Gaseous emissions from coal stockpiles

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Abstract

Stockpiled coal undergoes atmospheric oxidation and desorption processes during open air storage. These processes release gases to the environment which may effect health and safety by their toxicity and flammability. In extreme cases, this could lead to a fire. This report discusses gaseous emissions from coal stockpiles. It covers gas emission mechanisms, and gas sampling and testing methods, before examining in more detail the principal gases that have been emitted. It concludes that there is limited research in this area and more data are needed to evaluate the risks of gaseous emissions. Some methods used to prevent coal self-heating and spontaneous combustion can be applied to reduce emissions from coal stockpiles.

Acronyms and abbreviations

CAR-PDMS	Carboxen-Polymethylsioxane
CS_2	carbon disulphides
COS	carbonyl sulphide
DMS	dimethyl sulphide
FPD	Flame Photometric Detector
GC	gas chromatography
IPCC	Intergovernmental Panel on Climate Change
L/min	litres per minute
MSD	Mass Selective Detector
ppmv	parts per million by volume
SPME	Solid Phase Micro Extraction
VSC	volatile sulphur compounds

Contents

1 Introduction

The stockpiling of coal is carried out at a number of points along the transport chain to the end user – at coal mines; coal preparation plants; transport terminals; and the user site, including power plants, integrated iron and steel works, coke works and cement plants (Carpenter, 1999). Countries with no domestic coal resources but consuming large amounts of coal have to store appreciable quantities for relatively long periods of time in large stockpiles in the open air at harbours or in storage facilities at power plants. Assessing gas and dust emissions while storing coal has practical importance in risk assessment of the storage area and prevention of greenhouse gas emissions.

It is known that coal oxidation begins the moment that coal is mined and comes into contact with oxygen in the air. Oxidation results in loss of coal calorific value and allows gaseous emissions to the environment. Williams and others (1998) found that coal oxidation at low temperatures is an important contributor to greenhouse gas emissions. Coal that has been mined can be subject to increased temperature and reduced atmospheric pressure compared with coal in the ground conditions which are for degassing. Grossman and others (1994b) identified coal oxidation products of CO_2, CO, CH_4, C_2H_4 and H_2 from open air bituminous coal stockpiles in Israel. Kozinc and others (2004b) monitored gas emissions of CO_2, CO, C_2H_4, and dimethylsulphide (DMS) from a coal stockpile in Velenje, Slovenia.

Though there is a wealth of data on stack emissions from power plants, little consideration has been given to gaseous emissions from coal stockpiles. The only fugitive emissions from stockpiles routinely assessed are dust emissions. The purpose of this report is to investigate gaseous emissions from coal stockpiles. It begins by examining the gas emission mechanism before describing gas sampling and testing methods. The emitted gases, including hydrogen, carbon oxides, hydrocarbons, and sulphuric gases, are discussed in more detail in Chapter 4. Finally, Chapter 5 reports the lack of research for gaseous emissions from coal stockpiles.

2 Gas emission mechanisms

Possible sources of gases emitted from coal stockpiles are degassing, low temperature oxidation and, in extreme cases, spontaneous combustion.

2.1 Gas desorption

Coal beds contain reservoirs of gases, mainly CO_2 and CH_4. These gases are stored in coal beds on the internal surface of organic matter (adsorption mechanism) or within the molecular structure of the coal (absorption mechanism). Gas desorption depends on temperature and pressure. For coal stockpiles, temperatures can be higher (due to oxidation) and atmospheric pressures lower than those occurring in coal beds. These conditions are ideal for degassing. At first, it was believed that the gas desorbed from coal was pure methane. Now it is well known that coals also contain nitrogen, carbon dioxide, and sulphuric gases. Apart from CO_2 and CH_4, Zapušek and Marsel (1998) found that DMS was produced from the lignite by a desorption process.

2.2 Low temperature oxidation

Both low temperature oxidation and spontaneous combustion generate greenhouse gases. While low temperature oxidation and spontaneous combustion arise from the same basic processes and represent different extremes of the same phenomenon, greenhouse gas emissions from each are different. The major greenhouse gas emission from oxidation at ambient temperatures is CO_2. However, at the elevated temperature present in material affected by spontaneous combustion, parts of the coal can be starved of oxygen with the result that the chemical reactions change and appreciable quantities of CH_4 can be produced. Note that this methane is produced as a result of heating and is therefore separate from seam gas trapped in the coal (Carras and others, 2009).

From the moment that coal is exposed to air, it is subject to low temperature oxidation (weathering) by atmospheric oxygen. This process can be sustained if the heat produced by the exothermic oxidation (mainly chemisorption of oxygen at the coal surface and emission of carbon dioxide) cannot be sufficiently dissipated by heat transfer within the stockpile.

Low temperature oxidation of coal has been studied extensively. Davidson (1990) carried out a comprehensive literature research on 'Natural oxidation of coal' and stated that, even at ambient temperature, coal reacts with oxygen in air. However, it would be naive to assume that coal oxidation is a simple reaction involving just two reactants, coal and oxygen. Coal is a collection of reactants and should be viewed as such. He summarised coal oxidation as the sum of several constituent reactions:

- the reaction with oxygen to form CO_2 and CO directly;
- the physical adsorption of oxygen on the coal surface;
- the chemical absorption of oxygen on the coal;
- the formation of H_2O.

Davidson pointed out that although much work on weathering and low temperature oxidation has taken place, the parameters influencing the reactions remain unravelled.

Wang and others (2003a) also agreed that coal oxidation at low temperatures is a complicated process, involving four phenomena (*see* Figure 1), namely:

- oxygen transport to the surfaces of coal particles;
- oxygen transport within coal pores;

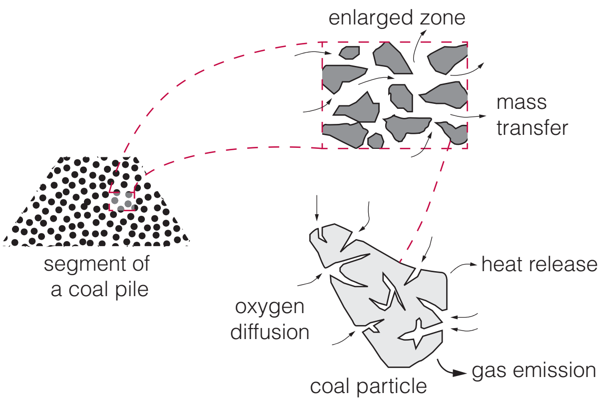

Figure 1 The fundamental phenomena occurring in the coal oxidation process (Wang and others, 2003a)

- chemical interaction between coal and O_2;
- the release of heat and emission of gaseous products.

The complexity of these phenomena is enhanced by the diversity of the composition and properties of coal, as well as by its porous structure. Chemical interactions between coal and O_2 molecules occur at the external surface of coal particles and on the coal pore surfaces, although the latter usually predominate.

Although the exact process of coal oxidation is complex and the mechanisms are not fully understood, some general features of the process are known. According to Wang and others (2003a,b), two parallel reaction sequences occur during coal oxidation at low temperatures – the direct burn-off and sorption sequences. This theory echoes Davidson's summary. The burn-off reaction sequence is suggested to be similar to the direct combustion reactions of solid fuel but it is not possible to describe this reaction sequence in the form of a series of fundamental steps due to a lack of understanding. It is proposed that the direct burn-off reaction only occurs at specific reaction sites in a coal's aliphatic or aromatic structure and results in the direct formation of gaseous products, including carbon dioxide, carbon monoxide and water. Figure 2 shows schematically the reaction sequences. In the sorption sequence, the following steps are suggested:

(a) chemisorption of O_2 on surfaces of coal pores and the formation of unstable carbon-oxygen complexes (for example, peroxides and hydroperoxides);
(b) decomposition of the unstable solid oxygenated intermediates to gaseous products and stable solid complexes, including hydroxyl (phenolic –OH), carbonyl (–CO) and carboxyl (–COOH) groups;
(c) degradation of these stable complexes and generation of new active sites for coal oxidation following the decomposition of the stable complexes.

Carbon dioxide emission is also accompanied by emissions of low molecular weight organic gases ($C_{1\text{-}5}$, for example, methane and ethane), carbon monoxide and hydrogen, all of which are flammable (Nehemia and others, 1999; Cohen and Green, 2009).

$\text{Coal} + O_2 \rightarrow O_2$ (physically adsorbed) (1)
O_2 (physically absorbed) $\rightarrow O_2$ (chemically absorbed) (2)
O_2 (chemically absorbed) $\rightarrow$ surface oxides (oxycoal) + heat (3)
surface oxides (oxycoal) $\rightarrow CO_2 + H_2O$ + heat (major reaction) (4a)
surface oxides (oxycoal) $\rightarrow H_2 + CO + C_{1\text{-}5}H_n$ (side reactions) (4b)

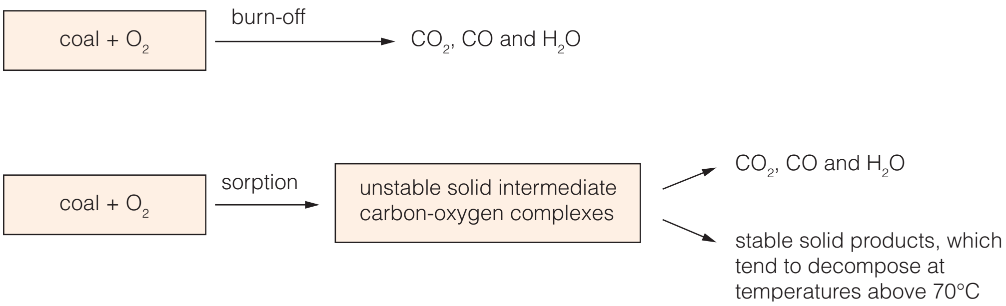

Figure 2 An illustration of the general reaction pathways occurring in coal oxidation (Wang and others, 2003a)

Reactions 1–3 are the main processes occurring during atmospheric coal oxidation. Surface oxides refer to several types and compositions of oxygenated functional groups (oxygenated intermediates as described above). A small percentage of the surface oxides (1–15%, depending on the temperature) decompose via reaction 4a and a much smaller percentage of certain other surface oxides decompose via reaction 4b. The source of the sulphur gases COS and CS_2, however, is oxidation of pyrite in coal. Kozinc and Zapušek (2003) and Kozinc and others (2004b) proved this theory with the gases detected from a lignite stockpile in Velenje coal mine.

2.3 Factors affecting low temperature coal oxidation

The coal oxidation reactions are affected by several factors. Apart from mass transport considerations, these factors can be classified as internal and external variables. The internal variables include composition and physical properties of coal, history of coal weathering/oxidation, as well as particle size. The external variables involve temperature, partial pressure of O_2, and moisture content in the gas medium. In terms of coal oxidation in coal stockpiles, the design of the stockpile and configuration of the stockpile also play an important part.

Other IEA CCC reports have studied factors affecting coal oxidation. Davidson (1990) analysed the reaction parameters and specially mentioned that mineral chemistry plays an extremely important role in coal weathering and low temperature oxidation. Nalbandian (2010) studied the factors which affect low temperature oxidation in order to understand the properties that influence the propensity of coal to self-heat/combust. This report only summarises some of the key factors which affect low temperature coal oxidation mainly based on Wang and others' (2003a) publication.

2.3.1 Composition and physical properties of coal

The influence of coal composition and its structure on oxidation is complicated and remains a source of debate. The established trend is that the rate of oxygen consumption by a coal decreases with an increase in carbon content (coal rank) of coal. Low rank coal with its low degree of carbonisation oxidises more easily even at low temperature than high rank coal. Some minerals, such as pyrite may act as a catalyst in the oxidation process. Inherent water, including water physically or chemically bonded in coal pores, plays an important role in the oxidation process, although controversy exists as to whether the inherent water acts as a promoting or inhibiting agent. Most investigators argue that a minimum amount of water (about 1% of coal mass) is necessary for the interaction between coal and $O_{2,}$ but high water loading inhibits oxygen adsorption because of the necessity for the O_2 molecules to diffuse through layers of free water present at the external surface and in the pores of the coal particles. Nelson and Chen (2007) think that inherent water prevents oxidation by 'chemical' and 'physical' occupation of active sites, and by providing a resistance to oxygen diffusion within the coal pores.

2.3.2 Oxidation history

Oxidation history has a significant effect on reactions between coal and oxygen at low temperatures. It was observed that a weathered or oxidised coal consumes oxygen at a rate far lower than a freshly mined or crushed coal. Nelson and Chen (2007) agree that preoxidation has a strong negative influence on the oxidation rate. The lower reactivity of aged coals is due to the removal of active sites by oxidation. The decrease in oxidation rate of aged coals is more noticeable at higher temperatures. The maximum rate of decrease in the reaction rate occurs when fresh coal particles are first exposed to oxygen.

2.3.3 Particle size

The oxidation rate increases with a decrease in particle size, which correlates to the diameter or the external surface area of coal particles until a critical diameter is reached. This follows directly from the fact that low temperature oxidation of coal involves reactions taking place at the internal surfaces of coal pores. For smaller particles, the rate is found to be basically independent of particle size and this may be due to a fast penetration of oxygen to the interior of small particles. The critical diameter corresponds to a size at which oxygen penetrates the particles without experiencing any mass-transfer resistance. The critical diameter depends upon factors such as reaction conditions and the porosity of the coal. It varies significantly between coals. According to Nugroho and others (2000), the effects of particle size are very significant for high rank coals, but almost negligible for low rank coals as the surface area hardly changes. For fresh coal, the influence of particle size on reaction rate is pronounced even at low temperature. However, for dry coal, the influence of particle size becomes important only at significantly higher temperatures or for considerably larger particle sizes. As the role of particle size on oxidation rate depends on the coal being studied, no simple generalisations are possible. For coal stockpiles, in addition to changing the reaction rate, the particle size also affects the permeability. It has been suggested that permeability exerts more control on the overall reaction rate than particle size in stockpiles.

2.3.4 Temperature

Temperature has a significant effect on the oxidation process. Normally, the temperature range considered is between ambient and 100°C, although sometimes this range is extended to 150°C. It has been reported that the rate of oxygen consumption almost doubles for a temperature rise of 10°C. Several studies have found that the oxidation rate of coal increases dramatically as the temperature crosses a threshold of approximately 70–80°C. Some investigators found the emission of gaseous products (especially carbon oxides) to be directly associated with temperature rise in a coal stockpile.

2.3.5 Partial pressure of oxygen

As early as the beginning of the 20th century, investigators observed a dependence of the rate of coal oxidation on oxygen concentration in the gas phase. A number of investigators suggested that over a wide range of oxygen concentrations, the rate of oxygen consumption can be expressed as a power of the partial pressure of oxygen in the oxidation medium with the exponent varying between zero and unity.

2.3.6 Moisture

It has been found that wet coal is more reactive than dry coal at room temperature but by 70°C the oxidation of dry coal exceeds that of wet coal. The effect of moisture on the oxidation rate of the coal is interrelated with the pore structure and inherent moisture content of coal. Carras and Young (1994) summarised two research groups' experiments on moisture content. The Sondreal and Ellman group determined the oxidation rate of lignite with a range of moisture contents. The lignite was sized to 12.5 mm by 6.3 mm and dried in an inert atmosphere. These workers found that the oxidation rate initially increased with moisture content up to a value of 20% water (by mass) and then decreased with increasing moisture content. The second group was Itay and others (1989) who used a dry coal crushed to 75 µm. The coal was oxidised at 56°C for about five hours and then a small quantity of water added. They observed an increase in the oxidation rate and concluded that the water had a catalytic effect on the oxidation reaction. However, more recent work at CSIRO laboratories tends to show that for coals which have not been dried, increasing the water content acts to depress the initial oxidation rate, particularly when the water content approaches the equilibrium moisture value (Carras and Young, 1994). This behaviour is probably due to liquid water blocking some of the pores and inhibiting the access of oxygen.

3 Gas sampling

Freudenstein and others (2000) reported an incident in which gaseous substances were released by a 7000 t coal stockpile at an opencast mine in the UK. Villagers living downwind from the mine complained to the local authority of strong, unpleasant odours, predominantly of a tar-like smell, and a sulphurous 'rotten-egg' smell. They also complained of upper airway and skin irritation, and exacerbations of asthma and eczema. The presence of skin irritations suggested that sulphur dioxide was unlikely to be the only gas present. Unfortunately, the small district council did not have all the expertise and technology required to measure the relevant airborne pollutants emitted. Measurement of the sulphur dioxide and sulphite levels at the stockpile were taken only after the health-related complaints had stopped, and could not be used to estimate either peak or personal exposure.

Indeed, it is a challenge to test the gas emissions from a large coal stockpile. The main barrier is sample collection. Laboratory test methods for gases are well established and well reviewed in other IEA CCC reports. In this chapter three methods for collecting gases from coal stockpiles are described.

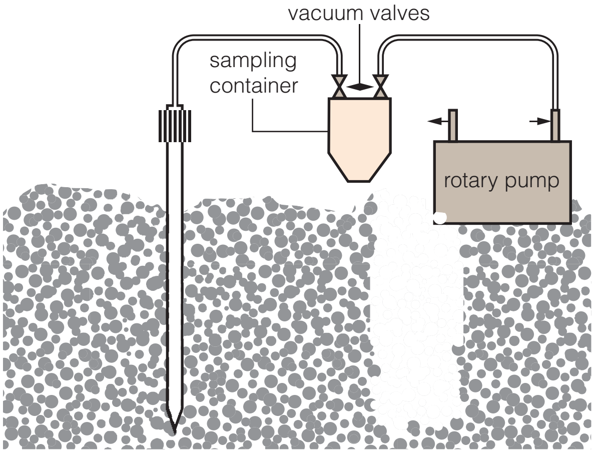

Figure 3 Schematic diagram of gas sampling from a coal stockpile (Grossman and others, 1991b)

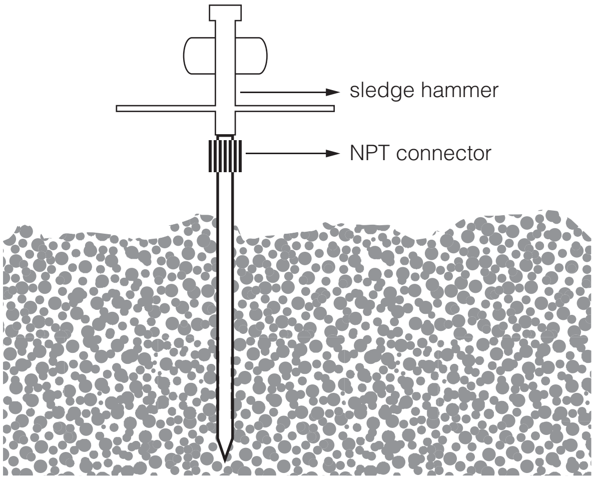

Figure 4 Penetrator of the sampling unit (Grossman and others, 1991b)

In order to test gas emissions from coal stockpiles, Grossman and others (1991b) developed a lightweight (37 kg) portable sampling unit to sample the gases found within a coal stockpile and monitor stockpile temperatures. The unit consisted of the following components (*see* Figure 3)

1. Penetrator which consisted of four sections of 1.5 m stainless steel pipe with a stainless steel membrane at the bottom (*see* Figure 4). A heavy duty handle at the top can withstand the blows of a 5 kg sledge hammer.
2. Gas sampling container which was made of glass.
3. Evacuation and power supply. Vacuum in the glass container was obtained by using a small direct drive rotary pump, which can achieve a vacuum of ~0.1 Pa. The power was provided by a small generator.
4. A thermocouple for temperature measurements. The thermocouple was inserted into the penetrator until the desired depth was reached.

After the first tube section was inserted into the stockpile, the handle was removed and an additional section was connected to the first section, the handle was then reattached to help the operator to penetrate the new section of the stockpile. The process was repeated until the required depth was reached. The glass container was attached on one side to a vacuum pump and on the other side to the penetrator. The pump was switched on and the glass container's valves were kept open for three minutes, during which time the original glass container atmosphere was removed and in its place was introduced the gas that had been pumped via the membrane at the tip of the penetrator. The vessel valve that led to the pump was closed, and after the system pressure equilibrated, with ambient pressure, the second valve was shut. The collected gas samples were then brought to the laboratory for further tests.

A decade after Grossman and others (1991b) work, Kozinc and others (2004b) studied gas emissions from a lignite stockpile at the Veleji coal mine. Kozinc and his colleague Zapušek (Kozinc and others, 2004a; Zapušek and others, 2003) established a direct sampling method to collect gas from the stockpile surface. The testing method they developed was guided by the Verein der Deutschen Ingenieuren (VDI) Directive (3790/1997). They made two 1 x 1 x 0.5 m (0.5 m in height) polycarbonate tents. The airtight tents were placed on the stockpile and after a certain time, the emitted gases were collected by air pump at a low flow rate in the tent. The gas samples were taken from the tents in gas sampling bags to the laboratory, where tests of the samples were performed by gas chromatography (GC) within 24 hours.

As the volatile sulphur compounds (VSC) level in air are low, separation and pre-concentration techniques are often required before the test. Kozinc and others (2004a) explored two pre-concentration techniques. The first one was cryogenic trapping which contained three traps, – a wet NaOH trap to remove carbon dioxide, a cold trap (0–4°C) to remove moisture and a cryogenic trap with liquid nitrogen. The components COS, CS_2 and DMS freeze at temperatures of –138.8°C, –11.5°C and –98.3°C, respectively. The trap was heated and flushed with synthetic air and the released gases were collected in a 10-litre sampling bag for further laboratory tests. The second technique is Solid Phase Micro Extraction (SPME) fibres. Developed in the early 1990s by Dr Pawliszyn's group, it is a simple and inexpensive technique where the use of solvents is unnecessary, and can be used both in the laboratory and on site (*see* www.sigmaaldrich.com). The gas collected in the sampling tent was pumped through a cold trap (0–4°C) to remove the moisture and placed into a 2-litre sampling bag. A 75 µm Carboxen-Polymethylsioxane (CAR-PDMS) sampling SPME fibre was inserted into the sampling bags for 15 min extraction to pre-concentrate COS, CS_2 and DMS. The VSC gases were tested by GC equipped with a Flame Photometric Detector (FPD) or a Mass Selective Detector (MSD). Kozinc and others (2004a) suggested that the SPME pre-concentrated technique combined with GC-MSD is a method of choice for the determination of VSC gases in the ppbv concentration level from coal stockpiles.

Although it was tested on spoil piles at eleven opencast Australian coal mines, the following method can be applied to coal stockpiles. Carras and others (2009) determined fluxes of greenhouse gases from sections of coal mine waste by placing a purpose-built chamber on the ground surface and measuring the concentration of CO_2 and CH_4 emitted into the chamber. For low emission rates, measurements were made using a cylindrical chamber 37.5 cm in diameter and 40 cm high with a total volume of about 45 litres and an area covering of 0.22 m^2. The chamber was placed on the ground and sealed by placing sand around its base. A small solar-powered fan inside the chamber ensured that the sample was well mixed during the measurement period. For higher emission rates, large chambers with a triangular cross section and made from lightweight polycarbonate sheeting were used where necessary (*see* Figure 5). The dimensions of the large chambers were 4 m long by 1 m wide, covering an area of 4 m^2 with an enclosed volume of approximately

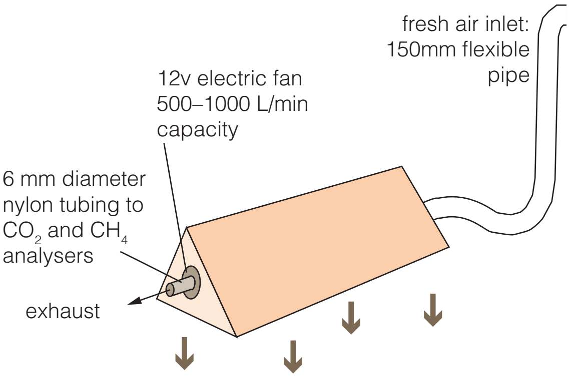

Figure 5 The large chamber used to measure gas flux (Carras and others, 2009)

1200 litres. The chamber was demountable, enabling it to be moved easily between test sites. The chambers were operated in a ‘dynamic’ mode where ambient dilution air was drawn through the chamber at a known rate by a fan fixed at one end of the chamber. The intake air was taken well away from emission fumes with a flow rate typically about 600 L/min. Concentrations of CH_4 and CO_2 were measured in the effluent from the chamber. In both the small and large chambers, sample air was withdrawn from the chamber at about 5 L/min and passed into a polyethylene manifold located inside a specially instrumented vehicle for testing for CO_2 and CH_4. A dilution system was used to cope with very high emission rates in which the sample air was mixed with high purity nitrogen in known ratios via two calibrated mass flow controllers.

4 Emitted gases

4.1 Hydrogen

Although it has been noted that hydrogen was emitted in self-heated mine workings, it was only in 1991 that Grossman and others (1991a) reported the production of molecular hydrogen at ambient temperatures as low as 40°C from coal oxidation. While studying coal oxidation in isothermal conditions in small batch glass reactors with four bituminous coals, which were commonly fired in Israeli power plants, a small amount of molecular hydrogen was detected. The group then further studied this topic with more coals and published the results in 1993, 1994 and 1995. Grossman and others (1994a) also reported that hydrogen emission does occur in industrial scale coal stockpiles.

Grossman and others (1993) tested five coals which had the same gross calorific value but different volatile matter and ash contents at temperatures of 55–95°C in a batch reactor. In all instances molecular hydrogen was detected in small but appreciable concentrations, $\geqslant$100 ppmv. Results in Table 1 show that the larger the amount of O_2 consumed, the higher is the concentration of H_2 evolved. This implies that H_2 is the product of an oxidation-related process. Labelling studies with deuterium oxide showed that more than 98% of the evolved molecular hydrogen originates from C-H bonds and not from moisture. This may indicate that the sources of H_2 are secondary reactions, which follow the oxidation process and the oxides are the source of production for molecular hydrogen.

Nehemia and others (1999) used the contamination of batch reactors with 3% volume equivalent of the gaseous atmosphere to check the source of the H_2 formed. Results in Table 2 show that the reactors contaminated with formaldehyde showed a big increase in the H_2 concentration. After studying in detail the mechanism of formaldehyde decomposition to yield hydrogen in the presence of bituminous coal, the authors proposed that formaldehyde is formed as a result of a low temperature coal oxidation process and undergoes an oxidative decomposition process catalysed by the coal surface to yield molecular hydrogen.

Cohen and Green (2009) also confirmed that the process by which molecular hydrogen is produced via atmospheric oxidation (temperature range 55–95°C) of bituminous coals is due to oxidative decomposition of formaldehyde, which is released from decomposition of different functional organic groups at the coal's surface. Formaldehyde is formed by cleavage of certain coal surface oxides that are then oxidised by coal-derived hydroperoxides to form the triatom heterocycle dioxirane (CH_2O_2). This compound subsequently decomposes to yield hydrogen and carbon dioxide.

Table 1 Effect of oxygen pressure upon hydrogen emission (Grossman and others, 1993)

Argon, %	Nitrogen, %	Oxygen, %	Hydrogen emitted, ppmv
100	–	–	80
–	100	–	34
–	80	20	342
–	60	40	443
–	40	60	583
–	20	80	954
–	–	100	1121

From 5 g USA coal, 75–250 µm, heated to 95°C in 95 ml reactor

Table 2 Effect of different atmospheres on hydrogen emission (Nehemia, 1999)

Atmosphere	Hydrogen, ppmv
N_2	<20
air	420
O_2	1870
air + 3% CO	410
air + 3% CH_4	390
air + 3% HCOOH	310
air + 3% CH_2O	7100

In 60 ml batch reactors containing 5 g coal in air heated at 95°C for 135 h

Research (Grossman and others, 1994a) has shown that H_2 emission is a fast process that occurs in under ten minutes from exposing coal to an O_2 containing atmosphere. The coal particle size did not affect H_2 emission. The results consequently proved that molecular hydrogen is produced on the surface of the macropores (if not micropores), which represent the major component of a coal's surface area. However, research by Cohen and Green (2009) has shown that although it is not linear, there is a correlation between coal particle size and yields of H_2 from formaldehyde. This may be because oxygen diffusion through the coal particles into the inner part of the sample is dependent on the sample size. Coal rank did not influence hydrogen emission. Results from tests investigating the effects of temperature on H_2 emission under different conditions were contradictory. The batch reactor simulation by Grossman and others (1993) confirmed that the production of hydrogen is a temperature and time dependent process (*see* Table 3). However, results from thermogravimetric flow reactor studies (Grossman and others, 1994a) showed that the amount of H_2 emitted at any given point of time was not directly dependent upon the temperature to which the coal had been heated or the temperature of the reactor (*see* Table 4). The field test results also showed that temperature had no effect on the emission of H_2 from coal stockpiles (*see* Table 5). Grossman and others (1994a) pointed out that, unlike batch reactors where relatively large quantities of H_2 (300–2000 ppmv) accumulate in the reactor prior to analyses, the simulation studies had online analyses of very low H_2 concentrations (2–10 ppmv). Additional work is needed before more convincing conclusions can be made concerning the temperature effect on H_2 emissions. In particular, attempts should be made to increase the sensitivity of the thermogravimetric-mass spectrometer studies which tended to show emissions of H_2 at much higher temperatures than the thermogravimetric-gas chromatography studies (190°C versus 50°C). Since the reactor conditions were similar for both systems, it is possible to conclude that the problem lies in the realm of present mass spectrometer levels of detection. For actual stockpiles, it is impossible to determine the mechanisms responsible for hydrogen emission due to the lack of parameter control.

Table 3 Rate of hydrogen emission as a function of time in an oxygen atmosphere (Grossman and others, 1993)

Oxidation duration, h	Temperature, °C	H_2 emission, ppmv	H_2 production rate, ppmv/h.g
12	55	25	0.090
48	55	370	0.335
168	55	1751	0.453
0	95	0	0
0.5	95	21	3.82
2	95	223	10.1
4	95	378	8.61
12	95	1347	10.2
24	95	2707	10.3

From US coal, <74 µm in 120 ml reactor, sample size 23 g at 55°C and 11 g at 95°C

Table 4 Thermogravimetric-Gas Chromatography results of H_2 emission from coal oxidation simulation studies (Grossman and others, 1994a)

Reaction temperature, °C	American	American 1	American 2	German
50	–	5.62	0	9.24
74	6.01	–	–	–
94	–	6.8	–	–
132	–	–	0	9.26
151	6.11	–	–	–
178	–	6.07	–	–
200	–	–	0	–
225	6.10	–	–	8.07
250	6.46	5.50	0	8.56

The heating rate for these experiments was 10°C/min, flow rate was 1.31 per min at 1 MPa pressure with an atmosphere of synthetic air (80% vol N_2, 20% vol O_2) except for American 2 which was performed in an inert atmosphere (100% vol N_2). Sample weight was 4.5 g except for American 1 which was 1.7 g

Table 5 H_2 and temperature monitoring at Ashdod coal terminal, Israel (Grossman and others, 1994b)

Coal type	Depth, m	Temperature, °C	H_2 emission ppmv
Columbian	1.0*	19.0	†
	0.2	59.6	†
	1.5	85.0	9812
	2.5	91.1	4.57
	4.5	89.2	483
American	0.2	44.0	111
	1.5	53.3	464
	3.0	36.0	932

All the coals had a bulk density of 850 kg/m^3 in the coal pile
* above ground
† not detected

These studies suggest that H_2 emission is an oxidation related mechanism and is therefore dependent on the amount of O_2 consumed by coal. Grossman and others (1993, 1994) indeed proved this suggestion with his experiment: no O_2, no H_2 emission; more O_2, more H_2 emission (*see* Table 4). As shown above, the amount of hydrogen produced from coal oxidation is quite small. Also hydrogen is a low molecular weight gas, which is lighter than air, so it is assumed that the hydrogen produced in the stockpile is dissipated. Despite this, hydrogen still should be taken into account when planning the transportation and storage of coal as it may accumulate in certain areas, especially in the areas where stockpiles are covered or in confined spaces. This may cause safety problems by forming explosive mixtures with air that could be a safety hazard. Attention should be paid to the fact that H_2 was detected in stockpiles at near surface level (111 ppmv at 0.2 m depth and 9821 ppmv at a depth of 1.5 m) as such significant molecular hydrogen concentrations will increase the potential of spontaneous combustion by lowering the self-ignition temperature.

4.2 Carbon oxides

It is well known that carbon dioxide is emitted from stored coal. Field experiments carried out by Grossman and others (1994b) and Kozinc and others (2004b) proved that carbon monoxide is emitted from coal stockpiles as well as carbon dioxide. Grossman and others (1994b) found quite a high concentration of CO (~6%) at a depth of 1.5 m within a stockpile, and a dangerous level of CO (400–600 ppmv) above the stockpile (1 m) at the Ashdod coal terminal in Israel. Kozinc and others (2004b) monitored gas emission from a coal stockpile at the Velenje coal mine in Slovenia. They also detected CO and CO_2 (*see* Table 6). Figures 6, 7 and 8 show that the increase and decrease of CO and CO_2 concentrations are connected with the daily temperature fluctuation. In addition, the concentrations of CO and CO_2 in the sampling tent are inversely proportional to the O_2 concentration. The authors conclude that the sources of CO and CO_2 emission from coal stockpiles are desorption and oxidation processes. This conclusion is supported by experiments discussed in Chapter 2.

As shown in Chapter 2, low temperature oxidation produces carbon oxides. Detailed reaction pathways responsible for the generation of carbon oxides have not been fully elucidated and remain controversial. Early work by some researchers suggests that the decomposition of chemisorption intermediates primarily generates CO, and the liberation of CO_2 comes from the decomposition of the carboxyl groups (–C=O(OH)–). However, this conflicts with the experimental findings which indicate no detectable production of CO at low temperature. Using an FTIR spectrometer, Gethner (1987) observed that the production of CO_2 and CO is a consequence of the decomposition of the carboxyl groups. More specifically, other researchers concluded that the decomposition of the carboxyl groups leads to the formation of CO_2 while CO is a result of the decomposition of carbonyl groups (C=O). Based on these early findings and their own experiments, Wang and others (2003c) proposed that the decomposition of chemisorption complexes (such as the unstable oxygenated intermediates) primarily generates CO_2 rather than CO. Consequently, during the initial stage of the experiment, CO mainly derives from the decomposition of the unstable chemisorption intermediates. The proposed reaction sequences proceeding during coal oxidation are shown in Figure 9. CO_2 is suggested to be generated by 1) the direct burn-off reaction; 2) the decomposition of the unstable chemisorbed intermediates; and 3) the decomposition of the stable oxygenated complexes containing –COOH groups. CO is produced by two independent reactions, namely the direct burn-off reaction and the decomposition of the stable oxygenated complexes containing –C=O groups.

Table 6 Evaluation of gas emissions calculated for the whole coal stockpile (Kozinc and others, 2004b)

Sampling time	Gas	Emissions in 24 hours from the ventilated tent	Emissions in 24 hours from the non-ventilated tent
9-12 June 2001	CO_2	1.3 t	1.1 t
	CH_4	3 kg	4 kg
	CO	0.2 kg	0.2 kg
22 June to 27 July 2001	CO_2	1.4 t	1.2 t
	CH_4	0.5 kg	0.4 kg
	CO	0.6 kg	0.7 kg
7-12 December 2001	CO_2	47 kg	57 kg
12-23 January 2002	CO_2	41 kg	45 kg

Average gas emissions were evaluated from the concentration of gases found in the sampling tents. For this evaluation the following data were used: surface of each tent ≈1 m^2 and stockpile surface ≈121,000 m^2 during June and July 2001 and ≈107,000 m^2 during December 2001 and January 2002

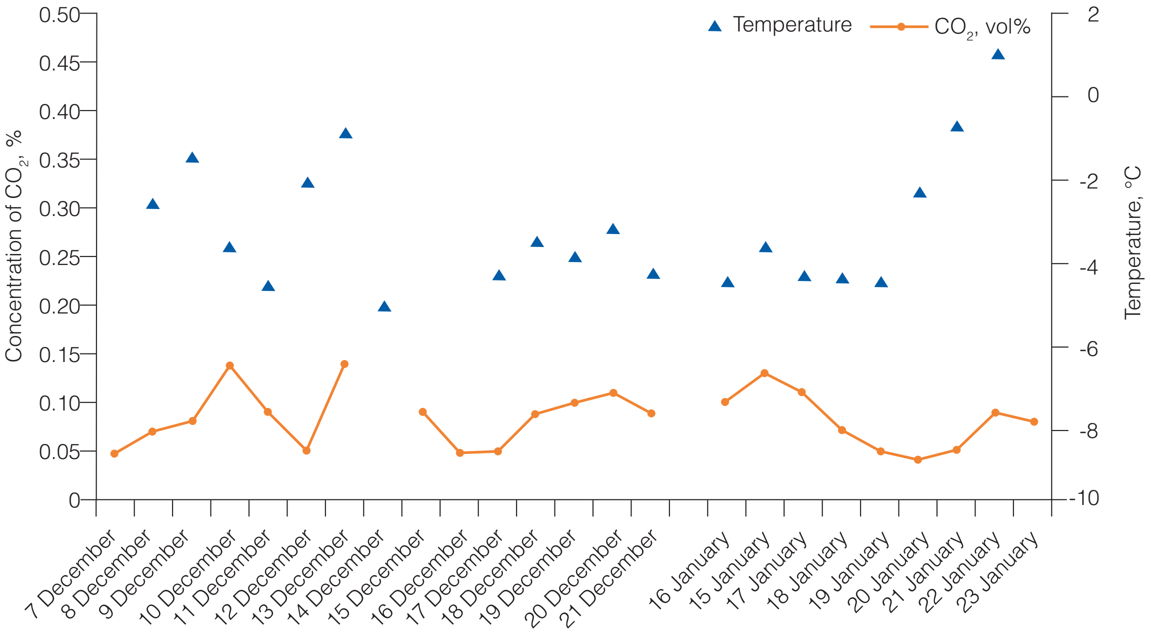

Figure 6 Concentration of CO_2 and temperature in December 2001 and in January 2002 from ventilated sampling tent in Velenje coal mine (Kozinc and others, 2004b)

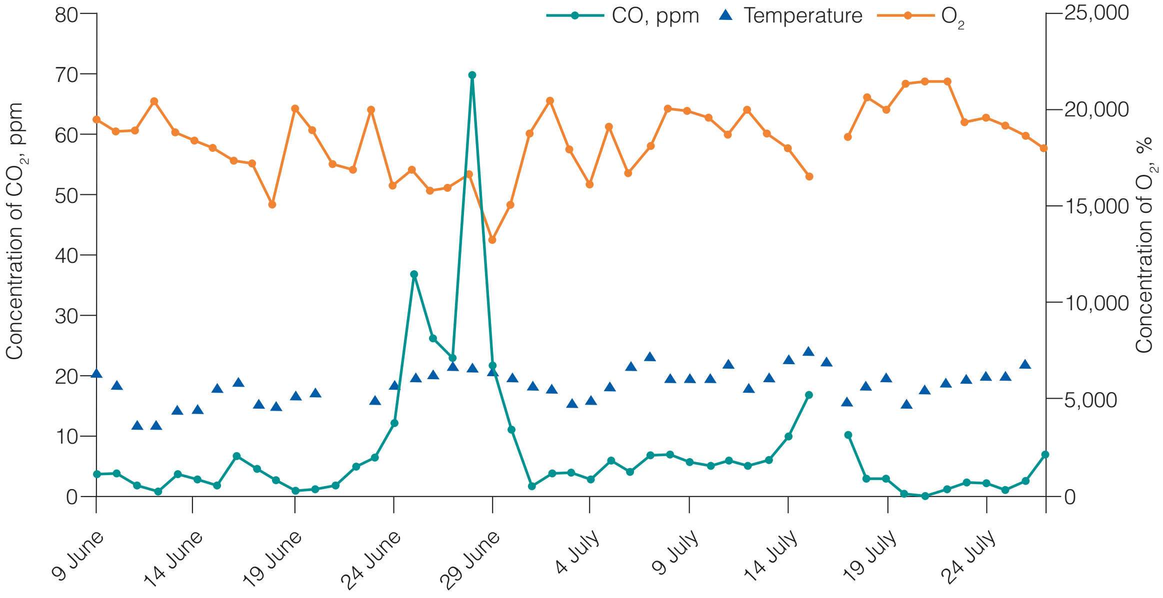

Figure 7 Concentration of CO, O_2 and temperature in June and in July 2001 from ventilated sampling tent in Velenje coal mine (Kozinc and others, 2004b)

However, the mechanisms detailed in Figure 9 tie the formation of carbon oxides only to a gas/surface reaction of the impinging oxygen molecule with the coal macromolecule surface. As the coal macromolecule also contains oxygen atoms, either as a part of the backbone of the structure (denoted as inherent oxygen, for example, ether groups C-O-C, carbonyl groups (C=O), or carboxyl groups (C=O(OH)–) or as chemisorbed water trapped in the pore structure, decomposition of these groups (denoted as surface oxides) might also contribute to carbon oxides formation. A third source of

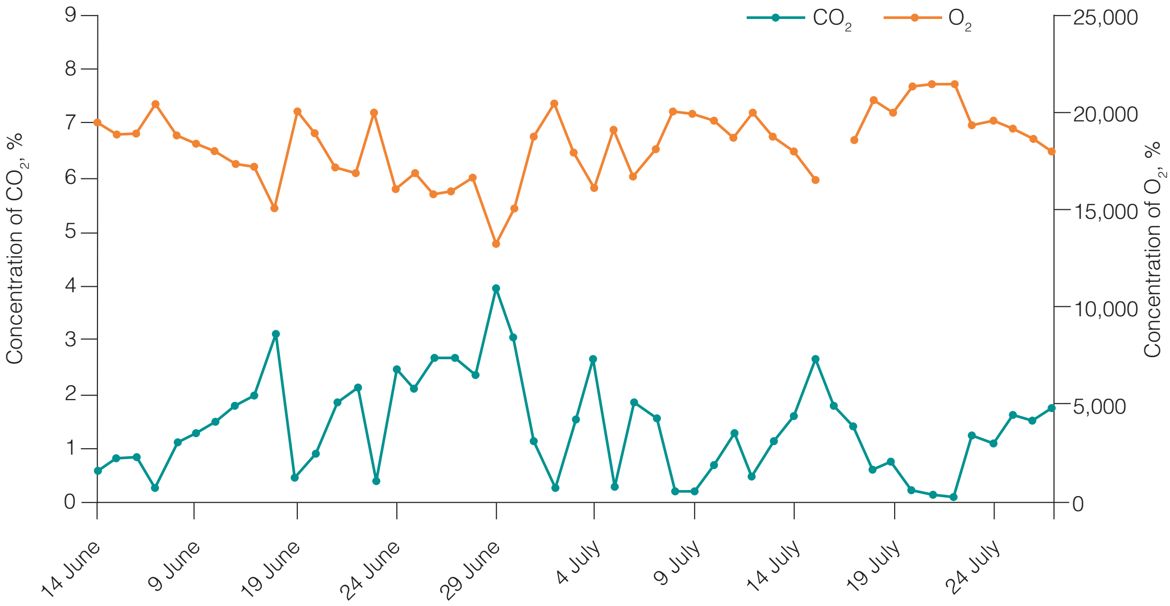

Figure 8 Concentration of CO_2 and O_2 in June and in July 2001 from ventilated sampling tent in Velenje coal mine (Kozinc and others, 2004b)

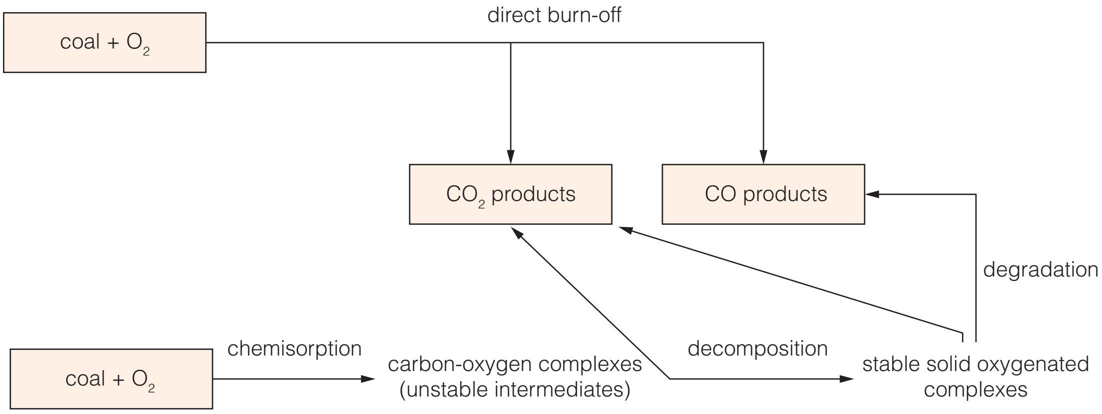

Figure 9 Proposed reaction pathways for production of CO_2 and CO in low temperature oxidation of coal (Wang and others, 2003c)

oxygen could possibly originate from the moisture (H_2O) in coal. However, water molecules are not expected to decompose at such a low temperature (30–150°C) to supply the oxygen atoms required for carbon oxide production. Research results from Aizenshtat and others (2010) have corroborated this option. For example, the amount of CO_2 emission from lignite as a result of low temperature oxidation exceeds the amount of O_2 which is consumed by the coal. The research group studied three types of coals (bituminous, subbituminous and lignite) in order to obtain a more accurate estimation of the amounts of carbon oxides formed at low temperature oxidation. They concluded that CO and CO_2 produced during weathering of stored coal resulted from two parallel processes: 1) thermal decomposition of oxygenated groups occurring at the coal macromolecule backbone (carboxyl groups -C=O(OH)- for CO_2 and aldehyde groups –(H)C=O for CO), and 2) chemisorption of atmospheric oxygen which subsequently decomposes to yield the carbon oxides. As mentioned in Section 4.1, coal catalysed the decomposition of formaldehyde to molecular hydrogen and CO_2.

Wang and others (2003a,b,c) observed from tests on Australian bituminous coal that the rate of

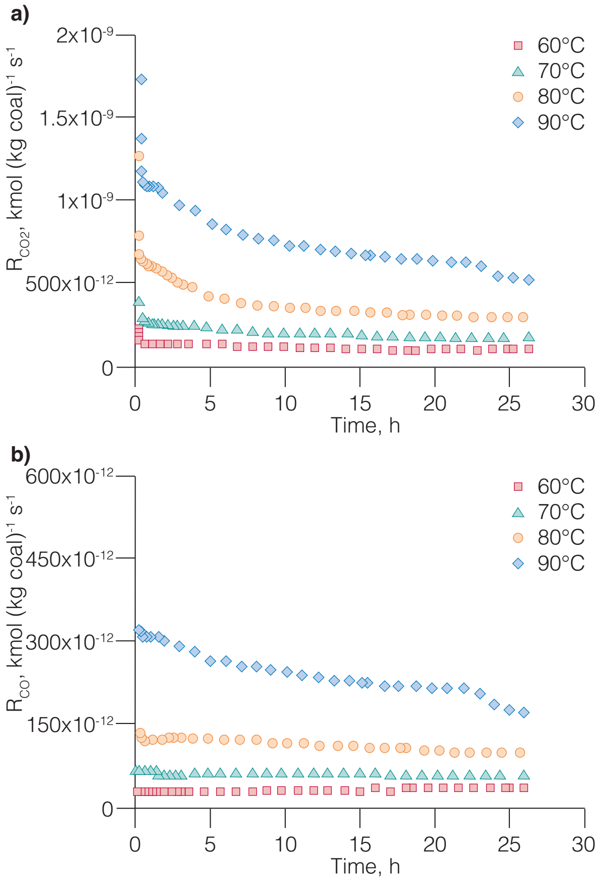

Figure 10 Formation rates of carbon oxides at various temperature (Wang and other, 2003c)

production of CO_2 decreases rapidly during the first few hours. After this period, the rate of production of CO_2 decreases at a slower rate. The rate of production of CO also undergoes a progressive reduction with time. Baris and Didari (2009) used high volatile Turkish bituminous coal to carry out tests on low temperature oxidation. Their results show that the rate of formation of CO_2 diminishes gradually with time. The rate of production of CO also exhibits similar behaviour. Although the observed decrease in the production rates of CO_2 and CO are not so rapid, a substantial decrease shown in their results supports the results of Wang and others. Yuan and Smith (2011) conducted experiments on low temperature oxidation in an isothermal oven to investigate the effect of ventilation on the CO and CO_2 emissions. The results indicate that CO was generated immediately after the airflow passed through the coal, while CO_2 was generated in a later phase under the experimental conditions. The concentrations of both gases increased to a maximum value quickly, then began to decrease. The maximum concentration of CO_2 was about five times the concentration of CO. The CO_2 concentration also declined more rapidly than the CO concentration. The oxygen consumption rate echos the production rates of CO_2 and CO. The results of Wang and others (2002) show that an elevated rate of oxygen consumption is present at the initial stage of oxidation, followed by a rapid decline in oxygen consumption. The rates of CO_2 and CO production decreased with time as well. Green and others (2011b) further prove that the emission of the carbon oxides stems from two major precursors:

a) decomposition of oxygenated groups from the inherent oxygen within the coal macromolecule structure. The rate of this process reduces appreciably with time;

b) decomposition of oxygenated groups formed by the reaction of atmospheric oxygen with the coal (defined as surface oxides). The rate of this process is not appreciably affected with time.

Temperature has a significant effect on the production of CO_2 and CO. As the temperature increases the levels of CO_2 and CO emissions also increase. The threshold for thermal decomposition of the oxygenated complexes to generate carbon oxides lies in the range 50–70°C. Results of laboratory and field tests all support this theory (Baris and Didari, 2009; Kozinc and others, 2004; Wang and others, 2002, 2003c). Figure 10 shows that a higher temperature enhances the rate of coal oxidation in the reactor resulting in a higher level of carbon oxides emission. It also shows the production of carbon oxides decreasing with time. For coal stockpiles, Kozinc and others (2004) reported the same trend (*see* Figures 6 to 8). In general, their results show higher concentrations of CO and CO_2 during spring and summer when the temperatures were high, and lower concentrations during autumn and winter when the temperatures were lower. The CO and CO_2 concentrations are inversely proportional to the O_2 concentration.

Results of a batch reactor test carried out by an Israeli research group (Aizenshtat and others, 2010; Green and others, 2011b) show that coal rank has a greater effect on CO_2 emission from low temperature oxidation than CO emission. The functional groups that are precursors to CO emission are much more stable than those that are precursors to CO_2 release, and do not appreciably depend upon coal rank. On the other hand, the amounts of CO_2 produced from low temperature oxidation are very much dependent on the coal rank, and the emission rate decreases as coal rank increases.

4.3 Hydrocarbons

Methane emission from coal seams has been reviewed in several IEA CCC reports (Smith and Sloss, 1992; Sloss, 2002, 2005). In coal, methane is primarily (>90%) stored as a monomolecular layer on the internal surface of the coal and is held in place by the hydrostatic pressure of the pore fluids in the surrounding strata. When the pressure changes, methane is released from coal. The release process is much faster once the methane has reached the surface of the coal. Although most of the methane is likely to be released within the mine, there is still a small amount of CH_4 emission from coal stockpiles. The *Guideline for Greenhouse Gas Emissions Reporting* published by the Ontario Ministry of the Environment (December 2010) describes how to report methane emission from coal storage piles. It provides methane source definition, reporting requirements, calculation methods, sampling, analysis, and measurement requirements, and procedures for estimating missing data.

Organic volatile emissions from coal stockpiles at the Ahsdod Coal Terminal are given in Table 7 (Davidi and others, 1995). Possible processes for the different hydrocarbon products that are released once the coal has been oxidised at low temperature have been proposed. One process might be desorption of gases that were trapped in the pores of the coal during the latter stage of the coalification process. Another process might be oxycoal surface reactions (*see* Chapter 2). The evolution of these hydrocarbons is most probably linked to the formation of coal surface oxides or the production of carbon dioxide.

Kozinc and others (2004) and Zapušek and others (2003) also measured organic hydrocarbon emissions from a stockpile in Slovenia (*see* Table 6). According to their observations, the concentration of CH_4 was under the quantification limit (100 ppmv) most of the time, except in June and July 2001 when it was quantified thirteen times. In June 2001, the test stockpile had just been formed. The evaluated emissions of CH_4 were higher in July when the average temperature was higher. This confirms that the main source of CH_4 was the desorption process. Zapušek and Marsel (1998) found that CH_4 is desorbed relatively quickly from coal; for example, a laboratory experiment showed that the concentration of desorbed CH_4 fell from 5% to less than 1% in approximately 30 hours.

Table 7 Results from test monitoring for hydrocarbons and temperature at Ashdod coal terminal, Israel (Davidi and others, 1995)

Site	Depth, m	Temperature, °C	CH_4, ppmv	C_2H_6, ppmv	C_3H_8, ppmv	C_4H_{10}, ppmv
A	0.3	30.9	71	4	0.5	–
	1.5	37.7	65000	3240	438	82
	4.0	36.3	75300	3380	397	72
B	0.3	39.8	7	–	–	–
	1.5	53.1	32600	1660	233	58
	3.0	44.0	85800	4000	548	141

A and B are two different sampling sites located on the windward side of the same coal pile approximately 50 m apart

It was observed (*see* Table 7) that the larger concentrations of hydrocarbons were not necessarily associated with areas of higher temperature or greater depth. However, the concentrations of the different saturated hydrocarbons decrease as the molecular weight increases. Undoubtedly, the gases that evolved in warmer parts of the stockpile may have migrated to colder areas, where due to the adsorptive properties of the coal they become less mobile. Thus in field testing, it is difficult to derive any mechanistic information concerning the evolution of organic hydrocarbons since the gas is mobile in nature and will not necessarily be concentrated near to where it is produced.

In order to gain more understanding of the hydrocarbon emission process, Davidi and others (1995) and Grossman and others (1991a, 1998) performed low temperature oxidation in small batch glass reactors with the purpose of simulating a coal pile 'hot spot'. At 95°C in air, methane emission exhibits two different processes (*see* Figure 11): a fast process that is prevalent during the first 15 hours and a much slower stage in the subsequent 140 hours. The first stage correlates to oxygen consumption. After approximately 15 hours, most of the oxygen has been consumed and a much slower rate is measured. This slower process is attributed to the slow evolution of coalbed methane that has been trapped in the pores of the coal. It is interesting to note that in a pure argon atmosphere, methane is also evolved although in smaller amounts, 100–140 ppmv compared to 300 ppmv in air. When coal was heated isothermally at 95°C in an argon environment, negligible amounts of ethane were detected. Ethane production appears to comprise two separate processes (*see* Figure 12), the first of which is fast and oxidation correlated. After all the oxygen has been consumed from the batch reactor, a slower process is observed. According to Grossman and Cohen (1998), propane follows the same trend. As shown in Figure 13, ethylene very much resembles the emission process of molecular hydrogen (*see* Section 4.1), namely it is produced only in the presence of oxygen and there is no slow emission process.

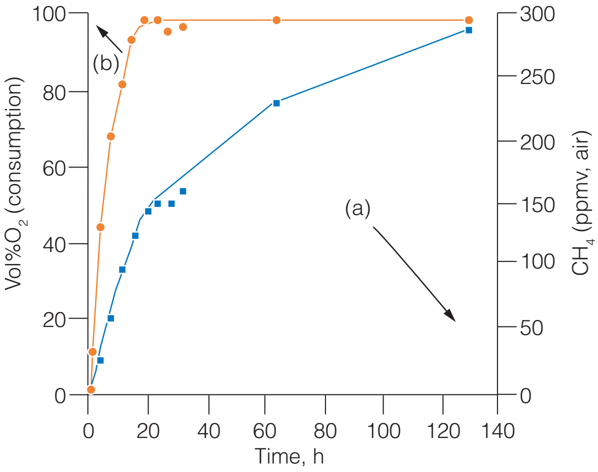

Figure 11 Time dependence of a) methane emission and b) oxygen consumption (Davidi and others, 1995)

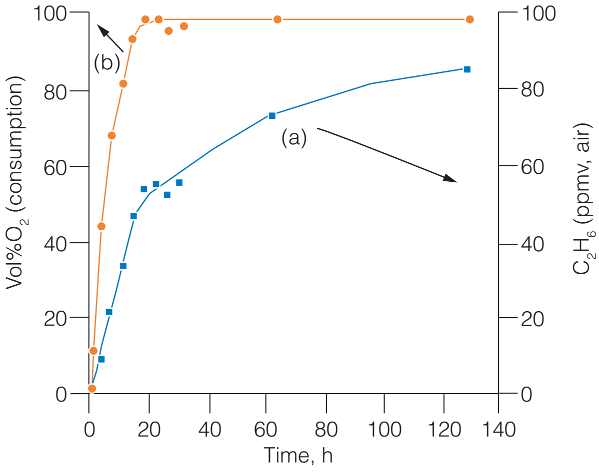

Figure 12 Time dependence of a) ethane emission and b) oxygen consumption (Davidi and others, 1995)

Coal particle size does not have a significant effect on the amount of hydrocarbons released. For the amounts of oxygen consumed, no appreciable ageing occurs and the decline of the emission process is only minor (Davidi and others, 1995).

Although Davidi and others (1995) concluded that the emission of organic materials was correlated to oxidation, except for methane, the two stages of the emission process they proposed conflicts with Zapušek and Marsel (1998) who found that gas desorption is a fast process.

4.4 Sulphur gases

Dimethyl sulphide (DMS), carbonyl sulphide (COS) and carbon disulphide (CS_2) were

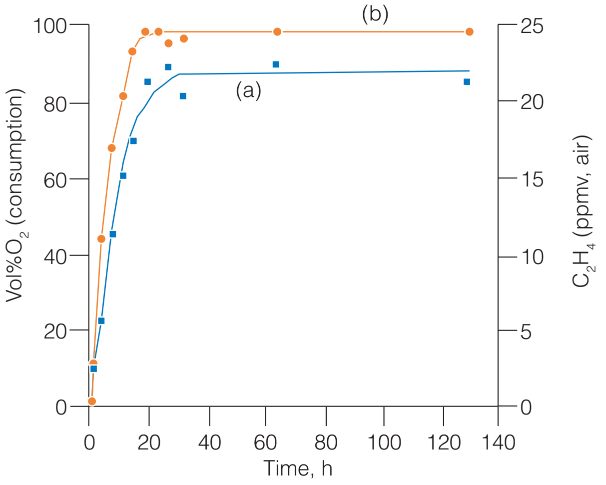

Figure 13 Time dependence of a) ethylene emission and b) oxygen consumption (Davidi and others, 1995)

detected from a coal stockpile at the Velenje coal mine by Kozinc and others (2004a). DMS was only quantified four times in the test which was expected, as the test stockpile was made approximately a year before the date of the sampling period. As has been reported by Zapušek and Marsel (1998), the source of DMS from coal is the desorption process and the concentration of DMS fell to below 1 ppmv in a few days. Zapušek and others (2003) monitored gas emissions from a lignite stockpile at the Sostanj power plant in Slovenia from June 2001 to the end of January 2002. DMS was also detected in June and July 2001 but its concentration was mostly below the quantification limit (1.0 ppmv). In June 2001 the test stockpile had just been formed and the detected concentration of DMS was mainly the result of the desorption process. However, the main reason for low DMS concentration could be its photodegradation.

COS and CS_2, on the other hand, were quantified almost every day in field tests carried out by Kozinc and others (2004a). Their results (*see* Figure 14) found that the concentration of COS and CS_2 followed the same trend as temperature although there is not a direct correlation between them. Zapušek and others (1998) suggested the source of COS and CS_2 in lignite is probably oxidation of pyrite. Kozinc and others (2004a) confirmed this by x-ray analysis. The content of sulphide sulphur was in the range 0.3-0.4%.

In order to confirm the formation of volatile sulphur compounds (VSC), Kozinc and others (2004a) incubated two coal samples in different atmospheres (nitrogen and synthetic air) and temperatures (25°C and 70°C). Results showed that COS concentration at both temperatures was approximately

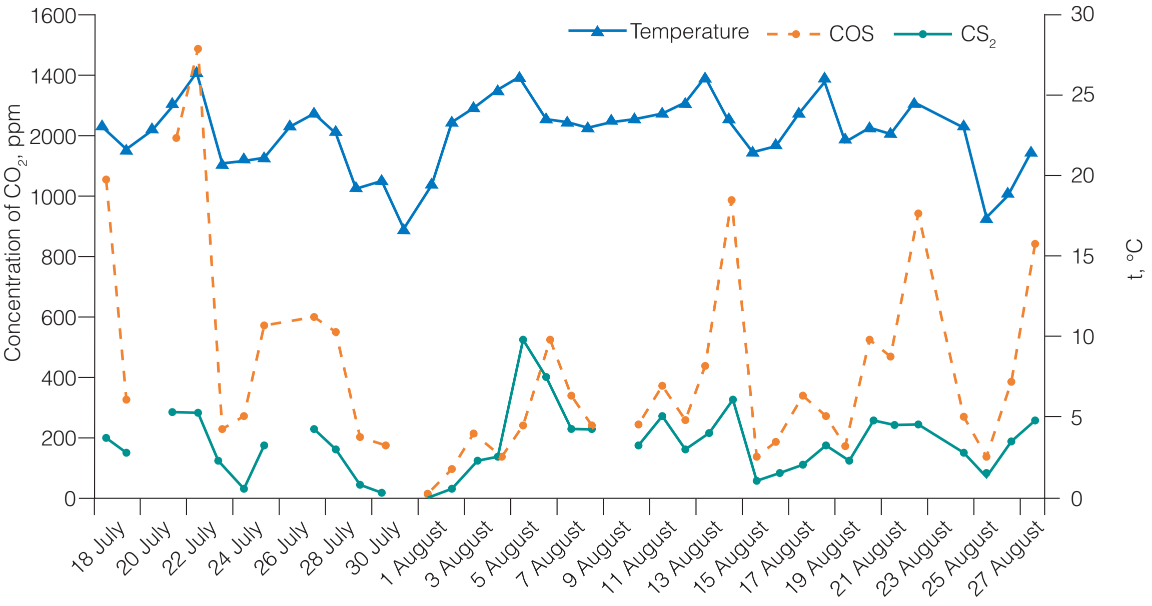

Figure 14 Concentration of COS and CS_2 versus temperature in gas samples from coal stockpile (Kozinc and others, 2004a)

seven times higher in the synthetic air than in nitrogen, confirming that the source of COS is oxidation. When the incubation temperature was higher (70°C), the increased CS_2 concentration in synthetic air compared to nitrogen showed that more CS_2 was formed in the presence of oxygen. A similar effect was observed in the stockpile, where at higher air temperatures, higher concentrations of COS and CS_2 were detected in the gas samples taken.

In summary, the concentration of COS and CS_2 are influenced by temperature, and oxygen is required for their formation. The presence of oxygen does not have an influence on the concentration of DMS in the same way as temperature does. This means that CO and CS_2 are emitted via an oxidation process and DMS by desorption.

5 Minimisation of emissions

After reporting the village air pollution incident mentioned at the beginning of Chapter 3, Freudenstein and others (2000) recommended the creation of a national database in England of companies and public bodies that have the necessary facilities to provide a rapid measurement of relevant airborne pollutants. A worrying fact to come out of this paper is that national data on the frequency of such incidents do not exist. An exhaustive literature search provided only two research groups directly working on gaseous emission from coal stockpiles: Grossman and others in the 1990s and Kozinc and others in the 2000s. Wang and others (2003a) also report that no work has been done on the prediction of gas emission from a coal seam or a stockpile. This has practical importance in risk assessment of the storage area and prevention of greenhouse gas emissions. More recently, Nalbandian (2010) could not trace work that has been undertaken to evaluate the quantity of gases emitted through the low temperature oxidation of the coal during transportation or whilst in a stockpile awaiting to be used in a power plant. There appears to be little information available in the public domain on gaseous emissions from coal during transportation, in stockpiles, in silos/bunkers or in pulverisers/mills. More work is needed.

However, greenhouse gas emissions from spontaneous combustion in opencast coal mines are recognised by the Intergovernmental Panel on Climate Change (IPCC). However, due to the lack of measurement methodology, they note in the most recent Guidelines for National Greenhouse Gas Inventories (IPCC, 2006) that these emissions are extremely difficult to quantify and it is unfeasible to include a methodology. Measurement methods for low temperature oxidation and uncontrolled combustion are still being developed. In 2005, a New Zealand government consultation paper, *Implementing the carbon tax*, questioned whether applying the carbon tax to coal stockpiles was necessary (Cullen and Hodgson, 2005). Should the answer be yes, development in measurement methods on gas emissions from coal stockpiles would be advanced.

But why is there a lack of research? Kozinc and others (2004b) calculated the emission of CO_2 from the Velenje coal mine stockpile and concluded that it was negligible compared to emissions from the Sostanj power plant. In addition, the author speculates that although they always exist, coal stockpiles are not part of a power plant's or coal mine's permanent assets. Unless a strict regulation is applied, management attention is usually on more valuable permanent assets.

According to International Energy Agency's *World energy outlook 2011*, coal demand is expected to continue to grow in the emerging economies for the next ten years, driven in particular by the power generation industry in China and India (IEA, 2011). More coal will be mined, transported and stored before being used to produce power. Consequently more coal stockpiles will be formed and more gaseous emissions from stockpiles will be produced. Now may be the time to invest more research into this topic and reassess whether it is necessary to regulate gaseous emission from coal stockpiles.

Although not significant compared to stack emissions, some gases emitted from coal stockpiles are toxic and explosive. It may be necessary to prevent these gas emissions in the future. Since the sources of the emissions are degassing and low temperature oxidation of coal, which are also the cause of self-heating and spontaneous combustion, methods to prevent the self-heating and spontaneous combustion of coal stockpiles are applicable. The methods are reviewed by Nelson and Chen (2007) and in other IEA CCC reports (Carpenter, 1999; Walker, 1999; Nalbandian, 2010).

Heat accumulation and an oxygen source are the keys to low temperature oxidation and the development of spontaneous combustion. Therefore, controlling ventilation is the main factor to prevent gaseous emissions and spontaneous combustion. Consequently, the following should be borne in mind when designing and constructing coal stockpiles:

- the amount of compaction;

- avoidance of particle size segregation;
- pile height;
- angle of the slope of the pile;
- shielding from the wind;
- reducing initial coal temperature;
- sealing the pile (in long-term storage)

Following these measures should reduce gas emissions from coal stockpiles.

6 Conclusions

Stockpiled coal undergoes low temperature atmospheric oxidation during storage in open air. If heat dissipation is insufficient then autogenous heating of the stockpiled coal will occur. It has been long known that coal beds are reservoirs of gases, such as carbon dioxide and methane. Gas desorption depends mainly on temperature and pressure. The temperature in the stockpile increases due to oxidation, and atmospheric pressure is lower than that in the coal beds. These conditions are ideal for gas desorption which emits gases to the atmosphere. Moreover, with temperature increases, the rate of oxidation increases. The rate of oxidation roughly doubles with an increase of 10°C in ambient temperature. The oxidation also yields gas emissions.

The multi-stage mechanism of low temperature coal oxidation is complicated and even today it is still not fully understood. The initial stages involve physical adsorption and chemical absorption of atmospheric oxygen. The next stage is the formation of surface oxide which then decomposes to produce low molecular inorganic gases, such as carbon oxides, hydrogen, water and low molecular organic gases, such as hydrocarbons (C_{1-5}).

There has been a limited amount of experimental work carried out on large-scale stockpiles, due to the expense and time-consuming nature of such work. A literature search could only find two research groups that have carried out field tests on gas emissions from coal stockpiles, one is from Ben-Gurion University of the Negev, Israel, and the other is from the Institute of Ecological Research, Slovenia.

The Israeli group developed a portable sampling system to monitor gas emissions from bituminous coal stockpiles at the Hadera power plant and Ashdod coal terminal. They detected CO, CO_2, hydrocarbons and hydrogen. Higher gas concentrations occurred in non-compacted stockpiles than partially compacted stockpiles and compacted stockpiles. This observation can be explained by the fact that uncompacted stockpiles have less restricted air flow and further proves that the emission of these gases is a low temperature oxidation process.

The second group used polycarbonate tents to collect gases from a lignite stockpile surface at the Velenje coal mine. They detected CO, CO_2, CH_4, DMS, COS and CS_2. Their results show that CO_2 emission was thirty times higher during spring and summer than during autumn and winter. CO also had the highest emissions during the summer. On the other hand, CH_4 and DMS both had the highest emission in June when the stockpile was first formed. This proves that the source of CO_2 and CO is from desorption and oxidation processes while CH_4 and DMS are mainly from desorption process. The concentrations of COS and CS_2 are influenced by temperature and oxygen, which means that they are the products of oxidation.

Gas emissions from coal stockpiles have not yet been regulated. However, the Intergovernmental Panel on Climate Change (IPCC) has recognised them. Due to the lack of work, the IPCC cannot nominate a measuring method. In fact, there appears to be very little information available on gaseous emissions from coal stockpiles. More data are needed to assess the emissions. Until more information is available, it would be difficult to establish a regulation or legislation on gas emissions.

Although gas emissions from coal stockpiles are negligible compared to coal-fired power plant emissions, caution should still be taken since some of the gases are toxic and explosive. This is especially important where the stockpiles are in enclosed areas. Some methods used to prevent coal self-heating and spontaneous combustion can be applied to reduce gaseous emissions from coal stockpiles.

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