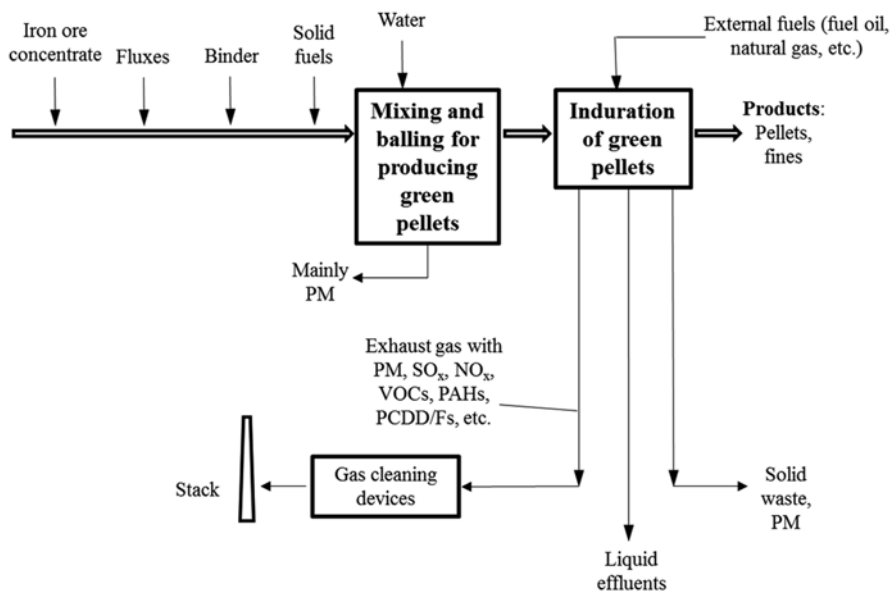


Fig. 19.2 Overall inputs and outputs of the pelletising process

For the pelletising process, the NO_x emissions are primarily generated through the fuel—NO_x route followed by the thermal—NO_x formation. However, the generation of induration NO_x is dominated by the thermal—NO_x route (Bolen 2014).

Several technologies have been applied to reduce the NO_x pollutant emissions in most modern pellet plants. Wet scrubbers, bag houses and ESPs are used for fugitive particulate removal at some points of the material handling such as cooler discharge (Bolen 2014). The recycled dust can be reused as a raw material for pelletising.

The fuel type and amount used in the pellet induration largely determine the NO_x emissions from pellet plants where NO_x is typically NO (Zahl et al. 1995). Generally, the combustion of the natural gas produces more NO_x than coal due to the reaction of nitrogen in the excessive air at the extremely high-temperature flame generated by the natural gas (Engesser 2004). It was also found that the NO_x amount increases with flame temperature. Thus, the addition of coal into the green pellets could be able to reduce NO_x production during the induration. 1% coal addition succeeded to decrease the NO_x production by 10–12% in the peak pellet temperature range of about 1200–1260 °C (Engesser 2004). An investigation into the NO_x formation in a rotary kiln test facility showed that the use of coal or biomass could result in lower NO_x emissions than the use of oil or gas (Johannes 2014). Reduction reactions of NO_x on char could also be responsible for decreases in observed NO_x.

Contrary to NO_x, SO₂ is hard to reduce during the pelletising process. SO₂ is formed by oxidation of sulphur which may be present in most raw materials and external fuels. Thus, reduction in SO₂ emissions can be achieved by using low-sulphur content raw materials and external fuels. More recently built pellet plants may also have installed desulphurisation devices for SO₂ removal, such as lime slurry, to react with SO₂.

19.3.2.2 Comparison of Sintering and Pelletising

Figure 19.3 presents typical amounts of several emissions from pelletising and sintering according to the date provided by Poveromo (2006). The amounts of different emission types from pelletising and sintering are distinct, especially SO_2 , CO and CO_2 . Pelletising of hematite and magnetite typically emits SO_2 of 200 and 100 g/t pellet respectively while sintering produces around 1700 g/t sinter. CO emissions from pelletising are lower than 1 kg/t pellet compared to the value of about 40 kg/t sinter for sintering. CO_2 production from pelletising is only 1/7–1/8 of that from sintering (Poveromo 2006).

The differences in emissions between the above pelletising of hematite and magnetite are mainly related to the variation in their fuel requirements. In addition, compared to sinter plants, pellet plants generally emit much less non-methane volatile organic compounds (NMVOCs) and PCDD/Fs but more heavy metals (such as Pb, Cd, Hg, Cr, Cu, Ni and Zn) and other hazardous nonmetal elements (such as As and Se) per unit mass of sinter or pellet product. For example, according to the data from the European Commission in 2001, sinter plants emitted uncontrolled NMVOCs of 138 g/t and Pb of 3.5 g/t sinter (European Environmental Agency 2013). For pellet plants, the emissions of uncontrolled NMVOCs and Pb are 14 and 20 g/t pellet respectively.

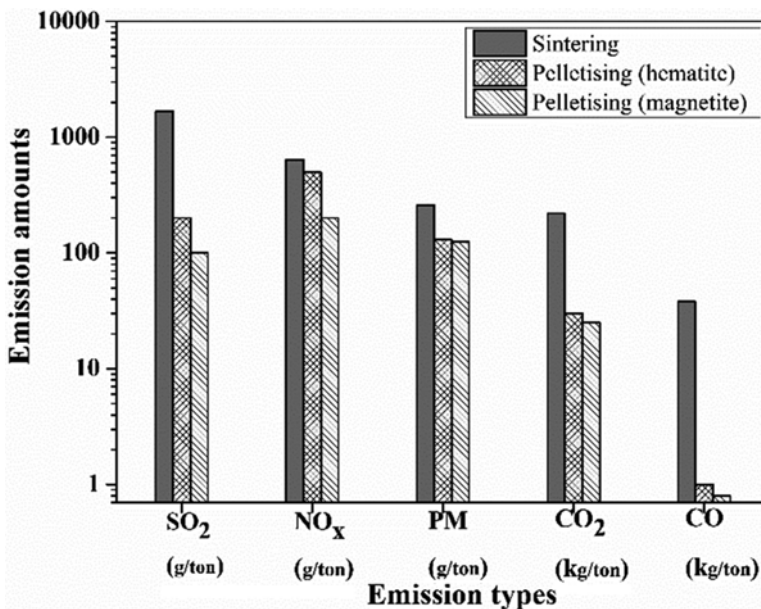


Fig. 19.3 Comparison of emissions from sintering and pelletising processes (Poveromo 2006)

19.3.3 Cokemaking

Cokemaking involves the decomposition of bituminous coals in the absence of oxygen to remove volatile matter, producing a solid residual of coke, and by-products including coke oven gas, coke breeze, tar, light oils and other chemicals. Cokemaking takes place in batteries which house 10–100 ovens. Coal is charged into the ovens from their top, and the heat required for coal decomposition is supplied by the combustion of recycled coke oven gas, natural gas or other gas fuels. Most coking plants integrate by-product facilities that are used to collect distilled volatile matters and purify the untreated coke oven gas ('foul' gas). By-product chemicals such as tar, light oils, naphthalene and ammonia can be recycled from the gas.

Figure 19.4 illustrates typical yields (wt%, based on the coal feed) of major products/by-products from cokemaking. The yields were calculated from the data found in the literature (Energetics 2000). Coke and coke breeze are the dominant solid products with yields of 63.5 and 6.8%, respectively. A considerable amount of the coal feed is converted to the coke oven gas with a yield of approximately 15%. Ammonia liquor and coal tar are the most outstanding liquid products with respective yields of around 6.5 and 5%. Other products such as light oil and ammonia sulphate are formed at yields of less than 4%.

Figure 19.5 illustrates a typical composition (vol%) of major species in coke oven gas. Hydrogen and methane are the dominant components with contents of around 52 and 30% respectively. The concentrations of other components are below 10%. The contained minor gas species generally involve benzene (C_6H_6) of 21–36 g/m³, PM of 2–36 g/m³, toluene (C_7H_8) of 2–3 g/m³, hydrogen cyanide (HCN) of 0.1–4 g/m³, etc. (US Environmental Protection Agency 1988; Nelson et al. 1991; Association of Iron and Steel Engineers 1998).

The cokemaking process with corresponding emission sources can be schematically described as illustrated in Fig. 19.6. The process is comprised of more than 10 modules, including production of blast furnace coke (consisting of coal preparation, coke oven batteries, coke removal with water quenching and coke screening with storage) followed by downstream treatments of foul gas consisting of ammonia spray, condenser/exhauster, tar extractor, saturator and condenser, absorption tower and a scrubbing tower. The final clean coke oven gas after treatment can be combusted for heat supply to the coke oven batteries, used in other processes or sold.

PM is released during the physical handling (e. g., pushing, charging and loading) of the raw coal material and the coke product as well as during the cokemaking in battery ovens. VOCs and other small-molecule gases, such as SO₂, NO_x and CO, are primarily generated as by-products of coking. Other dominant emissions include ammonia, coal tar, wastewater, sludge and tar residue which are produced along the streamline of foul gas treatment.

During cokemaking, ammonia results from the high-temperature (>700 °C) degradation of nitrogen-containing organics as part of the secondary decomposition reactions. Ammonia is irritating to skin, eyes and the respiratory system and can cause damage to lungs or even death if the ammonia concentration in the air is very

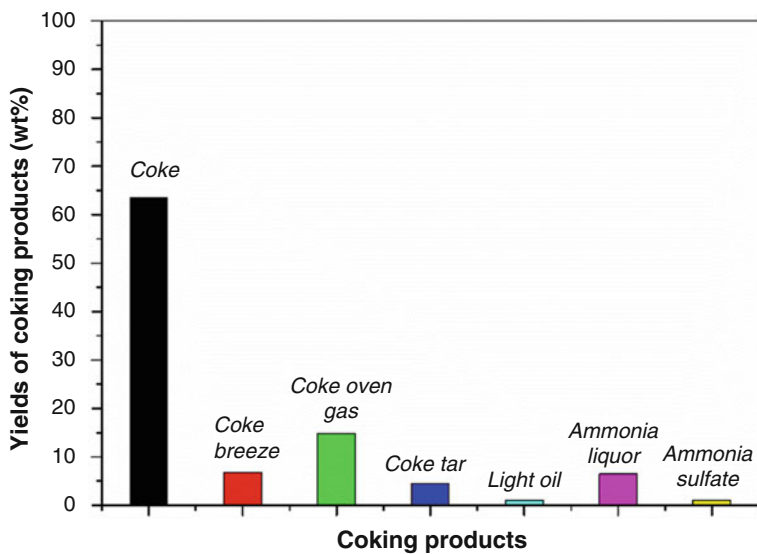


Fig. 19.4 A typical distribution (wt%, based on the coal material) of major products/by-products from cokemaking

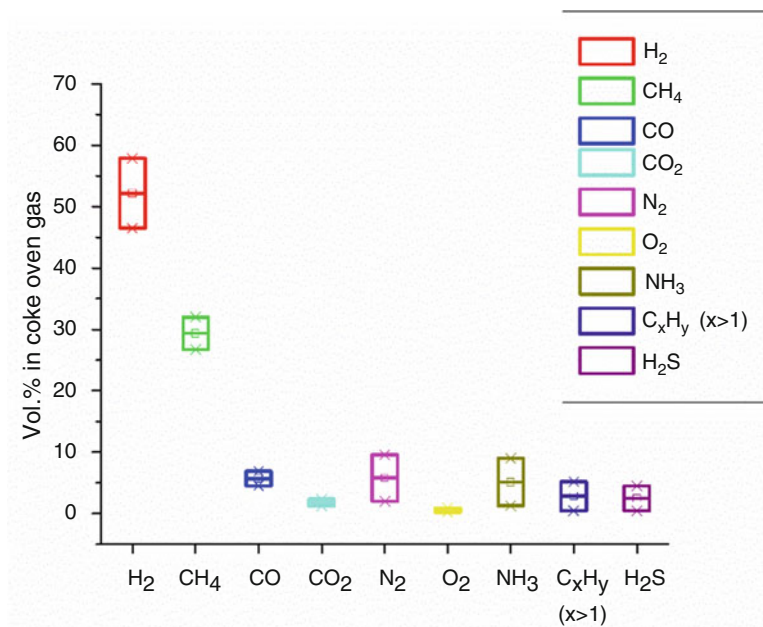


Fig. 19.5 A typical composition (vol%) of major species in coke oven gas

high. Ammonia may aggravate the eutrophication of some water resources. It can react with sulphate ions and return to the earth surface by rainfall. PAHs are released as fugitive emissions from leakages in the coke oven doors, lids, pipes and charging and pushing operations.

Large amounts of pollutant emissions are generated due to the enormous coke demand in ironmaking plants. Table 19.1 exhibits an example of pollutant production amounts (kg) per one tonne of coke manufactured.

19.3.4 Ironmaking in Blast Furnaces

The majority of ironmaking takes place in blast furnaces, although other ironmaking technologies have been developed. The basic process of blast furnace ironmaking with inputs and outputs is shown in Fig. 19.7. The overall inputs mainly include iron-bearing materials (lump ore, sinter, pellets, scrap, etc.), fluxes (e.g. limestone and dolomite), coke, other types of fuels (e.g. coal, coke breeze and coke tar), hot air blast, air, oxygen, coke oven gas, natural gas or fuel oil and water.

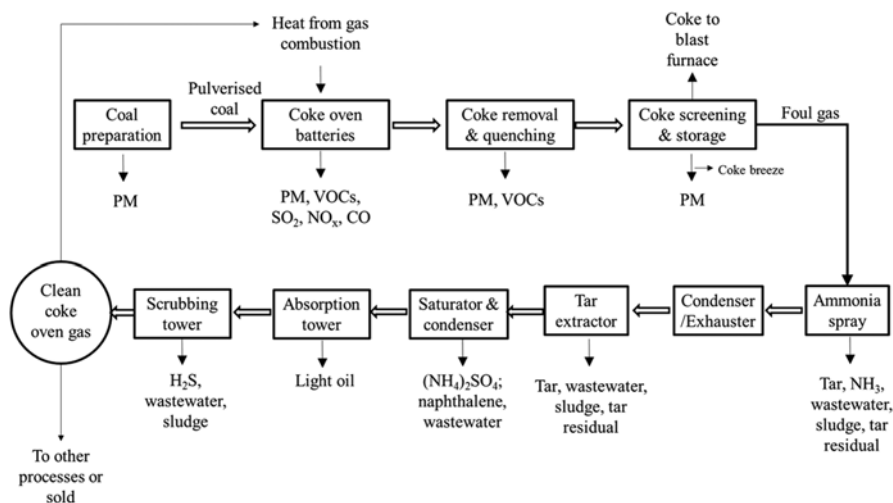


Fig. 19.6 The coking process and pollutant emissions (Energetics 2000)

Table 19.1 An example of pollutant production from cokemaking based on one ton of coke manufactured (Yaroshevskii et al. 1995)

| Amount of pollutant emissions (kg pollutant per ton coke) | | | | | |
|---|-----------------|------|-----------------|-----------------|--------|
| H ₂ S | SO ₂ | CO | NH ₃ | NO _x | Phenol |
| 2.3 | 1.0 | 0.46 | 0.3 | 0.16 | 0.09 |

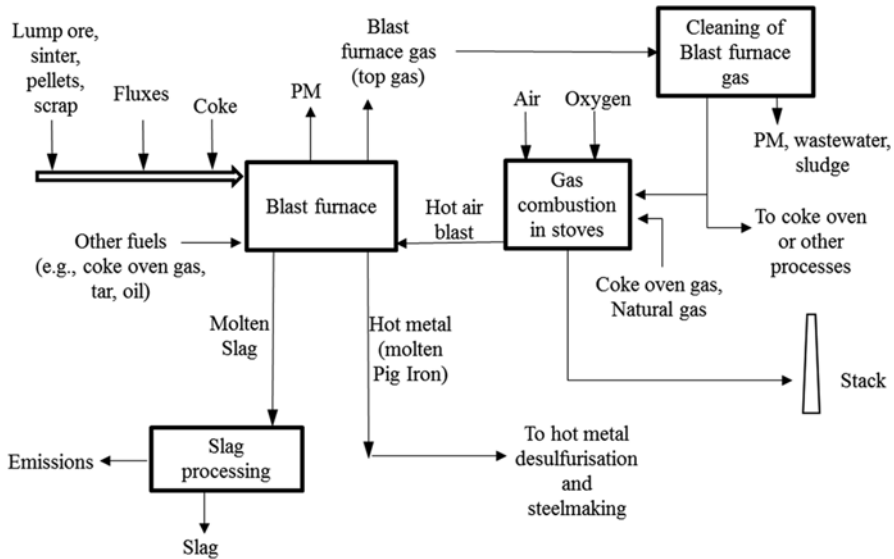


Fig. 19.7 Schematic diagram of blast furnace ironmaking process with inputs and outputs (Energetics 2000)

The outputs primarily include molten pig iron (iron saturated with carbon) which is then sent to steelmaking, molten slag, blast furnace gas, PM and wastewater and sludge.

Tapping of the blast furnace to extract pig iron and slag releases considerable emissions. During tapping, some metal oxides, such as magnesium oxide, and carbonaceous materials are released as particulates (European Environmental Agency 2013). Particle emissions also arise from the charging and conveying operations. VOCs can be released from the heating of the transport trough (after coating) and the plugging material (European Environmental Agency 2013).

The most abundant by-product from ironmaking in blast furnace is the slag which is then generally used as construction material or directly sent for landfilling. The slag contains large quantities of unwanted impurities such as sulphur. The generation rate of slag generally depends on the impurity content of the feed materials and is typically around 300 kg/t pig iron.

The blast furnace generates gas emissions mainly from the top where the blast furnace gas (top gas) is released. The blast furnace gas leaving the furnace top is hot, combustible and contains considerable dust. The size of the dust particles in the raw blast furnace gas ranges between several μm and about 6 mm. Multistage operations are employed for de-dusting. The first-stage dry cyclones or gravity dust catchers can remove over 60% of the particles from the gas stream. Besides the dust, the blast furnace gas typically contains CO_x (CO and smaller content of CO_2) of up to 40%, N_2 of 55–57%, H_2 of 1–5% and small amounts of other components such as VOCs, SO_2 and H_2S with a typical heating value of 2.5–3.6 MJ/Nm³ (Energetics

2000). SO_2 and H_2S are formed due to the sulphur content of coke and other materials. In Europe, NAFTA (North American Free Trade Agreement) countries and Japan, the sulphur content of coke charged to blast furnaces are generally 0.5–0.9, 0.6–0.7 and 0.5–0.6 wt%, respectively (Babich et al. 2008). The cleaned blast furnace gas is extensively used in blast furnace stoves to preheat the inlet air to supply hot air blast or for heat recovery to generate steam and electricity.

19.4 Emission Abatement Measures

Commonly used emission abatement measures can be utilised in ironmaking processes; however, some technologies are exclusively designed to fit the special requirements of ironmaking plants (mainly coking, sintering, pelletising and ironmaking blast furnaces).

Solid by-products from these plants, e.g. slag from blast furnaces, are treated and/or recycled by customised methods. Wastewater is processed in wastewater treatment plants prior to discharge to the environment. The measures for gas emission abatement include (1) primary measures aiming to prevent and minimise emissions during the production processes and (2) secondary (end-of-pipe) measures applied to abate emissions after their generation. Generally, primary measures should be given more priority, but the related environmental, economic and technical aspects should be also taken into consideration.

The commonly used primary and secondary measures for gas emission abatement in different production plants are depicted in Tables 19.2 and 19.3. Due to the low pollutant concentrations and huge amount of gases involved in these processes, the introduction of pollution control measures generally incurs high investment cost. Beside the measures listed in Tables 19.2 and 19.3, there are also measures for comprehensive control of pollutants specially developed for sintering and pelletising processes. These measures include (1) for sintering (emission optimised sintering (EOS[®]) (Menad et al. 2006; Bolen 2014), low emission and energy optimised sintering process (LEEP) (Eisen et al. 2004), environmental process optimised sintering (Eposint) (Alexander et al. 2007)) and (2) for pelletising (LKAB KK4 (operating) and Essar Steel Minnesota (under construction) (Bolen 2014)). Integrated ‘co-control’ of multi-pollutants and energy consumption is believed to be more efficient than single measures. Environmental regulations are putting pressure on the iron and steel industry to develop more efficient emission control technologies.

19.5 Conclusions

Iron production processes (including sintering, pelletising, cokemaking and blast furnace ironmaking) release significant amounts of pollutant emissions to the air, water and soil. This work is focused on the pollutants emitted to the air including CO , SO_2 , nitrogen oxides (NO_x), acid gases (H_2S , HCl , HF), polycyclic aromatic

Table 19.2 Measures for gas emission abatement in different iron industrial plants (US EPA 1994; Engesser 2004; Menad et al. 2008; Bolen 2014)

| Emission types | Primary measures | Pelletising | Coking | Ironmaking in blast furnace |
|-----------------|--|---|--|--|
| PM | <p>Sintering</p> <p>Restrict generation of SO_x and NO_x which are precursors for PM_{2.5}</p> <p>Equipping charging cars with dust collector</p> <p>Ensuring sealing of pipes and holes</p> | <p>Restrict generation of SO_x and NO_x which are precursors for PM_{2.5}</p> <p>Equipping charging cars with dust collector</p> <p>Ensuring sealing of pipes and holes</p> | <p>Equipping ascension pipe ejector with steam or NH₃ liquor systems</p> <p>Quenching tower with emission control system</p> | <p>Suppression of pollutant formation by minimising the contact between hot metal and air. It can be achieved by installing evacuated runner cover systems and local hooding ducted to a baghouse. This primary measure also applies for other pollutant emissions</p> |
| SO ₂ | <p>Use low-sulphur raw materials (e.g. coke breeze)</p> <p>Substitution of solid fuels by suitable biomass</p> <p>Use of additives, e.g. CaO, MgO and urea</p> | <p>Use low-sulphur raw materials</p> | <p>Use low-sulphur raw materials</p> | <p>In blast furnaces, most of sulphur is absorbed in slug by reaction</p> |
| NO _x | <p>Selective use of fuel with low N content</p> <p>Substitution of coke breeze by suitable biomass</p> <p>Use of additives, e.g. rice husk and sugar</p> <p>Minerals in coke generally suppress the transformation of coke N into NO_x</p> | <p>Selective use of materials of low N content</p> <p>Addition of coal or biomass into the green pellets</p> <p>Lowering the amount and temperature of the combustion air</p> <p>Adopting low NO_x burners in traditional air re-coup ducts with NO_x removal efficiency of 10–50 %</p> <p>Adopting low or ultra-low NO_x burners in separate combustion chambers with NO_x removal efficiency of up to 95 %</p> <p>Lowering the flame temperature by expanding the flame zone</p> <p>Generating partial reducing atmosphere within the flame</p> | <p>Improved heating system to avoid excessive oxygen</p> <p>Waste gas recirculation to reduce the local temperature and increase the residence time of the recirculated NO_x</p> | <p>Decreasing the flame temperature when blast furnace gas burns</p> <p>The NO_x concentration in blast furnace gas and stove flue gas is very low and thus is not a concern. Generally, no special NO_x controlling measures are needed</p> |

| | | | | |
|-------------|---|-------------------------------------|---|--|
| VOCs | <p>Removing oil from mill scale before its use in sinter plants Restricting oil content in sinter mixture</p> | Process and equipment modifications | / | Similar to SO ₂ and NO _x , these emissions are of less concern |
| PAHs | <p>Optimising the main sintering conditions such as the water content, suction pressure, bed height and type of hearth layer</p> | Process and equipment modifications | <p>Minimising leakages of coke oven batteries at doors, lids, pipes and charging and pushing operations</p> | |
| PCDD/ Fs | <p>Minimising the chloride and oil loading in the sinter bed Use of additives, e.g. ammonia and urea Setting the burn-through point at the sinter discharge Setting the burn-through point at the sinter discharge Using Taguchi experimental design to optimise process parameters, including oxygen and moisture contents of inlet gas, temperature in combustion chamber, temperature of outlet flue gas, residence time in cooler</p> | Optimising process parameters | Optimising process parameters | |

Table 19.3 Secondary measures for gas emission abatement in different iron industrial plants (Bohlen 2014; Philip 1999)

| Emission types | Secondary measures | | Comments | |
|-----------------|---|--|--|--|
| | PM removal devices/technologies | PM removal efficiency (%) | Typical discharge PM contents (mg/m ³) | Several devices/technologies could be combined to enhance the PM removal |
| PM | Mechanical collectors (e.g. cyclones and dropout boxes) | 50–80 | 45–150 | |
| | Fabric filters (baghouse) | 90–99.99 | 10 | |
| | Dry electrostatic precipitators (ESPs) | 90–99.99 | 20 | |
| | Wet electrostatic precipitators | 90–99.99 | 20 | |
| | Wet scrubbers | 70–99+ | 45 | |
| | SO ₂ removal devices/technologies | SO ₂ removal efficiency (%) | Typical discharge SO ₂ contents (ppmv) | |
| NO _x | Circulating fluidised bed or gas suspension absorber | 95–99 | 5 | |
| | Wet lime/limestone scrubbing | 80–95 | 10 | |
| | Spray dryer absorption | 70–90 | 25 | |
| | Wet electrostatic precipitator | ~80 | / | |
| | Lime/limestone injection | 30–50 | / | |
| | NO _x removal technologies | NO _x removal efficiency (%) | Reactions | |
| | Selective catalytic reduction (SCR) | 60–90 | Ammonia or urea + NO + O ₂ → N ₂ + H ₂ O (+ CO ₂ for urea) on vanadium-based catalysts at 300–500 °C | |
| | Low temperature oxidation (LoTOx) | ~80 | O ₃ + NO _x → HNO ₃ + H ₂ O at ~150 °C | |
| | Selective noncatalytic reduction (SNCR) | 30–50 | Direct injection of urea or aqueous ammonia into hot gas stream at 900–1010 °C | |
| | VOCs and PAHs | Adsorbents (e.g. activated carbon) | / | |

| | | |
|--------------|---|--|
| PCDD/Fs | Airline system Optimised de-dusting facilities, e.g. ESP with rotating electrode Entrained flow process | / / It mainly comprises of an adsorbent component of lignite coke of very fine particles and an electrostatic precipitator (ESP) where dust is separated. Results showed that this processing technology was able to restrain the PCDD/Fs concentration to 0.3-0.4 ng I-TEQ per m ³ |
| | Oxidative catalysis method | PCDD/Fs can react with H ₂ O and O ₂ and break down to form small molecules of CO ₂ , HCl and H ₂ O |
| Heavy metals | Heavy metals significantly adhere to particulates which can be removed by PM removal devices such as wet scrubbers. Zn, Pb and Cd emissions are the main concerns in sinter plants. Mercury emission is of concern in pellet plants. Soluble oxidised mercury can be removed by wet scrubbers. Elemental mercury can be removed by activated carbon injection into the off-gas duct followed by carbon particle capture by PM removal devices | |
| Waste water | Solids removal by sedimentation, heavy metal precipitation by physical/chemical processing, and filtration | Recycling and reuse of up to 98 % of water can be achieved by applying advanced technologies |

hydrocarbons (PAHs), volatile organic compounds (VOCs), dioxins and furans (PCDD/Fs), heavy metals and particulate matter (PM). Their effects on the environment and human health are summarised. The inputs and emission outputs for the above four iron production processes are also introduced, aiming to give readers the information on the sources and production mechanism of the major pollutants in each production process. Sintering contributes the largest share of most types of pollutant emissions among the iron production processes. Waste gases produced from the sintering bed reactions are the primary sources of emissions. Emissions from pellet plants are mainly generated during the thermal induration of green pellets. Comparison of these two iron ore aggregation processes shows that pelletising generally emits much less NO_x , SO_2 , CO, non-methane VOCs and PCDD/Fs but more heavy metals per unit mass of sinter or pellet product. Cokemaking is responsible for severe emissions of H_2S , SO_2 , NO_x , CO, PM, VOCs and heavy metals from the coke oven batteries and coke quenching process. As to the blast furnace iron-making process, tapping generates the primary emissions due to the contact of hot metal and slag with the air. Furtherly, the work describes the commonly used primary and secondary measures for gas emission abatement. More efficient and cost-saving measures and technological advances are required to respond to the increasing pressure from environment regulations.

References

- Alexander, F, Andreas, K, Anton, S (2007) New developments for achieving environmentally friendly sinter production-eposint & meros. In: The 6th ironmaking conference proceedings Association of Iron and Steel Engineers (1998) Steelmaking and refining volume. In: Fruehan RJ (ed) The making, shaping, and treating of steel, 11th edn. The AISE Steel Foundation, Pittsburgh
- Babich A, Senk D, Gudenau HW, Mavrommatis KT (2008) Ironmaking. RWTH Aachen University, Aachen
- Bolen J (2014) Modern air pollution control for iron ore induration. *Miner Metall Process* 31:103–114
- Cameron I, Huerta M, Bolen J, Okrutny M, O’Leary K (2015). Guidelines for selecting pellet plant technology. In: AusIMM iron ore conference, 13–15 July 2015
- Carmichael KR, Carson JR (1998) Process reduction of volatile organic compound emissions at a steel mill sinter plant. In: Environmental innovations in the metals industry for the 21st century: proceedings of a specialty conference
- Carvalho MMO, Cardoso M, Vakkilainen EK (2015) Biomass gasification for natural gas substitution in iron ore pelletizing plants. *Renew Energy* 81:566–577
- Chen YC, Tsai PJ, Mou JL (2008a) Determining optimal operation parameters for reducing PCDD/F emissions (I-TEQ values) from the iron ore sintering process by using the Taguchi experimental design. *Environ Sci Technol* 42:5298–5303
- Chen YG, Guo ZC, Wang Z (2008b) Application of modified coke to NO_x reduction with recycling flue gas during iron ore sintering process. *ISIJ Int* 48:1517–1523
- Ciaparra D, Aries E, Booth MJ, Anderson DR, Almeida SM, Harrad S (2009) Characterisation of volatile organic compounds and polycyclic aromatic hydrocarbons in the ambient air of steelworks. *Atmos Environ* 43:2070–2079

- Dean AM, Bozzelli JW (2000) Chapter 2. Combustion chemistry of nitrogen. In: Gardiner WC (ed) Gas-phase combustion chemistry. Springer Science+Business Media, New York
- Demirbas A (2008) Hazardous emissions from combustion of biomass. *Energy Source Part A* 30:170–178
- Eisen P, Husig KR, Kofler A (2004) Construction of the exhaust recycling facilities at a sintering plant. *Stahl Eisen* 124:37–40
- Energetics (2000). Energy and environmental profile of the U.S. iron and steel industry. Prepared for U.S. Department of Energy
- Engesser J (2004) Nitrogen oxide (NO_x) emission reduction during pellet induration by fuel addition to the green pellets and decreased excess air. *Miner Metall Process* 21:9–16
- European Environmental Agency (2013) EMEP/EEA air pollutant emission inventory guidebook – 2013
- Formoso A, Moro A, Fernandez-Pello G, Muniz M, Jimenez J, Moro A, Cores A (2000) Study of the iron ores mixture granulation in the sintering process. Part 2. Granulation index. *Rev Metal Madrid* 36:254–265
- Gan M, Fan XH, Chen XL, Ji ZY, Lv W, Wang Y, Yu ZY, Jiang T (2012) Reduction of pollutant emission in iron ore sintering process by applying biomass fuels. *ISIJ Int* 52:1574–1578
- Johannes H (2014) Evaluation of the NO_x formation in a rotary kiln test facility. Master's thesis, Chalmers University of Technology Göteborg, Sweden
- Lu L, Ooi TC, Li X (2015) Sintering emissions and their mitigation technologies. In: Lu L (ed) Iron ore: mineralogy, processing and environmental sustainability. Elsevier, Cambridge
- Menad N, Tayibi H, Carcedo FG, Hernandez A (2006) Minimization methods for emissions generated from sinter strands: a review. *J Clean Prod* 14:740–747
- Nelson D, Scheff P, Keil C (1991) Characterization of volatile organic compounds contained in coke plant emissions. Presented at the 84th annual meeting & exhibition of the air & waste management association
- Philip JA (1999) Reducing the emissions of dioxins from sinter plants. In: Workshop proceedings, steel research and development on environmental issues, Bilbao
- Poveromo JJ (2006) Agglomeration processes-pelletizing and sintering. In: Kogel JE, Trivedi NC, Barker JM, Krukowski ST (eds) Industrial minerals & rocks: commodities, markets, and uses. Society for Mining, Metallurgy, and Exploration, Inc. (SME), Littleton
- U.S. Environmental Protection Agency (1988) Air emissions species manual volume I: volatile organic compound species profiles (April)
- US EPA (1994) Alternative control techniques document - NO_x emissions from iron and steel mills
- World Steel Association (2015) Annual crude steel production per country and region 1980–2014. <http://www.worldsteel.org>. Accessed 27 Nov 2015
- Wu XC, Zhao LJ, Zhang YX, Zheng CH, Gao X, Cen KF (2015) Primary air pollutant emissions and future prediction of iron and steel industry in China. *Aerosol Air Qual Res* 15:1422–1432
- Yaroshevskii S, Baoich A, Tereshchenko V, Nozdrachev V (1995) In: 3rd international conference on combustion technologies for a clean environment, 3–6 July 1995, Lisbon, vol 1, 28.11, pp 60–90
- Yu YM, Zheng MH, Li XW, He XL (2012) Operating condition influences on PCDD/Fs emissions from sinter pot tests with hot flue gas recycling. *J Environ Sci* 24:875–881
- Zahl R, Haas L, Engesser J (1995) Formation of NO_x in iron oxide pelletizing. Iron Ore Cooperative Research (MnDNR), Minnesota Department of Natural Resources
- Zhang WH, Wei CH, Chai XS, He JY, Cai Y, Ren M, Yan B, Peng PA, Fu JM (2012) The behaviors and fate of polycyclic aromatic hydrocarbons (PAHs) in a coking wastewater treatment plant. *Chemosphere* 88:174–182