# Propensity of coal to self-heat

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## Abstract

When coal is exposed to air it undergoes exothermic chemisorption of oxygen which is followed by formation of surface oxides and to some extent oxidation of the coal, resulting in emission of various gases (the most prominent of which are $CO_2$, $H_2O$ and CO). Large coal stockpiles, especially those stored for long periods, may develop hot spots due to self-heating. In some cases spontaneous combustion may result. The self-heating process depends on many factors including coal rank, temperature, airflow rate, the porosity of the coal pile, ash and moisture content of the coal, humidity as well as particle size of coal. Emissions of molecular hydrogen, carbon monoxide and low molecular weight hydrocarbons can also accompany the oxidation process. These processes raise environmental and economical problems for coal producers and consumers, who transport and store large coal piles. This report reviews the propensity of coal to self-heat and in some cases, self-ignite. It includes the methods of evaluating the propensity for coal to self-heat and it covers aspects including self-heating in stockpiles, during transit, storage in bunkers as well as in the mill itself. Methods for determining the conditions at which the coal pile could undergo spontaneous combustion in order to predict the safe storage time under set conditions and the influence of the factors contributing to the spontaneous heating are reviewed. The significance of the greenhouse gas emissions resulting from the oxidation during transport and/or storage, especially $CO_2$ are investigated. However there appears to be no emphasis in research work or published material specifically quantifying these emissions. Thus, the potential for future regulation to control these emissions by introducing cooler stockpiling environments or specific transport and bunkering modes remains unexplored. Methods currently used in safety management to avoid spontaneous combustion and/or to deal with fires due to self-heating are presented.

# Acronyms and abbreviations

| | |
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| CEN | Committee for European Standardization (Comité Européen de Normalisation) |
| CFD | computational fluid dynamics |
| CPT | crossing point temperature |
| DRIFT | diffuse reflectance infrared fourier transform |
| DSC | differential scanning calorimetry |
| DTA | differential thermal analysis |
| daf | dry ash free |
| Ea | Activation energy |
| FFPR | Fire-fighting piercing rod |
| F-K | Frank-Kamenetskii |
| FTIR | Fourier transform infrared |
| HGI | Hardgrove Grindability Index |
| HRRM | heat release rate method |
| IMCO | International Maritime Consultative Organisation |
| IMO | International Maritime Organization |
| IR | infrared |
| ISO | International Organisation for Standardisation |
| PRB | Powder River Basin |
| TG | thermogravimetry |
| TGA | thermogravimetric analysis |
| V/A | volume/surface ratios |
| WKE | Western Kentucky Energy |
| USBM | US Bureau of Mines |

# Contents

# 1 Introduction

As the most abundant fossil fuel in the world, coal accounts for ~40% of the electricity produced throughout the world. Coal-fired power plants release to the environment $SO_2$ and NOx, as well as $CO_2$ and $N_2O$, particulate matter, mercury and other hazardous air pollutants such as cadmium, arsenic, vanadium and various other acid gases. However, prior to firing in the plant boiler, the coal is stored on site either in stockpiles or silos/bunkers.

Spontaneous combustion, or self-heating, of coal is a naturally-occurring process caused by the oxidation of coal. Oxidation is a chemical change involving the valence (outermost) electrons of an element. During the oxidation process, the positive valence of an element ion is increased, or the negative valence of an element ion is decreased, resulting in a chemical change or breakdown of the compound. Using the oxidation process, a coal research scientist can check for impurities in coal and then prepare the coal to be burned 'cleanly'. However, natural oxidation of coal during transport, in stockpiles, bunkers and mills is uncontrolled and therefore can result in unwanted emissions, such as $CO_2$, and where coal is exposed to heat, spontaneous combustion may occur resulting in a variety of unwanted emissions and environmental issues.

Spontaneous combustion that leads to coal fires in power plants can cause major destruction. Unless handled correctly, the results can be catastrophic in both damage to power plant assets and, in a worse case scenario, the loss of human life.

Spontaneous combustion, or self-heating, is most common in low-rank coals and is a potential problem in storing and transporting coal for extended periods. Major factors involved in spontaneous combustion include volatile content, the size of the coal (the smaller sizes are more susceptible) and the moisture content. Heat build-up in stored coal can degrade the quality of coal, cause it to smoulder, and lead to a fire. The amount of heat emitted during coal combustion depends largely on the amounts of carbon, hydrogen, and oxygen present in the coal and, to a lesser extent, on the sulphur content. Hence, the ratio of carbon to heat content depends on these heat-producing components of coal, and these components vary by coal rank. The higher the oxygen content of coal, the lower its heating value. Typically the oxygen content increases in lower rank coals. For example, PRB coals have a 12% oxygen content where bituminous coals have around a 6% oxygen content. This inverse relationship occurs because oxygen in the coal is bound to the carbon and has, therefore, already partially oxidised the carbon, decreasing its ability to generate heat. However, the oxygen content in itself is not an indicator whether the coal is oxidised or not. There are tests and methods currently in use, and others under development, to evaluate the propensity of coal to self-heat in order to suppress and/or control spontaneous combustion.

This report reviews the propensity of coal to self-heat as well as methods of evaluating the propensity for coal to self-heat and in extreme cases self-ignite. It covers aspects including self-heating in stockpiles, during transit, storage in silos/bunkers as well as in the mill itself. Methods for determining the conditions in which the coal pile could undergo spontaneous combustion are reviewed. This is in order to predict the safe storage time under set conditions and the influence of the factors contributing to the spontaneous heating. The significance of the greenhouse gas emissions resulting from the oxidation during transport and/or storage, especially $CO_2$ were researched. However there appears to be no emphasis in experimental work or published material specifically quantifying these emissions. Thus, the potential for future regulation to control these emissions remains unexplored. None the less, the attempts to determine whether future regulation may be required to control these emissions by introducing cooler stockpiling environments or specific transport and bunkering modes are presented briefly. Methods currently used in safety management in real world applications are also presented.

# 2 Coal self-heating considerations

In this review, two main areas of coal production and utilisation are discussed in which uncontrolled burning can be a major concern. These are coal storage and, to a lesser extent, transport. The self-heating of coal is dependent on a number of controllable and uncontrollable factors. Controllable factors include close management in the power plant, of coal storage in stockpiles, bunkers and mills and management during coal transport. Uncontrollable factors include the coal itself and ambient conditions. Huitema (1999) describes the different storage systems in a coal-fired power plant.

Before coal burns openly, in a stockpile, silo or bunker, an unnoticed process of oxidation takes place. The natural oxidation of coal was the subject of a review by Davidson (1990). The chemistry of coal oxidation, that is oxygen consumption, oxidation products and reaction mechanisms are discussed in detail by Wang and others (2003a). In this process oxygen from the air reacts with the carbon in the coal and carbon dioxide is generated. This is an exothermic reaction, where heat is released. Normally, the heat is transported away by circulation of air which has a cooling effect. For conditions favouring spontaneous combustion the air supply needs to be high enough to support the oxidation, but too small for sufficient cooling. As a result the coal heats up. The phases or sequential stages involved in spontaneous combustion are shown in Figure 1. The temperature rises and at about 80ºC gases such as carbon monoxide (CO), carbon dioxide and water vapour are released. CO is an odourless gas, slightly lighter than air and has flammable limits in air. It is toxic by inhalation. Carbon dioxide is a greenhouse gas. Above a certain critical temperature the combustion begins. The grain size and the surface structure of coal may also influence its susceptibility for spontaneous combustion. In the centre of a large fire, temperatures of 1000°C and higher can be reached. Some factors that influence the spontaneous combustion of coal are:

- air-ventilation in the stockpile, silo/bunker;
- atmospheric conditions;
- coal quality: low carbon content and large amounts of volatile components support combustion;
- coal moisture content;
- particle size: the smaller the particles, the larger the surface area, the higher the risk.

Walters (1996) discussed the theory and practical implications of coal self-heating. Using analytical data from the late 19th century and combining it with modern predictive equations, the author demonstrated that the coal carried by sailing ships was extremely prone to self-heating and the situation was further aggravated by the conditions of the voyage. Spontaneous combustion incidences increased when sailing ships were replaced by coal-fired steam ships despite the reduction in voyage duration. However, as a result of the replacement of coal by oil as vessels' transport fuel, spontaneous combustion at sea was greatly reduced by the 20th century. Following the growth in the steel industry and the 1970s oil crisis, marine transportation of coal became widespread and in 1996 over 400 Mt of coal was transported in ships. In 2006, more than 570 Mt of steam coal was transported in the same manner. According to Walters (1996), with improved safety precautions in place and safer vessels, the percentage of incidents is small, but the large tonnage being shipped means that some coal cargoes are still prone to self-heating and therefore spontaneous combustion. Walker (1999) discussed the detection, prevention and control in coal transport by rail and sea.

The increasing international trade in both metallurgical and steam coal has led to renewed interest in the potential for spontaneous combustion to occur during transport, particularly by bulk carrier. This problem is becoming greater as the tonnage of lower-rank (subbituminous) coals transported by both rail and sea is increasing. This tendency exhibited by some coals to self-heat and result in spontaneous combustion, can preclude their widespread utilisation.

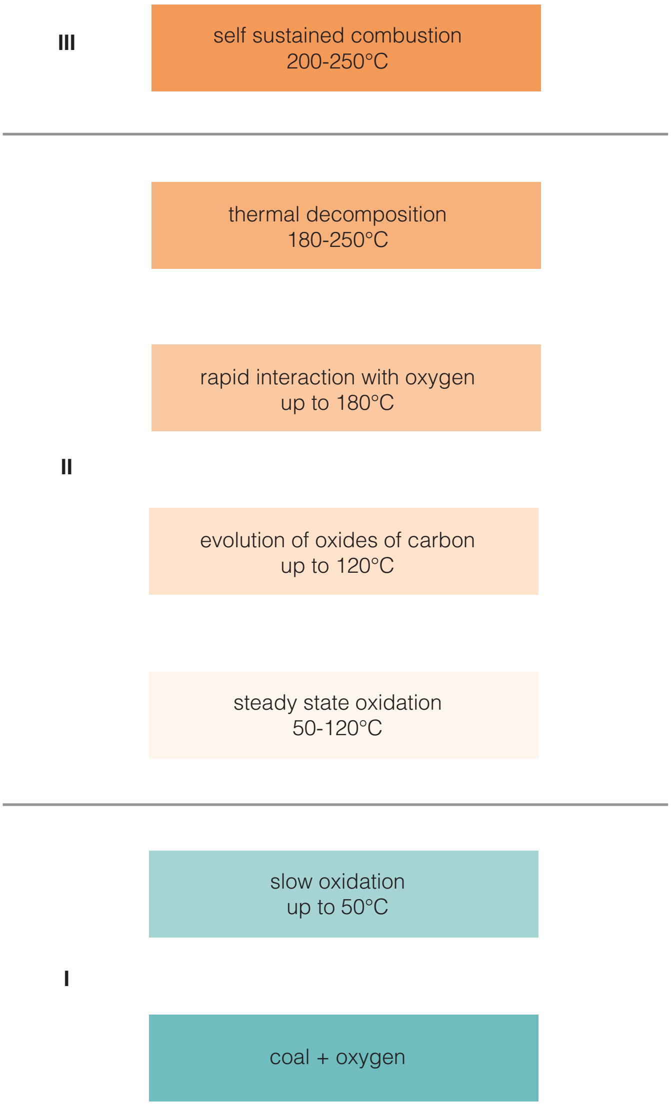


**Figure 1 The phases/sequential stages involved in spontaneous combustion** (Nijhof, 2007)

## 2.1 Burning process of coal

The amount of heat emitted during coal combustion depends largely on the amounts of carbon, hydrogen, and oxygen present in the coal and, to a lesser extent, on the sulphur content. Hence, the ratio of carbon to heat content depends on these heat-producing components of coal, and these components vary by coal rank.

Carbon, by far the major component of coal, is the principal source of heat, generating about 14,500 Btu/lb (~33 MJ/kg). The typical carbon content for coal (dry basis) ranges from more than 60% for lignite to greater than 80% for anthracite. Although hydrogen generates about 62,000 Btu/lb (~144 MJ/kg), it accounts for only 5% or less of coal and not all of this is available for heat because part of the hydrogen combines with oxygen to form water vapour. The higher the oxygen content of coal, the lower its heating value. This inverse relationship occurs because oxygen in the coal is bound to the carbon and has, therefore, already partially oxidised the carbon, decreasing its ability to generate heat. Variations in the ratios of carbon to heat content of coal are due primarily to variations in the hydrogen content (Hong and Slatick, 1994).

Combustion (oxidation) of coal can take place rapidly as in a furnace or slowly in a stockpile. If it takes place slowly, there is a degradation or loss of energy content and hence in the value of the fuel. Factors that influence spontaneous combustion and can lead to a fire include (McGraw Hill International, 2002):

- coal rank: low-rank coals are most susceptible because of their higher porosity;
- amount of surface area exposed to air;
- ambient temperature, with high solar insulation aiding it;
- the oxygen content of coal;
- the free moisture in coal;
- configuration of the coal stockpile; steep conical piles with coarse coal at the edges and fines near the top are more susceptible because they promote natural convection (chimney effect) and good air flow through the pile to support combustion as it develops.

In order to minimise self-heating and prevent spontaneous combustion, it is important to maintain a dry pile and compaction at regular intervals.

## 2.2 Properties that influence the propensity of coal to self-heat/combust

The self-heating of coal is due to a number of complex exothermic reactions as discussed above. Coal will continue to self-heat provided that there is a continuous air supply and the heat produced is not dissipated. Walker (1999) discusses self-heating of coal which results in uncontrolled fires in coal and coal wastes. Self-heating of coal and related materials using models, application and test methods was the subject of a study by Carras and Young (1994). The intrinsic coal properties that control the propensity for self-heating have been the subject of many investigations. Relationships between these properties and self-heating indices have been published in a number of studies including Beamish (2008), Beamish and Arisoy (2008), Beamish and others (2005) and Blazak and others (2001).

Following the development of a large database over seven years that included adiabatic testing of coals from Australia, New Zealand, Indonesia and the USA, Beamish and Arisoy (2008) present what they describe as the establishment of definitive relationships and trends for the effects of various intrinsic coal properties on self-heating rates and the identification of anomalous coals. They examine previously-held views on the effects of coal rank, type and inorganic constituents on coal self-heating properties. The authors consider that many of the published relationships do not hold true in terms of coal self-heating rates. However, they conclude that significant relationships exist between coal self-heating rate and intrinsic properties of coal rank, mineral matter composition and coal type. The relationship with coal rank is non-linear and can be expressed in the form of a third order polynomial for coals ranging in rank from subbituminous to low volatile bituminous. The effect of mineral matter on coal self-heating rates can either be in the form of a simple heat sink effect or a more complex physico-chemical inhibition of access to oxidation sites. McManus and others (1999) discussed in detail the influence of mineral matter on the self-heating of coals. These effects can only be determined by actual testing of the coal and hence a coal ply sampling strategy is recommended to obtain site specific data. Additional coal analyses such as ash analysis and coal mineral matter identification may be required to obtain a fuller interpretation of the self-heating rate data.

In the USA, the higher propensity for spontaneous combustion of the low sulphur, subbituminous, Powder River Basin (PRB) coal, compared to eastern and mid-western bituminous coal, represents a great threat to coal handling systems and personnel safety (Power, 1999). A combination of high moisture and high volatile content results in this condition and affects the collection system in three areas: collector housing design, dust disposal and duct design. Jones (1999) discusses the importance of controlling coal dust when firing PRB coal. Purutyan and others (2001) present fuel-handling considerations when switching to PRB coals. PRB coal degradation causes and cures are discussed by Hossfeld and Hatt (2005).

The property of coal to self-heat is determined by many factors, which can be divided into two main types, properties of the coal (intrinsic factors) and environment/storage conditions (extrinsic factors). Self-heating results in degradation of the coal by changing its physical and chemical characteristics, factors that can seriously affect boiler performance. The risk of spontaneous combustion during final preparation such as in bunkers and mills also presents concerns in some cases. The properties which influence the propensity of coal to self-heat are discussed in the following sections.

### 2.2.1 Volatile content

As stated above, many factors influence the oxidation process of coal and it is difficult to determine their relative effects by varying one factor while holding the others constant. According to Nelson and Chen (2007), a popular approach has been to test a variety of coals using some measurement of self-heating tendency and then apply a regression analysis on coal components such as ash content, calorific value, density, fixed carbon content, iron content (total), iron content (non-pyritic), moisture content, pyrite content, sulphur content (organic), sulphur content (total), volatile matter content and other components.

Smith and Glasser (2005a,b) studied the spontaneous combustion of carbonaceous stockpiles. In part I they presented the relative importance of various intrinsic coal properties of the reaction system, and in part II they discussed the factors affecting the rate of the low-temperature oxidation reaction. In part II, they measured the initial rate of oxidation for 70 coals at an ambient temperature of 23ºC and pressure of 625 mm Hg. The temperature and pressure chosen represented typical conditions at South Africa's main coal shipping terminal. A regression analysis was carried out to relate the measured initial rate of oxidation, as determined on an ash free basis, for these 70 coals to their composition, as determined by petrographic, proximate and ultimate analyses. Petrography is the microscopic study of rocks, minerals or man-made materials. Proximate analysis of coal essentially involves the determination of ash, moisture, volatile matter and fixed carbon using standard specified procedures and provides a first hand idea of coal properties and behaviour. Ultimate analysis of coal involves the determination of carbon, hydrogen, nitrogen, sulphur and oxygen content. The authors found that the most significant regressor was always volatile matter followed by the inherent moisture content of the coal.

Smith and Glasser (2005b) also concluded that adsorption of water vapour does not in itself compete with the low-temperature oxidation in terms of 'heat generation,' but appears to speed up the oxidation rate, and possibly plays a catalytic role. The effect of the moisture content of the air on the spontaneous heating process was dependent on coal rank and temperature. The same conclusion was reached by Smith and Lazzara (1987) in a report of investigations for the US Bureau of Mines (USBM), which was founded in 1910 and was closed in 1995. However, in that report, the effect of water vapour was not considered and only coal oxidation was simulated (Yuan and Smith, 2009). Although many studies have identified the importance of the regressors's volatile matter and the inherent moisture content of the coal in its spontaneous combustion, in contrast, some studies found no correlation between volatile content and tendency for self ignition for German coals (Nelson and Chen, 2007).

Inherent and inorganic matter in coal influences its low-temperature oxidation. The critical ambient temperatures of acid-washed and water-washed coals are higher than that of raw coal, indicating that removal of the inherent inorganic matter from coal reduces its propensity to self-heat. When the critical ambient temperature of the acid-washed coal is used as a baseline, additives are identified as inhibitors or promoters if they lower the critical ambient temperature. The effect of the additive, whether a promoter or inhibitor, does not depend on the method of application. For example, Nelson and Chen (2007) report that copper acetate was found to have a stronger promoting influence on self-heating when it was ion-exchanged into the coal than when it was bulk mixed. The lower reactivity of the ion-exchanged coal was reportedly due to its significantly lower surface area and micropore volume. The change in surface area and volume was due to the absorbed $Cu^{2+}$, which provided a resistance to oxygen diffusion within the coal pores and reduced the number of available active sites. Wet-mixing potassium acetate into the coal resulted in a lower surface area than when the additive was ion exchanged into the coal. Where calcium acetate loading was increased, the critical ambient temperature remained unchanged although its inhibiting effect was noted as stronger when the additive was bulk mixed with the coal. The critical ambient temperature decreased as the loading of sodium acetate increased. The inhibiting effect of calcium acetate and sodium acetate are, according to Nelson and Chen (2007), mainly physical in nature; the additive increases resistance to oxygen diffusion by blocking the coal pore structure. The inhibiting/promoting effect of potassium chloride was also enhanced by an increase in additive loading.

The total surface area of a coal particle is given by the sum of its external and internal surface areas. The former is insignificant for particles with a large effective internal surface area. Conversely, for particles with low effective internal surface areas, the external surface area plays a key role during low-temperature oxidation of coal. The internal surface area of a particle depends upon its size, structure and porosity. Smaller coal particles have a larger surface area per unit volume of the particle and a lower diffusional resistance. According to Nelson and Chen (2007), other factors being equal, this means that smaller particles have a higher oxidation rate and release more heat than larger particles. Particle size is therefore an important factor in determining whether self-heating leads to spontaneous combustion.

Studies have shown that the propensity for spontaneous combustion increases as the coal particle size decreases. In addition to the increased oxidation rate of smaller particles, the rate of heat transfer between particles increases as their size decreases. The rate of oxidation increases with decreasing particle size until a critical diameter is reached. The critical diameter corresponds to a size at which oxygen penetrates the particle without experiencing any mass-transfer resistance. It depends upon factors such as the reaction conditions and the porosity of the coal and varies significantly between coals. In addition to changing the reaction rate, the particle size also affects the permeability of a stockpile. Nelson and Chen (2007) state that it has been suggested for stockpiles, the permeability exerts more control on the overall reaction rate than particle size. The relationship between particle size and permeability accounts for the greater tendency to self-heat in stockpiles in which segregation of coal particles has occurred, that is the larger particles allow more air to enter the stockpile, which reacts with the smaller particles that have a higher surface area (Nelson and Chen, 2007).

Other properties of coal which affect its tendency to self-heat include rank, heat capacity, heat of reaction, the oxygen content of coal and pyrite content. As stated above, the propensity of coal to self-heat and spontaneously combust tends to increase with decreasing rank. Thus, lignites and subbituminous coals are more prone to spontaneous combustion than bituminous coals and anthracites. Fei and others (2007) compared the spontaneous combustion behaviour of as-mined brown coal with a range of dried coal products. Their findings indicated that provided the iron content is limited, the dried products are not much more likely to combust spontaneously than raw brown coals. The science of Victorian brown coal (Australia) including structure, properties and consequences for utilisation was the subject of a textbook edited by Durie (1991). Li (2004) discusses advances in the science of Victoria brown coal. Both publications discuss the low temperatures oxidation and self-heating of Victorian brown coals and the use of experimental and model studies of self-heating and ignition of these coals. Factors influencing the spontaneous heating of low-rank coals were the subject of a review by Jones and Vais (1991).

Nelson and Chen (2007) state that it needs to be reinforced that the relationship with rank is a tendency, not an absolute fact. However, as risk decreases, moisture content, oxygen content and internal surface area of a coal increase. As a result, oxidation rate is enhanced and the propensity for the coal to self-heat is increased. Heat capacity and heat of reaction differ greatly depending on the coal type/rank. However, coals with higher oxygen content have a higher self-heating capacity. As discussed above, the presence of inorganic impurities in coal can promote self-heating. Pyrite ($FeS_2$) is known to enhance the risk of spontaneous combustion by accelerating the reaction process. Pyrite acts in two ways. It first catalyses the oxidation reaction then, in moist air, pyrite provides secondary heat and accelerates the self-heating process (Nelson and Chen, 2007).

## 2.2.2 Moisture and humidity

The temperature of coal increases due to self-heating until a plateau is reached, at which time the temperature is temporarily stabilised. At this point, heat generated by oxidation is used to vaporise the moisture in the coal. Once all the moisture has been vaporised, the temperature increases rapidly. On the other hand, dry material can readily ignite following the sorption of water. Thus, dry coal in storage should not be kept in a damp place because this can promote self-heating (Nelson and Chen, 2007). Therefore, the authors recommend that dry and wet coal be stored separately.

Under normal circumstances, coal in a stockpile contains moisture that is in equilibrium with the humidity of the surrounding atmosphere. Therefore, there is no heat transfer due to adsorption and desorption. However, under non-equilibrium conditions this is no longer the case, and adsorption and desorption processes have a strong controlling effect. According to Nelson and Chen (2007), this was first realised in the 1950s. When dry air flows over moist coal, desorption of water occurs. The endothermic process decreases, or restricts, the coal temperature. On the other hand, when moist air flows over a dry coal, adsorption of water occurs. This is an exothermic process and it releases the heat of wetting, which is about 2261 J/kg ($H_2O$). This can increase the coal temperature and enhance self-heating. Heat released by water adsorption is particularly significant for dry coals.

In 2005, Lohrer and others carried out a study on the influence of liquid water and water vapour on the self-ignition of lignite coal. The study included experiments and numerical simulation. They found that water, in a liquid or vapour state influences the self-heating process in coal in that extra heat is generated due to condensation and wetting of the coal. Consequently, a subcritical deposit of a dry coal can become supercritical if the humidity increases. Experiments with German lignite consisting of two different particle size fractions showed that a moist atmosphere led to a significant increase in temperature. Where the surrounding temperature is slightly below the self-ignition temperature of the dry coal, the threshold to ignition could be passed. In addition, further experiments showed that wetting can also result in self-ignition of the lignite. A numerical model was also created to describe the effect of self-heating until ignition of the coal including transportation of moisture. The simulated values agreed with those obtained with the experiments (Lohrer and others, 2005a). Lohrer and others (2005b) also studied the self-ignition of coal under various ambient conditions.

The moisture contained in coal may be bound to active sites on the surface of the particles or it may be loosely bound filling a portion of the coal pores, known as free water. The mechanisms by which moisture content affects self-heating include the following (Nelson and Chen, 2007):

- heat sink: when water is present, the heat released by oxidation is used to evaporate the moisture. Once the moisture in the area has evaporated, self-heating starts to occur;
- prevention of oxidation by chemical occupation of active sites: the adsorption and desorption of water changes the number of active sites that are available for the oxidation process to occur. Moisture desorption increases the number of active sites available for oxidation, thus increasing the oxidation rate;
- prevention of oxidation by reducing access to smaller pores: adsorbed moisture can provide a resistance to oxygen diffusion within the coal pores. Therefore, removal of this water exposes more surface area for oxidation, increasing the oxidation rate;
- prevention of oxidation by physical occupation of active sites: in areas of the coal matrix where free water is present, the oxidation rate becomes negligible because, before oxidation can occur, oxygen has to first dissolve in the water and then to diffuse to an active site. The solubility of oxygen in water is low and the diffusion rate of oxygen in water is four orders of magnitude lower than that of oxygen in air.

At temperatures above 70ºC, the oxidation of coal occurs more rapidly in dry rather than in moist air. This may be linked to the change in the mechanism of coal oxidation that occurs at about 70ºC. Below 70ºC, acid functions and peroxides are generated during coal oxidation and a higher moisture content is thought to promote these functions. At higher temperatures, peroxides form only transiently or not at all. Thus, it is possible that humidity plays a promoting role at lower temperature and an inhibiting role at higher temperatures (Nelson and Chen, 2007).

In general, PRB coal has between 20% and 30% water compared to 10% for a mid-western bituminous coal. The presence of water vapour does not pose problems in the dust collection system until the dew point is reached. Dew points in the dust collection airstream generally occur because of changing weather conditions, space heating of coal handling structures or differences in temperature of the coal versus the ambient air (Jones, 1999).

Blazek (2001) discussed the influence of coal oxidation and moisture on the spontaneous combustion of coal. The author considered that proper stockpile formation that limits the introduction of oxygen into the pile is critical in mitigating spontaneous combustion. Stockpile design and construction measures include (Blazek, 2001):

- avoidance of particle segregation as segregation encourages introduction of air. Drop heights at the stacker should be minimised to control segregation;
- proper pile compaction as compaction reduces air movement within the pile. Dense compaction can be achieved by compacting the coal layers. The pile should be contoured to provide adequate rainfall runoff and minimise erosion of the sides;
- elimination of potential ignition sources;
- proper pile height. For short-term storage without compaction a maximum pile height of 27 ft (~8.23 m) for fine coal is recommended;
- proper side slope angles. Shallow pile angles (15–30º) allow compaction equipment to work safely. Steeper angled piles are more prone to spontaneous combustion;
- shielding from the wind. A greater pile slope creates greater wind resistance, forcing air into the pile. Shielding the windward side of the pile minimises air movement through the pile. Spontaneous combustion typically occurs on the windward side of a pile. Mathematical modelling supports these observations;
- reducing initial coal temperature. Higher initial coal temperatures reduces the amount of time required to reach critical temperatures where spontaneous combustion accelerates rapidly. It is not recommended to store coal above 95ºF (35ºC) without compaction and a pile sealer;
- sealing the pile. Pile sealers and encrusting agents minimise air ingress and air movement in a pile.

Other practical, preventative measures to minimise the occurrence of spontaneous combustion listed by Blazek (2001) include:

- coals of different rank and propensities to spontaneous combustion should not be stacked together;
- differently sized coals should not be stacked unless fines content is sufficient to fill void spaces;
- weathered and fresh coals should not be stacked together;
- wet or partially wet coals should not be stacked together with dry coals;,
- run-of-mine coals and washed coals should not be stacked together;
- the storage site should be free of debris including combustible materials such as timber;
- a solid pile base without uncompacted material is critical to prevent air infiltration;
- the pile base should be contoured such as to allow for proper water drainage away from the pile. Drains should not extend under the pile as these can facilitate air entry into the pile;
- external heat sources such as steam lines or sewer lines should not run under the pile;
- the use of proprietary dust suppressants must also be reported to reduce the oxidation of individual coal particles.

Blazek (2001) concluded that research undertaken at the University of Wyoming (USA) that attempted to tie together much of the past research into a series of mathematical models could be used to predict the likelihood of spontaneous combustion. Parametric analysis with these models indicated that parameters such as pile slope, the availability and movement of air through the pile, material segregation, coal reactivity, particle sizing, temperature and moisture play important roles in the spontaneous combustion of coal in stockpiles.

## 2.3 Spontaneous combustion of coal

Spontaneous combustion means an oxidation reaction without any externally applied heat from a spark or a pilot flame, so that the departure of the internal temperature profile from being flat is due entirely to the material's own heat release by reason of chemical reaction (Querol Aragón and others, 2009).

Combustible matter reacts with the oxygen in the air at ambient temperature releasing heat. Under certain conditions the heat energy, due to the self-heating propensity of the matter, would accumulate and may lead to spontaneous combustion. Although at ambient temperature the reaction may be very slow, when heat accumulates the temperature increases and according to the Arrhenius Law the reaction rate will increase exponentially (Querol Aragón and others, 2009):

$$v = c_r \,.\, c_o \,.\, A \,.\, e^{\frac{-Ea}{RT}}$$

Where: v = reaction rate
$c_r$ = combustible concentration (kg/m$^3$)
$c_o$ = oxygen concentration
A = Arrhenius Frequency Factor (s$^{-1}$ or s$^{-1}$ C$^{1-n}$)
Ea = activation energy (kJ/mole)
R = universal gas constant = 8.314 J mole$^{-1}$K$^{-1}$
T = temperature (K)

According to Querol Aragón and others (2009), the problem is a heat balance, involving the heat produced inside the bulk material and the heat loss to the surroundings. The balance is decisive as to whether a steady state temperature is reached at a slightly higher temperature level (that is, heat loss is larger than heat production), or whether the temperature in the bulk material will continue to rise until it self-ignites (that is, heat production is greater than heat loss). The most important parameters in heat balance and therefore self-heating are particle size, quantity of reactive surface molecules, gross calorific value, heat conductivity, geometry and dimensions of the bulk material, heat transfer coefficient on the outside surface of the material, its size, ventilation and compactness.

Querol Aragón and others (2009) discuss experimental techniques used at laboratory scale for characterisation of the propensity of coal to self-heat. The different techniques they used are grouped as classical techniques, thermal analysis, activation energy and isothermal heating. The different techniques are presented here briefly but discussed in detail in Chapter 4.

**Classical techniques** include minimum ignition temperature on a layer, minimum ignition temperature in a cloud, ignition temperature of emitted volatile matter and Maciejasz Index (oxidation reaction by means of hydrogen peroxide attack). In minimum ignition temperature on a layer, a 5 mm sample layer is heated to a defined temperature and the temperature of the sample is registered. The test is repeated at several temperatures with new samples of the same material until the sample ignites. The minimum temperature at which the ignition occurs is known as minimum ignition temperature on a layer. The minimum ignition temperature in a cloud is determined by the introduction of a dust cloud in a preheated oven. The minimum temperature of the oven at which flames are observed is called minimum ignition temperature in a cloud. In ignition temperature of emitted volatile matter, a sample is heated until its temperature reaches 300ºC. At which point an ignition source is applied to the volatile matter of the sample and the appearance of flames is observed. This provides a good assessment for organic products that are flammable, such as coal, which makes them hazardous. The Maciejasz Index measures the required time (t) to produce a temperature increase of 65 K in a sample when it is bombarded with hydrogen peroxide. The Maciejasz Index is calculated as IM = 100/t. It determines the susceptibility of the sample to self ignite due to the oxidation of some compounds in the substance, for instance pyrites in coal. This method is used frequently for coals, especially where the sulphur content of the coal is high (Querol Aragón and others, 2009).

**Thermal analysis**, which comprises thermogravimetry and differential scanning calorimetry. The first yields combustion induction temperature, the maximum weight loss temperature and the increase in weight at the beginning of the heating process as typical parameters. In thermogravimetric analysis, the weight of the sample is measured as a function of its temperature. This is a very sensitive technique as changes in the weight of the order of micrograms can be registered. The most significant parameters are combustion induction temperature, maximum weight loss temperature and increase in weight at the beginning of the heating process. Figure 2 shows a thermogravimetric analysis test results highlighting characteristic points. The weight of the sample is plotted on the Y-axis and the temperature on the X-axis. Standard thermogravimetric analysis in air flow produces a characteristic curve for the loss of weight of the sample when heated at a predetermined rate. The reaction lasts a long time, so it is not easy to assign a definite temperature for that oxidation. When air is replaced by oxygen (thermogravimetry in oxygen flow), the reaction is much faster and a unique value of temperature can be obtained. This value has been used for comparative purposes between different coals to establish a graduation of the reactivity to the oxygen reaction. Figure 3 compares thermogravimetric analysis with air and oxygen showing the differences in the results obtained. The results of the thermogravimetric analysis in Figure 4 illustrate that the characteristic temperature varies with different coals. A number of coals from different parts of the world and different ranks were included in the analysis. Differential scanning calorimetry provides the minimum temperature at which the exothermic reaction begins, the maximum temperature reached during the exothermic reaction and the temperature at which the fast exothermic reaction commences. The sample in differential scanning calorimetry is placed in a crucible and heated at a regular rate that is

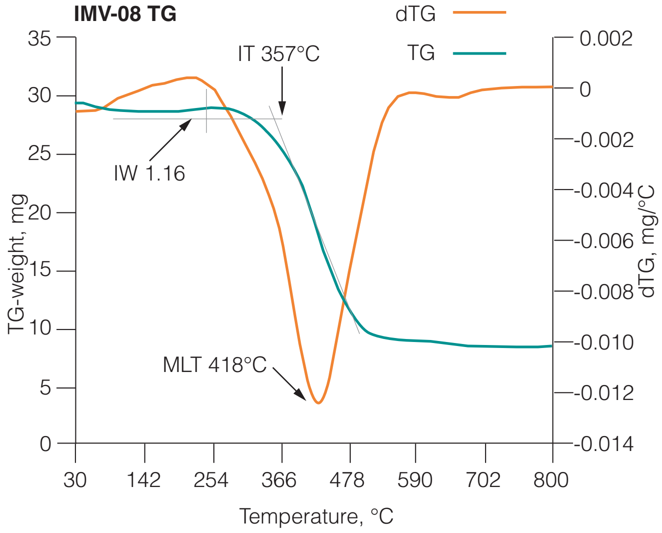


**Figure 2 Thermogravimetric analysis test results highlighting self-heating characteristic points** (Querol Aragón and others, 2009)

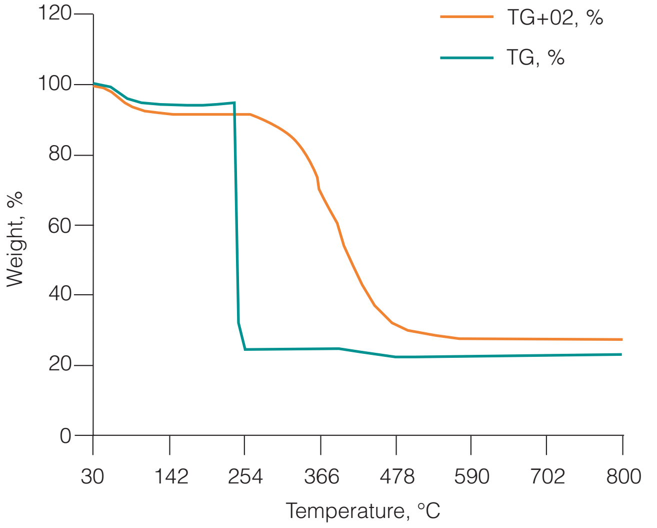


**Figure 3 Spontaneous combustion comparative thermogravimetric analysis results with air and oxygen** (Querol Aragón and others, 2009)

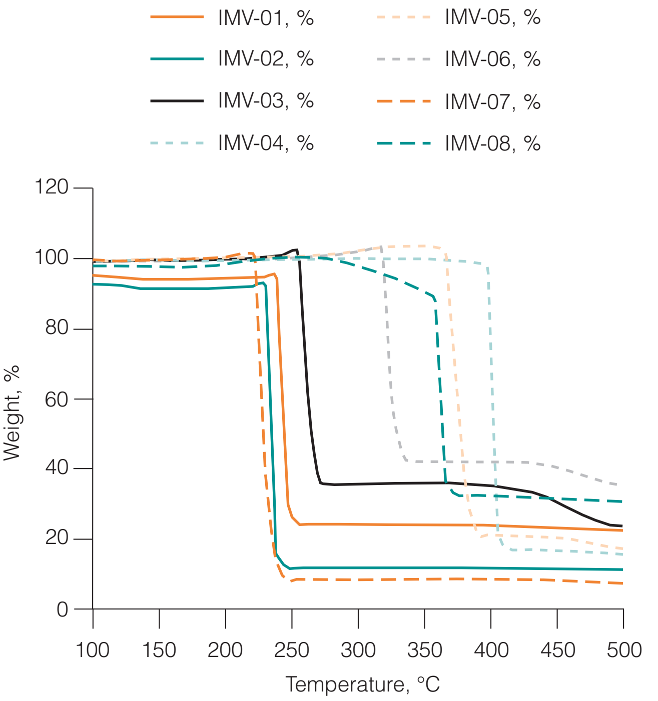


**Figure 4 Thermogravimetric analysis with oxygen only test results** (Querol Aragón and others, 2009)

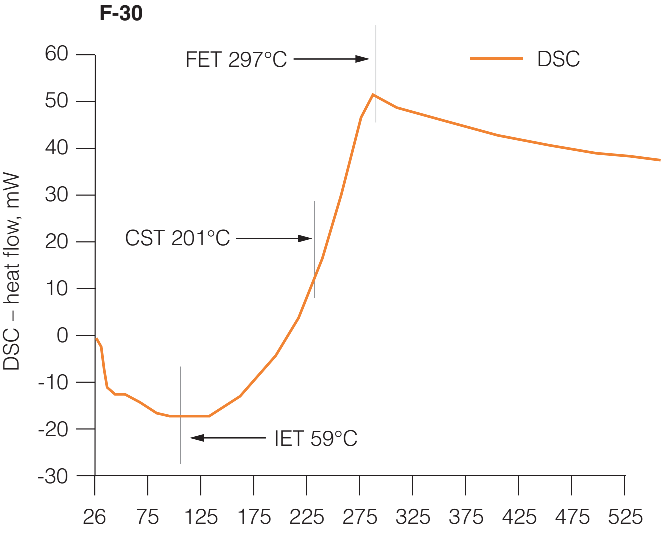


**Figure 5 Spontaneous combustion test results with differential scanning calorimetry analysis** (Querol Aragón and others, 2009)

established previously. The difference in temperature between the sample and a reference point is measured and recorded against the temperature of the oven and the exchanges of heat in the sample determined. The parameters used to characterise different substances are minimum temperature at which the exothermic reaction begins (initial temperature), maximum temperature reached during the exothermic reaction (final temperature) and the temperature at which the fast exothermic reaction commences (change of slope temperature). Figure 5 shows the result of a differential scanning calorimetry analysis. The heat flow is plotted on the Y-axis and the temperature on the X-axis (Querol Aragón and others, 2009).

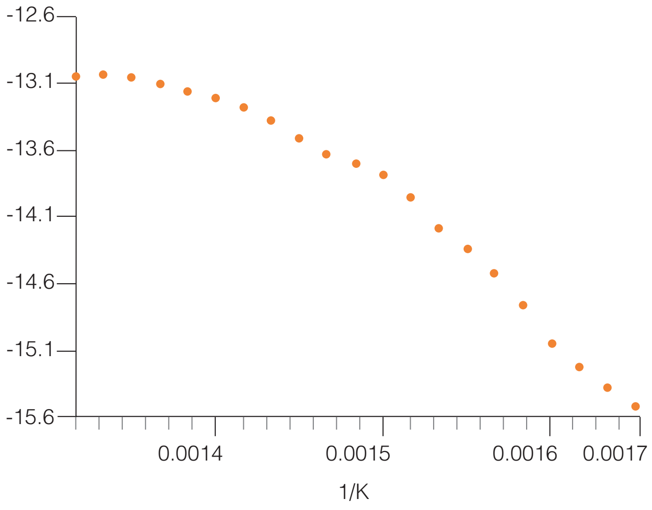


**Figure 6 Sample weight loss versus temperature** (Querol Aragón and others, 2009)

**Activation energy,** where thermogravimetry is the main tool used in the analysis but kinetics are also explored. One method is through the study of heat rate and its influence on the maximum weight loss. In addition, a kinetics based study can be carried out to estimate the activation energy of solids through standard software or applying Cummings kinetic model. The model is based on the loss of weight produced during the heating process of coal samples and establishes a relationship between the activation energy (Ea) and the rate of weight loss (Querol Aragón and others, 2009):

$$ln\left(-\frac{1}{w}\cdot\frac{dw}{dt}\right) = ln\ A - \frac{Ea}{RT}$$

where $w$ = weight of unburned combustibles
$dw/dt$ = instantaneous rate of weight loss
$A$ = frequency factor
$E$ = activation energy
$R$ = universal gas constant
$T$ = absolute temperature

Thermogravimetry is used as the analysis technique. Dust samples are subjected to a heating ramp, increasing the temperature at a constant rate, and measuring the weight loss. After recording the rate of weight loss, a rather simple algorithm may be used to fit a line to the experimental points in the region of the maximum rate, thus obtaining an apparent activation energy which is useful for comparing the behaviour of different substances. During heating of the samples, the weight loss can be measured. Figure 6 shows the loss of weight against temperature. By selecting the part of the curve near to the maximum slopes and filtering it, a straight line can be fit, the slope of which provides the activation energy (Querol Aragón and others, 2009).

**Isothermal heating** involves the use of an oven for testing samples at different temperatures and scaled sample volumes. Different conclusions may be reached depending on the testing conditions and procedures used. In isothermal heating, the Frank-Kamenetskii Theory for the heating process is used frequently. A standard procedure is actually under discussion within the standardisation working groups of the Committee for European Standardization (Comité Européen de

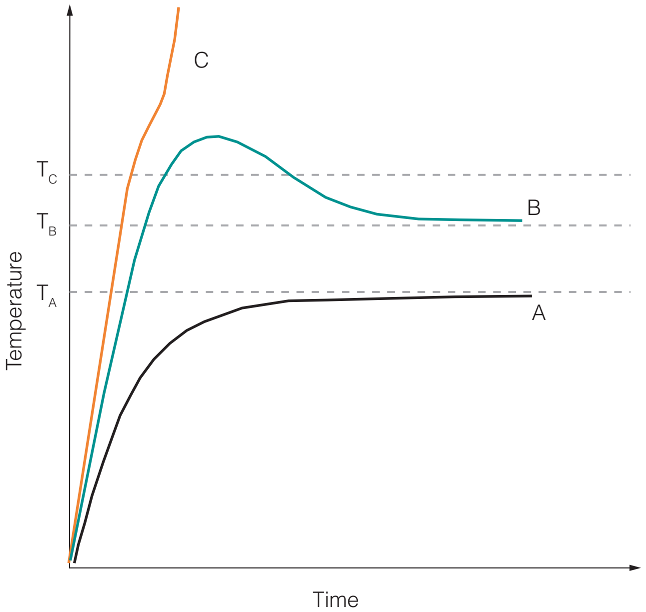


**Figure 7 Subcritical and supercritical behaviour of the test samples** (Querol Aragón and others, 2009)

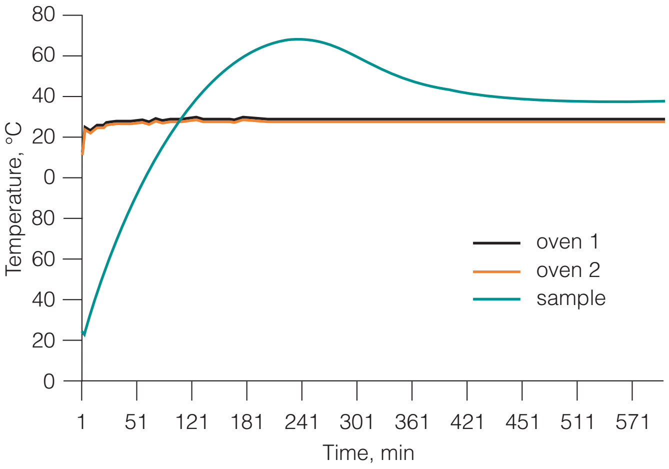


**Figure 8 Temperature records in tests for a 150 $cm^3$ cell of a coal sample: no ignition at 130°C** (Querol Aragón and others, 2009)

Normalisation (CEN)). For information on CEN visit www.cen.eu. The experimental basis for describing the self-ignition behaviour of a given material is to determine the self-ignition temperature of variously sized bulk volumes of the material by isothermal hot storage experimental process (storage at constant ambient temperatures) in commercially available drying ovens. The results reflect the dependence of self-ignition temperature upon material volume. A sample is kept in an oven at a fixed temperature which is increased in 5 K increments until it self-ignites. The temperature of self-ignition is the mean between the last subcritical and first supercritical temperature (*see* Figure 7, curves B and C respectively).

Subcritical conditions are defined as those where no ignition occurs whilst supercritical conditions are those that lead to ignition. The test is repeated for different volumes of samples, typically ranging from 15 $cm^3$ to 1500 $cm^3$. Figures 8 and 9 show the temperatures recorded in tests carried out for a 150 $cm^3$ cell of a coal sample reaching self-ignition at 135ºC and no ignition at 130°C. Once the self-ignition temperature is reached for different sizes of the test cell, it is possible to relate the temperature and the volume, and also to extrapolate the induction time (time required to reach ignition at every initial temperature). By plotting the logarithms of the volume/surface ratios (log V/A) of different sized dust heaps versus the reciprocal values of the respective self-ignition temperatures (1/T in $K^{-1}$), straight lines may be produced allowing interpolation and extrapolation to characterise the self-ignition behaviour of dust heaps of practical scale. This experimental testing procedure is currently being studied at the standardisation working groups of CEN to develop a draft proposal which will be discussed by experts from different countries. In particular, it is a task of CEN/TC305/WG1 (European Committee for Standardisation: Test methods for determining flammability characteristics), which will be carried out by Sub Group 5: 'determination of the spontaneous ignition behaviour of dust accumulations' (Querol Aragón and others, 2009).

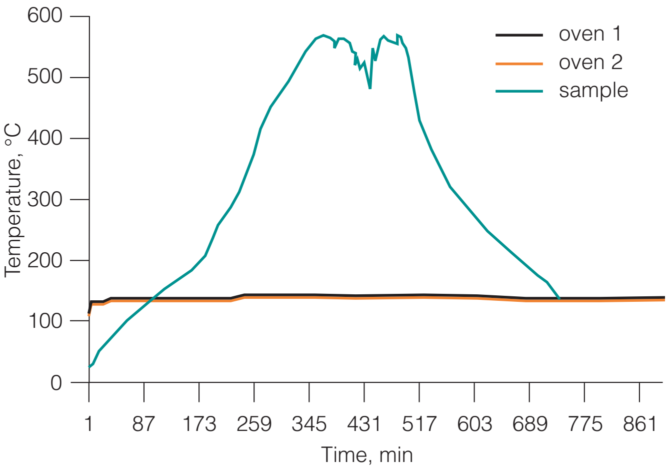


**Figure 9 Temperature records in tests for a 150 $cm^3$ cell of a coal sample: ignition at 135ºC** (Querol Aragón and others, 2009)

After studying a number of coals from different parts of the world and different ranks, a grouping of their reactivity has been proposed. The main feature of the classification is to include two experimental techniques based on a

**Table 1 Classification of self-ignition risk based on experimental data** (Querol Aragón and others, 2009)

| Risk | Thermogravimetry in oxygen flow characteristic temperature, °C | Apparent activation energy, kJ/mole |
|---|---|---|
| Very high | ⩽250 | ⩽79 |
| High | 250–299 | 80–89 |
| Moderate | 300–349 | 90–94 |
| Low | ⩾350 | ⩾95 |

thermogravimetric tool: thermogravimetry in oxygen flow characteristic temperature and apparent activation energy. Querol Aragón and others (2009) propose the grading of risk shown in Table 1. The authors suggest that this classification criteria could be used for other combustible matter such as low rank fuels, biomass and residues.

### 2.3.1 During transport

The International Maritime Organization (IMO) is a specialised agency of the United Nations with 169 Member States and three Associate Members. The IMO is based in the United Kingdom with around 300 international staff. The Convention establishing the IMO was adopted in Geneva in 1948 and the IMO first met in 1959. The IMO's main task has been to develop and maintain a comprehensive regulatory framework for shipping and its remit today includes safety, environmental concerns, legal matters, technical co-operation, maritime security and the efficiency of shipping. The IMO requires all coal carriers to provide suitable equipment for the early detection of cargo heating. Shipboard fires due to spontaneous combustion have been reported when coals from the USA were exported to the Far East (Smith and Lazzara, 1993). Measures introduced to prevent the loading of coal with temperatures greater than 40°C and compacting the coal in the cargo hold could be used successfully in stopping a fire. For more information about the IMO visit www.imo.org.

The IMO code of safe practice for solid bulk cargoes includes detailed recommendations for the safe loading and carriage of coal cargo. It states the propensity of coal to self-heat which could lead to spontaneous combustion. The section 'general requirements for all coals' stresses important advice for the safe loading and carriage of coal, including (Minton Treharne & Davies Group, 2008):

- prior to loading, the shipper or agent shall provide in writing to the master the characteristics of the coal, which includes whether or not the cargo is liable to self-heat. The master should be satisfied that he has received such information prior to accepting the cargo, and means are to be provided for measuring the temperature of the cargo while being loaded;
- if, at the time of loading when the hatches are open, the temperature of the coal exceeds 55ºC, expert advice should be obtained.

Minton Treharne & Davies Group (2008) report recent experience of several problems relating to the loading of heated coal at offshore loading terminals. Many of the problems were related to long storage periods on shore and/or extended journey times in the barge. Difficulties were encountered in discharging rejected 'hot' coal from the barge to the original loading terminal. The company focuses on an incident at an offshore loading terminal where coal at a temperature in excess of 55ºC had already been loaded to the bulk carrier and white ash was observed in some areas of the stow. The terminal provided no means for the discharge of the cargo. The advice to the master was to seal the hatch covers, ventilators and other hold openings tightly. The atmosphere in the hold was then monitored closely with sampling instruments. A steady reduction in oxygen and CO were observed indicating that the spontaneous heating process had been restricted. The hatch covers were opened after four days and the cargo trimmed level with bulldozers in order to compact the stow. The remainder of the cargo was then loaded into the holds in stages to enable regular compacting. Once loading was complete, the hatch openings were closed tightly to prevent air from entering the cargo. The hold continued to be monitored. The CO and oxygen levels dropped and after seven days the oxygen content in all holds had been reduced to 1%. The inert atmosphere was monitored and maintained throughout the voyage until delivery. Minton Treharne & Davies Group (2008) conclude that it may not be possible to always follow these procedures. However, with careful attention to detail and expert guidance, a heated cargo may be stabilised to a condition safe for carriage to the port of discharge and not have to be dug out from the ship's holds.

Today, power generating facilities import coal from different parts of the world. In 2010, worldwide trade in coal amounted to about 300 Mt/y. Special care must be exercised in the transportation of coal to avoid spontaneous combustion in ship holds and it is therefore important to have a method that appraises the safety of any coal that is to be shipped. According to Nelson and Chen (2007), bulk materials are commonly transported in cubic containers with 3 m sides. The maximum mean ambient temperature that a container in a shipping hold will be exposed to for a reasonable amount of time during transport is 38ºC (311 K). If spontaneous combustion occurs within a container, a dust explosion may result which could significantly enhance the rate of combustion due to the increased air supply. In addition to the danger of spontaneous combustion due to self-heating, an additional hazard in the transport of bituminous coal is the slow release of molecular hydrogen. Over the course of transport, hydrogen concentrations in the dead space above the coal can reach levels close to the lower explosion limit for hydrogen in air (Nelson and Chen, 2007).

The 1970s International Maritime Consultative Organization (IMCO) shipping standard test was developed from experimental work, which suggested that the activation energies for carbonaceous materials were very similar. In designing the IMCO standard, it was therefore assumed that carbonaceous materials had the same activation energy. This allows a simple test to be developed to distinguish between non-hazardous and hazardous materials. According to Nelson and Chen (2007), in the IMCO test, the material to be transported is packed into a 10 cm cubic gauze container and is placed in a recirculating air oven at 140ºC for 24 hours. Definition of cubic centimetre is the volume of a cube of side length one centimetre (0.01 m) which is equal to a millilitre, that is 1 $cm^3$ = 0.000001 $m^3$ = 1 ml.

The temperature at the centre of the sample is recorded by a thermocouple. If the sample fails to ignite, the material is judged safe to ship in a 3 m cube, while if it ignites, it is judged unsafe to ship in a 3 m cube. The advantage of the IMCO method is that it is a 'single point' test that gives a definitive answer within 24 hours. However, the assumption of a single activation energy for all materials to which the test is applied is an inherent flaw in the method. In the mid-1990s, a provisional International Organisation for Standardisation

(ISO) standard was proposed for assessing the propensity for spontaneous heating of carbonaceous materials. This method was also based on the assumption that the failure of a 10 cm cube to ignite at 140ºC indicates safety for shipping purposes in a 3 m cube. It therefore has the same disadvantage (flaw) as the IMCO test. The United Nations recommendations for the transport of goods susceptible to self-heating involves tests of various container sizes to produce various classifications of hazard. For example, a material that fails the IMCO test can be retested in a 10 cm cube at either 373 K or 393 K. If the material passes the retest, that is: it does not ignite, then it is safe to store or transport the material in either a cube of volume 450 L (side 0.77 m), if it passed the test at 373 K, or a cube of volume 3 $m^3$ (side 1.44 m), if it passed the test at 393 K.

Nelson and Chen (2007) consider that it can be shown that both of these criteria assume that the activation energy of the combustible material is 87 kJ/mol. The authors consider that this test is simply a variant of the IMCO test and, accordingly, has the same disadvantage (flaw) as the IMCO test. Nelson and Chen (2007) conclude that it is obvious that test procedures that predict the propensity to combust, based upon an assumed activation energy, are unreliable.

Due to the use of an arbitrary activation energy for all materials leading to unreliable predictions, new procedures have been proposed to assess the propensity of spontaneous combustion of combustible solids in which the value of the activation energy is determined as part of the test procedure. The first of these methods uses heat-release-rate measurements made with a micro-calorimeter. The second of these methods augments a hot-storage-test with the heat-release method. Both methods are discussed in detail by Nelson and Chen (2007).

According to Nelson and Chen (2007), it has been suggested that it can be safe to ship materials under conditions that are nominally supercritical, provided that the anticipated shipping time is less than the time to ignition of the assembly. If the calculated ignition time is higher than the shipping time, a practical upper bound, which is three weeks, then there is no hazard in practical terms. Table 2 shows the calculated critical ambient temperature for six Scottish coals stored in a 3 m cube. For each coal, this temperature is lower than the maximum ambient temperature that a container will be exposed to during shipping (311 K). On this basis, none of these coals should be transported as a 3 m cube assembly if the coal is supercritical. However, for two of the coals, the calculated ignition time is much longer than any shipping time and these might therefore be deemed safe to transport. However, such stipulations do not apply to coal carried by train, another form of transport that can experience localised self-heating incidents.

**Table 2 Calculated time to ignition under adiabatic conditions of six Scottish coals** (Nelson and Chen, 2007)

| Coal | E, (kJ/mol) | A/s | $(T_a)_{cr}$ | $T_{ad}$ (d) |
|---|---|---|---|---|
| Rosslynell | 54 | 9 | 256 | 2 |
| Dalquhandy 1 | 74 | 4 x $10^3$ | 285 | 11 |
| Killoch 6015 | 93 | 1 x $10^6$ | 302 | 73 |
| Killoch 5561 | 78 | 3 x $10^3$ | 301 | 71 |
| Dalquhandy 2 | 50 | 1 | 262 | 4 |
| Killoch 5736 | 57 | 15 | 268 | 4 |

Where $T_{ad}$ (d) = time to ignition in days, E = activation energy,
A = pre-exponential factor and T = temperature
Note: The value of $(T_a)$cr is for a 3 m cube. Other parameter values:
Q (heat reaction) = 25 MJ/kg, TR = 300 K, c = 1260 J/g.K
Remaining data are from (Jones, 1998, 2000).
Calculation of time to ignition, in seconds, under adiabatic conditions is calculated as follows:

$$T_{ad} = \frac{RT_R^2}{E}\,\frac{c}{QA}\,exp\left[\frac{E}{RT_R}\right]$$

## 2.3.2 Stockpiles

With regard to stockpiling, coals that exhibit the greatest tendency to self-heat (that is lignites, subbituminous and brown coals) are rarely stored for any length of time at the power station. Self-heating occurs more commonly at power plants than transfer points or ports. This is a reflection on the relative length of storage time involved at each stage. Spontaneous combustion in stockpiles poses significant safety, environmental, economic and handling problems. As well as the economic loss of coal due to fires, the heat-affected coal may become partially or totally unsuitable for its intended use. Thus prevention and early detection of spontaneous combustion is of paramount importance. It is not always clear how frequently fires occur as there is a lack of information published on this topic.

The three main functions of any coal pile management system are buffering, composing, and homogenising (Oberrisser, 2008):

- the buffering function ensures that there is enough coal in the plant's coal bunkers for the plant to continue operating. Buffering keeps brief supply interruptions from becoming a problem;
- the composing function ensures that a completed coal pile has the required composition – the correct proportions, by weight, of coals with different chemical and/or physical characteristics;
- the homogenising function manages the layering of various coal types over the length of the pile. This layering reduces the average deviation of a chemical or physical property over successive pile cross sections, compared to the deviation from average of the characteristic in arriving coal. If the plant served by the pile will be burning coal blends, a stockpile pre-homogeniser is a good system management design choice because its capacity can be increased simply by extending the length of the rails on which the stacker and reclaimer ride.

Coal stockpiles are prone to spontaneous combustion especially where large quantities are stored for extended periods (Nelson and Chen, 2007).

Experience has shown that in stockpiles, hot spots occur frequently after rain. For very dry coals, the problems are more serious. According to Nelson and Chen (2007), if almost all of the surface and inherent moisture has been removed, then moisture from saturated air condenses not only onto the external surface of the coal but throughout its internal pore structure. This results in the rapid increase in temperature so that very dry coals can ignite by water sorption. The risk of explosions, as a result of coal self-heating, has led to a reluctance towards using water for cooling in stockpiles. Furthermore, moist air has a higher thermal conductivity and heat capacity than dry air. Therefore, the flow of moist air transfers more heat to a coal pile than that of drier air; this is a secondary heat-transfer effect. In large coal systems dry and wet regions can both occur. Another ancillary heat effect is that heat released in a wet area in a stockpile increases the local temperature, which in turn increases heat flow into a dry area, thus enhancing its rate of oxidation (Nelson and Chen, 2007). Temperature profiles of coal stockpiles are discussed in detail by Sensogut and others (2008).

## 2.3.3 Silos/bins/bunkers

Coal silos/bunkers present a particular problem in relation to self-heating. Coal is usually stored only temporarily – perhaps a matter of a few hours or less – in silos used in rail load-outs, so there is little chance for self-heating unless the design of the structure allows coal to build up inside. Long-term silo/bunker storage can provide the possibility of air movement thus providing ideal conditions for accelerated self-heating. Therefore, ventilation is essential at the top of the silo or bunker to remove gas emitted from the coal; sealing the silo/bunker will help prevent self-heating. An alternative prevention method is flooding the upper parts of the silo with inert gas.

According to Nelson and Chen (2007), in June 1991 an undetected fire in a coal bunker at a coal-fired plant, believed to have started by spontaneous combustion, gave rise to a minor explosion, which ignited coal dust that resulted in a massive explosion. The estimated cost of this explosion exceeded US$ 4 million.

Chemetron Fire Systems (2000) discuss coal storage in silos and bunkers. In a common power plant configuration, the coal is fed by conveyor into the top of the silo, it then flows by gravity out of the bottom to the coal feeder, as shown in Figure 10, or to a conveyor to the coal feeder and then on to the coal pulveriser system. According to Chemetron Fire Systems (2000), coal stored in silos, before it is fed into the coal mills or other similar short-term storage applications, continually oxidises and generates heat. In the event of an unscheduled shut-down, coal trapped in the silo may oxidise enough to eventually start to burn. The length of the time that it takes to heat the coal to burning point is a function of the reactivity of the coal. Some Western US coals will reach this point in just a few days. In addition, fires are more frequent if

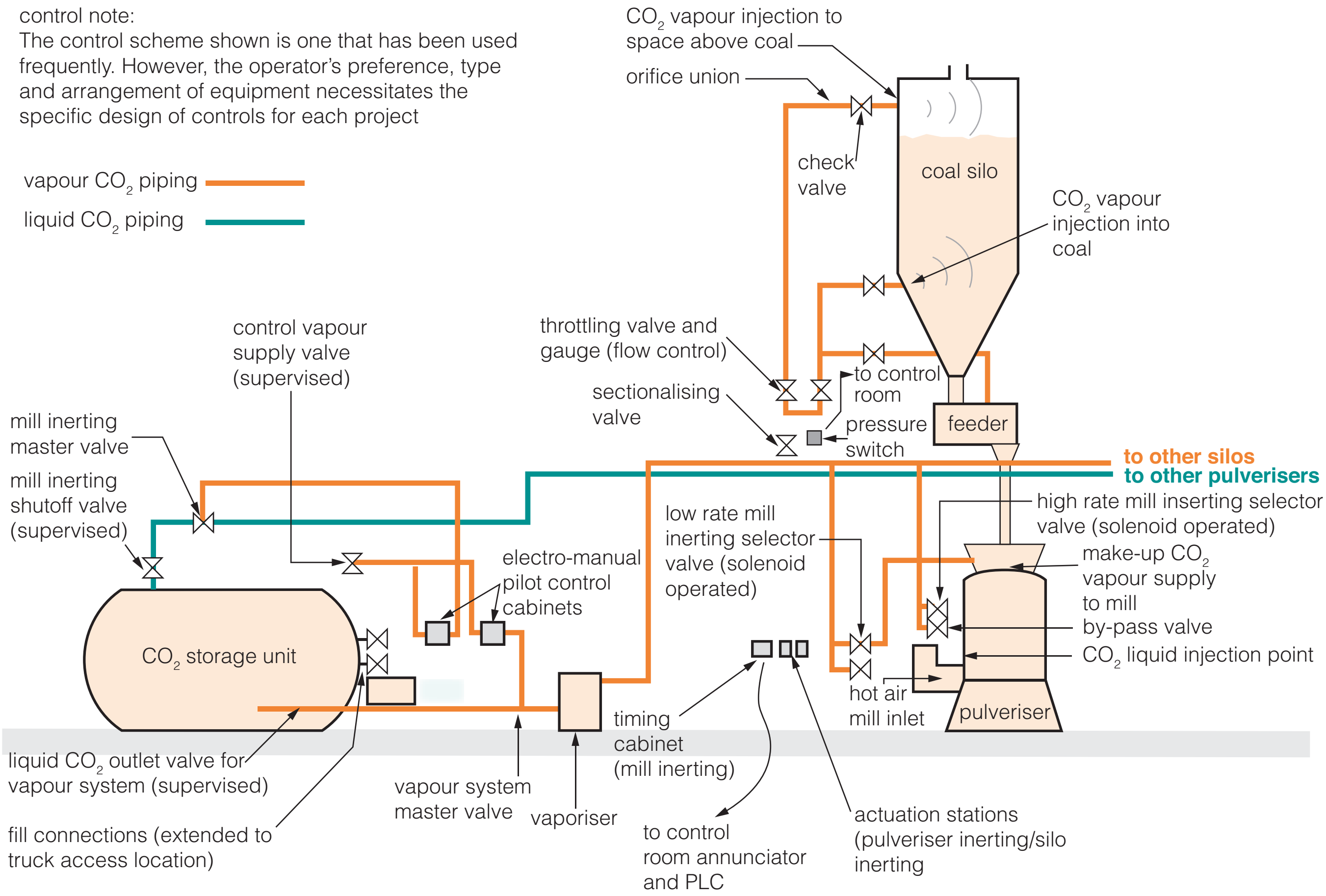


**Figure 10 Low pressure CO$_2$ fire protection and inerting system for coal silo and pulveriser** (Chemetron Fire Systems, 2000)

the silos/bunkers are not cleaned periodically and/or proper filling procedures are not followed. In the event of a fire, it is usually not practical to run the coal from the silo out onto the ground, therefore fire control in the silo/bunker is necessary. Inerting and fire control with $CO_2$ vapour is used widely and is discussed in Chapter 4 (Chemetron Fire Systems, 2000).

## 2.3.4 Pulverisers/mills

Coal pulveriser/mill fires and explosions can be a chronic problem at coal-fired power stations. The extent of the problem at coal-fired power stations and utility measures used to mitigate such incidents have been documented in a series of papers presented at many symposia on coal pulverisers/mills. Today, typical explosion scenarios, as specified for example, in terms of ignition sources and fuel and oxygen concentrations, are being identified from incident reports and from in situ measurements. Similarly, the success and limitations of alternative explosion prevention measures are being assessed from actual plant experience and test data.

A pulveriser system may be defined as the section from the coal silo feeding the pulveriser, the burners fed from that pulveriser and the points at which the hot air and cold air ducts leave their respective main supply ducts. The pulveriser system incorporates grinding to reduce coal particle size to allow its circulation within the pulveriser, drying using hot air (primary air input and residence time in the mill) and classification to produce coal so that 70% will pass through a 200 mesh screen. The term is known as coal fineness (Nag, 2007).

Usually, the first step taken in the pulveriser system is inerting by steam. This is to remove any hot deposits of coal inside the pulveriser system which can cause spontaneous combustion. The air fuel ratio of the mixture has an explosive range between 4:1 and 50:1. It is most reactive within the range 5:1 and 12:1. That is, if the primary air is fed into the pulveriser system while containing hot coal deposits and the explosive ratio is met, fire or explosion is likely to occur. A minimum primary air flow through a pulveriser should be 65 t/h (141 lb/h). If the air flow is less, the pulveriser may not start operation due to potential blockage in the long coal pipe to the burner. A minimum coal feed into the pulveriser should be 20 t/h (44 lb/h). This air fuel ratio is below the explosive range (3.25:1) and should avoid spontaneous combustion, however this ratio is difficult to achieve.

Usually operators set primary air flow at 75 t/h and feed coal minimum at 15 t/h. Thus the potential to meet the explosive ratio (5:1) is always there. However, in order to achieve safe operation, it is very important to set the outlet temperature at no more than 65°C. After stabilised operation, the air fuel ratio is around (2.5:1).

Pulverising is the process of applying a grinding force between a rotating ball and stationary roll wheel assemblies. Since the roll wheels do not touch the ball surface, both crushing and attrition take place by attrition of coal against coal. The capacity or output of a pulveriser, in general, depends on three factors. These are grindability, moisture content and fineness desired.

Grindability is not an inherent quality of coal like moisture content or heating value. The grindability index indicates the comparative value and ease with which a specific type of coal can be pulverised. On the Hardgrove Scale, a fifty Hardgrove Grindability Index (HGI) is the standard from which base or nominal capacities are calculated. A high grindability index indicates the coal is relatively easy to grind and, therefore, increases pulveriser capacity while coal with a lower grindability index is harder to pulverise and decreases pulveriser capacity.

Moisture content of the coal affects pulveriser capacity, but the effect is not as significant as grindability. Very high moisture coal tends to reduce pulveriser capacity. This is due to the fact that the higher moisture coals react differently and tend to resist the grinding process. On the other hand, as discussed above, dry coal in storage should not be kept in a damp place because this can promote self-heating. So, dry deposits of coal particles in coal mills become particularly susceptible to spontaneous ignition, through adsorption of moisture, under conditions of high humidity (Nelson and Chen, 2007).

Pulveriser capacity is greatly affected by the fineness requirement of the pulverised coal. In simple terms, more energy is required to achieve a greater fineness of the coal leaving the pulveriser. Therefore, without changing the energy input to the pulveriser, its output will be reduced if fineness of the product is increased. The fineness of the pulverised coal is expressed in terms of the percentage that will pass through a 200 mesh screen. The method of arriving at this value is as follows. A 50 g sample of pulverised coal, obtained from a composite collection taken after each pulveriser discharge valve in the pulverised coal system, is put on top of a series of three screens. The first screen is called a 50 mesh because it has fifty openings to the inch, or two thousand five hundred divisions per square inch. The next screen is the 100 mesh. The final screen is the 200 mesh, which is the screen with the smallest openings. To be exact, two hundred openings per inch or a total of four thousand per square inch.

Nag (2007) reviews coal pulveriser fire and explosion incidents and attempts to determine their consistency with current laboratory data on coal dust flammability and explosibility. An incident database, composed primarily of relevant factory mutual loss reports, is used together with data on the pulveriser internal environment during normal operations and incipient fires and explosions. The incident database is presented following a brief synopsis of pulveriser design and operation.

Uludag (2007) summarises self-heating theory and findings on coal characteristics and factor relationships as follows:
- a rise in temperature greatly accelerates the rate at which coal is able to absorb oxygen;
- the relationship between the air and coal reaction can be given as $r=k^{-E}_{RT}$ (r: the rate of change of the measured index (oxidation rate)), k: a constant, E: the activation energy of the reaction, R: the gas constant and T: the absolute temperature);
- the lower activation energies for lignites confirm the higher tendencies of low rank coals to spontaneously ignite;

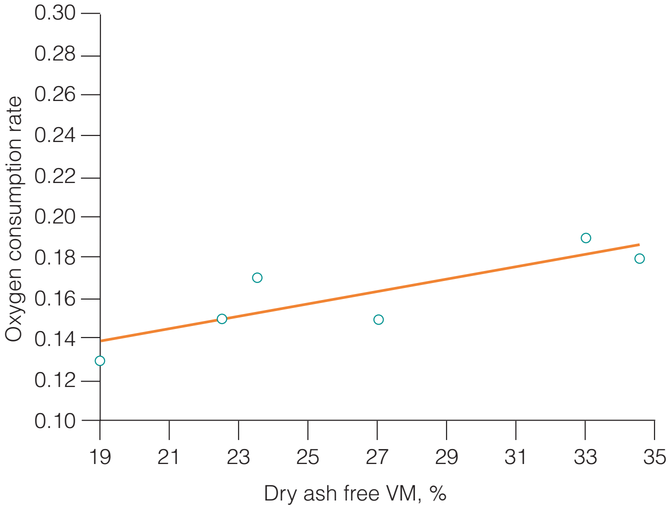


**Figure 11 Rate of oxidation and rank of coal** (Uludag, 2007)

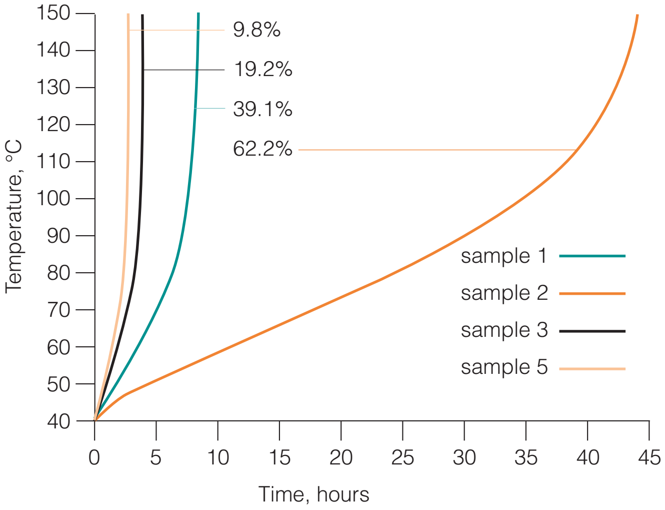


**Figure 12 The effect of ash content on time to self-heating of coal** (Blazak and others, 2001)

- when the humidity of the air falls relative to that of coal, the incidence of spontaneous combustion increases;
- heat of wetting is greater than heat of oxidation and is the cause of ignition in some coals;
- it is generally agreed that spontaneous combustion is a rank-related phenomenon (*see point 3 above*). As volatile matter and oxygen content increase (indicative of decrease in rank), the rate of self-heating is also raised (*see* Figure 11);
- the ash content of some coals can slow down the self-heating process and act as heat sink (*see* Figure 12).

Beamish and Blazak (2005) discuss in detail the relationship between ash content and $R_{70}$ self-heating rate of Callide coal while Beamish and Hamilton (2005) present the effect of moisture content on the $R_{70}$ self-heating rate of Callide coal.

In summary, before coal burns openly, in a stockpile, silo or bunker, an unnoticed process of oxidation takes place. In this process oxygen from the air reacts with the carbon in the coal and carbon dioxide is generated. If the heat released by the reaction is not controlled, spontaneous combustion may occur.

The grain size and the surface structure of coal can also influence its susceptibility for spontaneous combustion. Factors that influence the spontaneous combustion of coal include, air-ventilation in the stockpile or silo/bunker, atmospheric conditions, coal quality (that is, low carbon content and large amounts of volatile components support combustion), coal moisture content and particle size (that is, the smaller the particles, the larger the surface area, the higher the risk of self-heating). Other properties of coal which affect its tendency to self-heat include rank, heat capacity, heat of reaction, the oxygen content of coal and pyrite content. The propensity of coal to self-heat and spontaneously combust tends to increase with decreasing rank. Thus, lignites and subbituminous coals are more prone to spontaneous combustion than bituminous coals and anthracites. Proper stockpile design, construction and formation that limits the introduction of oxygen into a pile is critical in mitigating spontaneous combustion. Today, power generators import coal from different parts of the world. Thus, special care must be exercised and guidelines followed in the transportation of coal to avoid spontaneous combustion in ships' holds and it is therefore important to use methods that appraise the safety of any coal that is to be shipped.

# 3 Coal fire evaluation, monitoring and detection

Numerous methods are currently in use and some are under development in order to evaluate, monitor and detect coal-fires in stockpiles, silos and bunkers. Three of the major techniques used to monitor and detect a fire in a silo or bunker are carbon monoxide (CO) monitoring, thermal monitoring and infrared scanning.

A major consideration in minimising not only the potential for a fire but also its impact is where to install gas- and/or temperature-monitoring devices in bunkers and silos. Each type of instrument has its own application criteria that must be considered. These types of monitoring devices have proven effective at early detection of fires at plants burning coals with a propensity to self-heat (Douberly, 2003).

Monitoring for the presence of carbon monoxide (CO) gives the fastest indication of a fire in the making. CO is an odourless, toxic gas that is liberated at the very early stages of incomplete combustion. It is flammable at 12–75% volume in air. According to Douberly (2003), although it may be normal to experience a rise and fall of background CO levels in bunkers and silos during standard operation, monitoring provides a warning if the gas begins to rise consistently from background levels. Desired alarm set points are established once the normal background level of CO is determined in a power plant. Setting CO monitoring to detect a continuing upward trend of CO is advisable rather than waiting for the level of CO to reach a specific set point according to Douberly (2003).

There are many advanced coal fire detection systems that provide warning of the onset of coal mill or silo fires through the build-up of CO. One such system is the Land mill/silo fire detector. The system is designed to detect the rapid build-up of CO inside a pulverising coal mill and silo. It monitors the atmosphere in the mill or silo on a continuous basis and responds rapidly to any significant increase in the levels of CO. Features and benefits of the system according to Land Instruments International (2006), include:

- advanced fire detection that protects costly mill equipment loss and prevents downtime;
- a robust and low maintenance system designed for fire detection specifically in mills and silos;
- high level, reliable, continuous reading and integrated measurement integrity;
- easily set, site-specific alarm thresholds tailored to each individual application;
- easy connection to the plant control system with standard analogue and discrete contact outputs.

According to Land Instruments International (2006), CO monitoring, as opposed to thermal monitoring (temperature sensing), provides a more time-effective detection of combustion and subsequent prevention of mill fire. The system operates by extracting sample gases from the mill (often mill outlet) or silo and monitors the CO level on a continuing basis. Dual sensors are used with self-checking and automatic calibration to maintain the integrity of the system. The alarm threshold levels are set to suit the plant operating conditions. Where mills are using recycled combustion air for coal feed heating, the settings can be modified to compensate for externally introduced CO. Measurement of oxygen is an option when using a single stream instrument. This is because silos with limited oxygen can benefit from this additional measurement as an extra fire protection technique. Also, plants that use flue gas recirculation can monitor oxygen levels continuously with the system. The technology is suitable for monitoring CO on both horizontal and vertical mills, typically on the pulverised coal outlet, as well as in silos and bins.

Thermal monitoring or detection, using thermocouples can also provide an indication of a fire inside a bunker or silo. However, thermal detection does not provide the early warning that CO monitoring does. Thermal detection relies on the presence of heat for activation, so a fire may already be of considerable size before the thermal detector senses the excess heat (Douberly, 2003).

Coal is a good insulator, therefore a deep-seated fire may not produce extremely high temperatures on the exterior surface of a silo or bunker. Periodic monitoring of a bunker or silo using an infrared thermographic camera (that is infrared scanning) to scan the outside and/or inside of the enclosure is a common practice. Such a scan, *see* Figure 13, provides a visual picture of the thermal condition of the coal and is especially useful at pinpointing the exact location of a hot spot deep inside a silo or bunker.

In 2006, Ozdeniz and Sensogut studied computer controlled measurement of spontaneous combustion in coal stockpiles in Turkey. In 2008, Ozdeniz and others presented their findings on the monitoring and artificial neural network modelling of coal stockpile behaviour under different atmospheric conditions. In their study, the authors developed a measurement system that collects physical data from coal stockpiles. The obtained data, including heat values in a coal

**Figure 13 A thermographic image of a PRB coal silo fire** (Douberly, 2003)

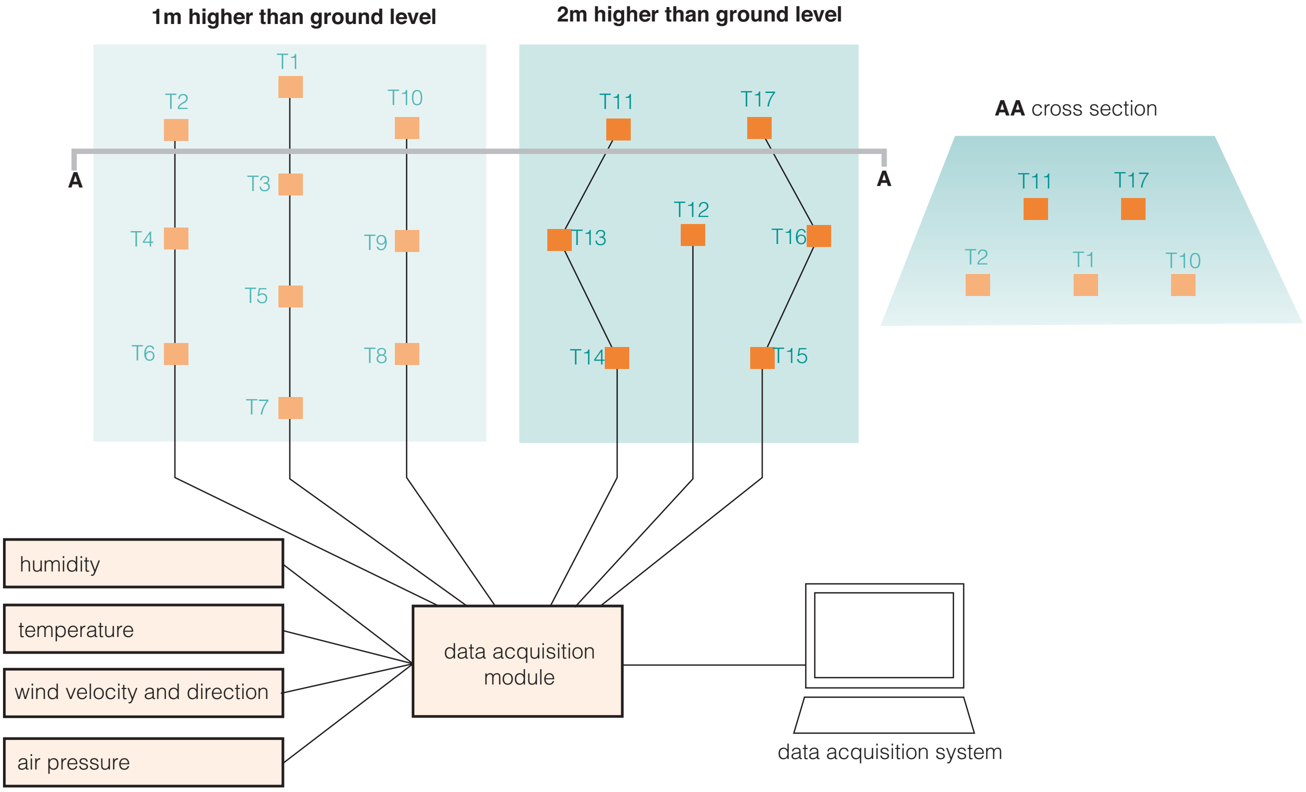


**Figure 14 Schematic presentation of heat sensors in stockpiles and measurement system** (Yilmaz and Ozdeniz, 2010)

stockpile, temperature and humidity, can be recorded into a database at desired time intervals. Thus a compact measuring and evaluating system is obtained, which can be used in academic research and by coal companies. Following that study, Yilmaz and Ozdeniz (2010) discussed an internet-based monitoring and prediction system for coal stockpile behaviour under atmospheric conditions. The tests were performed in Turkey on coals processed in coal preparation plants and particle sizes between 10 and 18 mm. The system was used on a triangular prism shaped stockpile with the following dimensions: 5 m width, 10 m length, 3 m height and 120 t of weight/mass. Seventeen heat sensors were placed in points in the stockpile. Ten sensors were placed at the first metre of the stockpile from the bottom and seven were placed at the second metre. The distances between the sensors at the first and second layers were set homogeneously. The plan view of the sensors is shown in Figure 14. The measuring unit was connected directly to the internet. All measured values and system prediction outputs were sent to a web server (and database), as shown in Figure 15, thereby enabling easy access to the continuously monitored data. Three types of users were created for the system, administration, active and passive users. Administration users were able to control and adjust the parameters of the system while active users could change prediction parameters. Passive users could only view continuously refreshed values (measured and predicted). Access time and rights of active users were determined by the system administrator. The continuously recorded data were stored in a database and artificial neural networking and statistical modelling were used to predict the stockpile behaviour. The detailed methodology used in the testing is discussed by Yilmaz and Ozdeniz (2010).

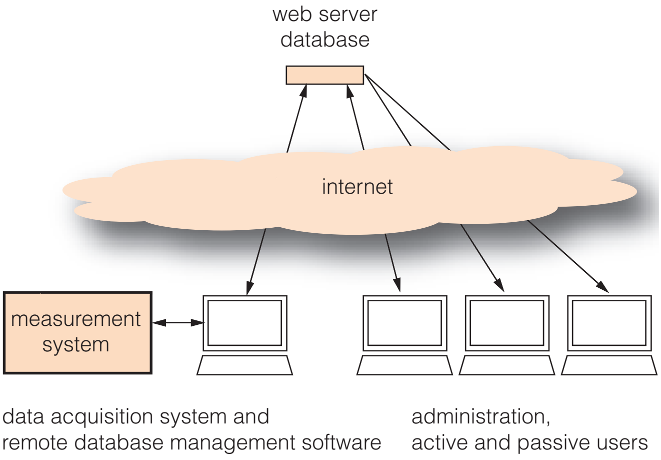


**Figure 15 General structure of internet-based monitoring and prediction system** (Yilmaz and Ozdeniz, 2010)

Yilmaz and Ozdeniz (2010) observed self-heating inside the stockpile leading to spontaneous combustion. They considered that the spontaneous combustion was caused by the smaller grain sized coal due to its larger surface area and greater contact with oxygen. The heat accumulated continuously in the middle of the stockpile and therefore could not be controlled. Thus, spontaneous combustion became inevitable. The statistical modelling showed high correlation coefficient values with the actual stockpile behaviour used in the study. The artificial neural networking model predictions were compared to measurement values obtained from experimental studies. The results were found to be compatible with each other to a great extent. The accuracy of the trained and tested artificial neural network model was found to be greater than 99%. The authors state that subsequent studies will be undertaken to estimate some stockpile parameters that cannot be measured experimentally. Also the advantages of using internet-based measurement and analysis include the possibility of following the behaviour, measured and predicted values at a distance from a stockpile on a continuous basis as well as provide real-time monitoring and controlling of the system via the internet with standard web browser and without the need for any additional software.

Experimental work on the self-heating propensity and spontaneous combustion of coal has been the subject of extensive fundamental and practical research for well over a hundred years and continues today. Zhou and others (2004) discussed testing methods for the propensity of coal to self-heat while Sen and others (2009) presented analytical methods, instrumental techniques and test methods for the oxidation of coal. Nelson and Chen (2007) carried out a survey of testing methodologies covering the period 1996-2005.

A wide variety of techniques are applied to gain insight into the processes that govern the self-heating propensity of coal. These include oxidation mechanisms, ranking the propensity of different coals to self-heat and the detection and suppression of self-heating. In the following sections methods for evaluating the propensity of coal to self-heat are presented including mathematical modelling, chemical kinetics, small-scale experimental procedures and laboratory testing methods measuring the propensity of coal to self-heat (such as crossing point temperature (CPT), differential thermal analysis (DTA), adiabatic calorimeter usage), infrared/fourier spectroscopy and other techniques. For initial temperature determination, coal is subjected to a current of air/oxygen in a thermostat. It shows signs of heating creating a curve which reaches a maximum and flattens out. The temperature of the medium used to heat the coal is kept constant in such tests. Then the coal is tested again with a different temperature setting. In this way, the coal is tested until the minimum temperature is reached at which the temperature of the coal does not rise. This is a time consuming test which is not used widely today. There are other, less widely used, means of analysis that are not described in this review including the Russian method of ignition temperature testing, the Olpinski Index, the SHT index, the Peroxy Complex Analysis, aerial oxidation studies, oxygen absorption methods such as Russian U Index, Glasser Index and the Wits-Ehac Index. The latter is discussed in detail by Uludag (2007).

## 3.1 Mathematical modelling

The self-heating process of coal is due to a number of exothermic reactions. Nelson and Chen (2007) discuss how the rate of oxygen consumption in the low-temperature oxidation reaction of coal can be expressed by a single Arrhenius expression. Many assumptions are made in mathematical modelling, for example that the spontaneous combustion of solid fuels undergoing self-heating consumes negligible amounts of oxygen. It is also often assumed that all coals have the same activation energy, for example, in the International Maritime Consultative Organization (IMCO) self-heating test. This assumption, according to Nelson and Chen (2007), has led to methods for determining safety in shipping coal that are not reliable.

Nelson and Chen (2007) also discuss the Frank-Kamenetskii self-heating analysis which has been applied to evaluate the hazards posed by self-heating of many bulk materials including coal. The Frank-Kamenetskii theory is the simplest spatially structured model that accounts for the phenomenon of spontaneous combustion. It provides an insight into the competing influences of heat production and dissipation, and provides a means to calculate the kinetic parameters involved. These kinetic parameters are A, the pre-exponential factor that goes with the heat reaction and E, the self-heating activation energy. These parameters are required for more detailed spontaneous combustion models. The Frank-Kamenetskii theory does not include many factors that are known to be important in the oxidation of coal at low temperatures. According to Nelson and Chen (2007), these include (but are not limited to) the oxygen concentration in the surrounding atmosphere, the transport of oxygen and moisture within the coal pores by convection and diffusion, gas absorption, the formation of gaseous and solid products, the moisture content of both the surrounding atmosphere and the coal, the evolution of heat by secondary mechanisms, the transport of heat within the coal by convection, the coal-pore structure, the particle size of the coal, and the exposed surface area of the coal. In addition, physical and chemical properties of coal may be a function of both temperature and chemical composition (water moisture, oxygen, reaction products). There is now extensive modelling literature investigating how these processes influence self-heating within a coal pile (Nelson and Chen, 2007).

Three dimensional computational fluid dynamics (CFD) modelling was conducted to simulate spontaneous heating in a large scale coal chamber (Yuan and Smith, 2009). As discussed in Chapter 2, the chemical reaction between coal and oxygen at low temperature is complex and not well understood. The gaseous reaction products evolved during coal oxidation are primarily CO, $CO_2$ and $H_2O$. Generally, three types of processes are believed to occur including physical adsorption, chemical adsorption, which leads to the formation of coal-oxygen complexes and oxygenated carbon species, and oxidation in which the coal and oxygen react with the release of gaseous products, typically carbon monoxide, carbon dioxide and water vapour. Oxidation is the most exothermic of these processes. Physical adsorption can begin at ambient temperature where coal is exposed to oxygen. Chemical adsorption takes place from ambient temperature up to 70ºC. The initial release of oxygenated reaction products starts from 70–150ºC, while more fully oxygenated reaction products occur at 150–230ºC. Rapid combustion takes places over 230ºC. The start of this rapid temperature rise is also known as thermal runaway. The time it takes to reach a thermal runaway stage is called induction time. The induction time can be used to indicate the potential hazard of coal self-heating. The temperature rise from ambient to 230ºC is a slow process compared to the fast temperature increase after 230ºC, which can lead to major fire hazards and even explosions (Yuan and Smith, 2009).

The goal of the CFD study was to understand the mechanisms of spontaneous heating. The modelling focused on the spontaneous heating mechanism at temperatures below 500 K (230ºC) and was conducted in a large-scale coalbed chamber. The results indicate that the development of the heating process can be divided into four stages. In the first stage (induction), the temperature rises slowly. During the second stage, as the temperature increases, the heat also increases. In the third stage, as the rate of temperature rise increases, more oxygen is consumed leading to insufficient oxygen for coal oxidation to occur. Therefore, the high temperature zone starts to move toward the front of the coalbed. During the fourth stage, the high temperature zone is limited to a small central area in the coalbed. In real applications, Yuan and Smith (2009), state that prediction of induction times is very important to prevent spontaneous heating fires. Under the conditions studied in the project, the higher air flow rate in the coalbed chamber resulted in a shorter induction time. The authors concluded that the order of reaction has a major effect in predicting the induction time. Lower values of order of reaction resulted in shorter induction times.

Humphreys (2005) reported a study that attempted to combine comprehensive knowledge of the many aspects of the oxidation behaviour of coal and the heat loss mechanisms that play a role in spontaneous combustion in order to assess the likely in situ or field behaviour of coal leading to self-heating. The knowledge was then combined into a number of numerical modelling techniques to simulate laboratory tests and to model the spontaneous combustion behaviour of coal in stockpiles. Fundamental oxidation parameters of reactivity and heat of oxidation were used as the basis for all models. Thus, a direct link was established between the results obtained from the laboratory tests and the predicted field behaviour. According to Humphreys (2005), the study provided a fresh understanding of the many aspects of coal self-heating leading to the development of a new, more quantitative assessment of the potential for spontaneous combustion that takes into account factors such as the initial pile temperature, pile size and mass, and coal particle size.

Akgun and Essenhigh (2001) discuss theoretical prediction of self-ignition characteristics of coal stockpiles using a two-dimensional unsteady-state model. The most significant results obtained were that physically realistic values of ignition times (>15 days), temperature (60–80ºC) and hot spot locations can be predicted for a packed coal bed, and when spontaneous ignition would not occur (about 2 m). The model also showed the significance of coal type and bed porosity on self-heating. The predictions of the model were (Akgun and Essenhigh, 2001):

- the existence of 'hot spots' of maximum temperature in the coal piles, not located on the centre-line, are typically about 2 m in from the sides;
- hot spots migrate;
- the temperature of the hot spots increases steadily with time, with bifurcation leading either to an unignited steady state with a small temperature rise, or to ignition;
- ignition occurs only for coal piles greater than a minimum critical height (of the order of 2 m for the coals in the study);
- the time to ignition is in excess of half a month or more;
- moisture may accelerate ignition by thermal coupling of heat transfer with evaporation/condensation;
- ignition temperature and time to ignition are predictably dependent on the bed porosity, pile shape and coal type.

Agun and Essenhigh (2001) concluded that the results have a significant practical (engineering) value. The findings supported the standard practice of compression as coal piles are created; they indicated the value of low grade slopes or better location of piles in depressions; they identified the optimum locations for thermal monitoring in the piles; they indicate optimum pile heights and provide predictions for dependence on packing density.

In 2006, Zarrouk and O'Sullivan discussed the diminishing reaction rate in the self-heating process of coal using several models. They compared the various mathematical forms used to represent the diminishing part of the reaction and introduced a new formulation in the form of a generic power-law model. Results attained with the new model were then compared with those obtained using previous models. The authors concluded that it is not possible to gain support for preferring one model rather than the others.

## 3.2 Chemical kinetics

Low temperature oxidation of coal has been studied extensively. Nelson and Chen (2007) state that although the exact process by which this happens is complex and the mechanisms are not fully understood, some general features of the process are known. The first step in the process of coal oxidation is the chemical sorption of oxygen at active sites on the surface of the coal. At temperatures below 40ºC, the interactions between coal and oxygen are mainly due to physical adsorption and chemisorption of oxygen in coal pores. The next step of the low-temperature oxidation of coal is the formation of unstable surface oxygen-coal complexes, generally through the attack of molecular oxygen on certain aliphatic bonds to produce peroxides and hydro-peroxides. An aliphatic bond can be either in a non-aromatic ring or in a carbon chain. At these temperatures there is little evolution of gaseous products. At higher temperatures, ~40–70ºC, the unstable oxygen compounds break down to give gaseous products, stable oxygen-coal complexes, and heat. At temperatures below 70ºC, carbon dioxide is the major gaseous product. Nelson and Chen (2007) consider that this is a change of view, since early studies indicated that carbon monoxide was the main product below 70ºC. The overall oxidation rate is significantly more rapid at these temperatures than below 40ºC. At even higher temperatures, the stable oxy-complexes degrade, generating new active sites for coal oxidation. Accompanying the chemical changes that occur as a consequence of oxidation are changes in the macromolecular structure of the coal (Nelson and Chen, 2007).

Wang and others (2003b) showed that carbon dioxide and carbon monoxide are produced by two parallel reaction sequences. One sequence which predominantly generates carbon dioxide rather than carbon monoxide and a second mechanism, which occurs at specific reaction sites in coal and results in the direct formation of gaseous products, including carbon dioxide, carbon monoxide and water. The authors found that the 70ºC temperature was a critical one for both reactions. According to Nelson and Chen (2007), several studies have found that the oxidation rate of coal increases dramatically as the temperature crosses a threshold of ~70ºC. In simple representation of the oxidation rate, this means that the values for the kinetic parameters (A and E) differ on either side of the threshold. The homogeneity of coal hinders an understanding of the oxidation mechanism, therefore the development of kinetic models that can be used to predict self-heating will represent an important step forward in developing a better understanding of when and why spontaneous combustion occurs (Nelson and Chen, 2007).

A number of test methods have been developed to investigate the low-temperature oxidation of coal, which leads to self-heating. Each has advantages and disadvantages. Sen and others (2009) published a detailed survey of analytical methods, instrumental techniques and test methods for low temperature oxidation. According to Sen and others (2009), despite current knowledge on the process of coal oxidation, a considerable grey area still exists and the exact phenomenon continues to be rather poorly understood. As a consequence a large number of techniques have been developed and used, some extensively, such as for example infrared/Fourier transform infrared spectroscopy (IR/FTIR) and thermogravimetry (TG)-FTIR. However, it is generally accepted that no single technique is able, on its own, to give complete information on the coal oxidation phenomenon.

Due to the complexity of the process, a combination of techniques can still be inadequate. According to Sen and others (2009), certain differences of opinion exist amongst various authors on the comparative merits of the various techniques. As a general opinion, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy is considered to be a useful technique because of the sensitivity combined with a high level of chemical information generated with the technique. Gieseler plastometry is considered by Sen and others (2009) to be the most sensitive technique. Gieseler plastometry involves determination of the coal's softening temperature, re-solidification temperature and maximum fluidity. However, it does not provide chemical information and is therefore of greater use for detection purposes. Mössbauer Spectroscopy is considered a versatile technique that can give precise information about the chemical, structural, magnetic and time-dependent properties of a material such as coal. Key to the success of the technique was the discovery of recoilless gamma ray emission and absorption. Many other techniques are currently in use and presented in the following sections (Sen and others, 2009).

## 3.3 Infrared/Fourier transform infrared (FTIR) spectroscopy

In infrared (IR) spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through/transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. No two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. Infrared/Fourier transform infrared (FTIR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments in which the main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was developed. The solution employed a simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies 'encoded' into it. The signal can be measured very quickly, usually in the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. FTIR can rapidly identify unknown materials. It can determine the quality or consistency of a sample and the amount of components in a mixture. For an introduction to FTIR see Thermo Nicolet Corporation (2001).

Thermogravimetric Analysis (TGA) measures weight changes in a material as a function of temperature (or time) under a controlled atmosphere. Its principal uses include measurement of a material's thermal stability and composition. Thermogravimetric analysis is routinely used in all phases of research, quality control and production operations. The application of TGA combined with FTIR to determine the organic oxygen content in a number of coals of differing ranks was the subject of a study by Charland and others (2003). The results indicated that the organic oxygen content determined by the technique (TGA-FTIR) was accurate. However, the authors concluded that, in their experience, the same sample could show relatively wide variations in oxygen content when protected from atmospheric oxidation and analysed over a period of time.

## 3.4 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a technique used for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. There are two types of DSC systems in common use. In power compensation DSC the temperatures of the sample and reference are controlled independently using separate, identical furnaces. The temperatures of the sample and reference are made identical by varying the power input to the two furnaces; the energy required to do this is a measure of the enthalpy or heat capacity changes in the sample relative to the reference. In heat flux DSC, the sample and reference are connected by a low resistance heat flow path (a metal disc). The assembly is enclosed in a single furnace. Enthalpy or heat capacity changes in the sample cause a difference in its temperature relative to the reference; the resulting heat flow is small compared with that in differential thermal analysis (DTA)

**Table 3 Basic characteristics of three bituminous and one subbituminous coal samples** (Taraba and Peter, 2003)

| Sample | Ash, % (dry) | Volatiles, % (daf) | C, % (daf) | H, % (daf) | S total, % (dry) |
|---|---|---|---|---|---|
| C4 | 2.4 | 25.1 | 90.9 | 4.9 | 0.35 |
| C2 | 3.5 | 35.3 | 88.9 | 6.4 | 0.5 |
| PV1 | 11.5 | 31.2 | 76.6 | 4.1 | 2.6 |
| HN2* | 9.9 | 60.2 | 75.8 | 8.5 | 1.3 |

* subbituminous coal

**Table 4 Results of the calorimetric measurements of the immersion heat Q (values of W correspond to the coal moisture content before immersion)** (Taraba and Peter, 2003)

| Sample | C4 (W=0.7%) | C2 (W=1.3%) | PV1 (W=5.6%) | HN2 (W=3.6%) |
|---|---|---|---|---|
| Additive (10% wt, aqueous solution) | Q, J/g | Q, J/g | Q, J/g | Q, J/g |
| Sodium chloride, NaCl | 1.5 | 1.8 | 5.7 | 11.2 |
| Sodium acetate, $NaOOCCH_3$ | 1.2 | 2.0 | 5.7 | 10.0 |
| Potassium chloride, $Na_2SO_4$ | 1.6 | 1.8 | 5.8 | 11.5 |
| Sodium sulphate, $Na_2SO_4$ | 1.9 | 1.8 | 5.9 | 11.2 |
| Sodium tetraborate, $Na_2B_4O_7$ (cca 33%) | 1.0 | 2.2 | 6.2 | 9.5 |
| Sodium nitrate, $NaNO_3$ | 1.2 | 1.7 | 6.5 | 9.9 |
| Sodium formate, NaOOCH | 1.3 | 1.9 | 6.9 | 9.8 |
| Sodium dihydrogen phosphate, $NaH_2PO_4$ | 1.3 | 2.0 | 7.5 | 10.9 |
| Ammonium chloride, $NH_4Cl$ | 1.1 | 1.9 | 7.7 | 10.7 |
| Calcium chloride, $CaCl_2$ | 1.9 | 2.4 | 8.2 | 12.4 |
| EDTA | 1.4 | 1.8 | 6.7 | 8.0 |
| Sodium sulphite, $Na_2SO_3$ | 7.2 | 16.8 | 22.7 | 39.8 |
| Urea, $(NH_2)_2CO$ | 1.5 | 1.8 | 8.8 | 14.2 |
| Thiourea, $(NH_2)_2CS$ | 1.3 | 1.9 | 17.7 | 15.4 |
| Phenol, $C_6H_5$-OH* (cca 8%) | 3.1 | 8.6 | 22.0 | 26.0 |
| Comparative basis | | | | |
| Deionised water, $H_2O$ | 1.2±0.1 | 1.7±0.1 | 5.8±0.2 | 9.0±0.3 |

* saturated solution at 25°C

because the sample and reference are in good thermal contact. The temperature difference is recorded and related to enthalpy change in the sample using calibration experiments (Bhadeshia, 2002).

Taraba and Peter (2003) studied the interaction of coal with additives inhibiting the self-heating process. With the use of DSC they were able to study the interactions occurring between inhibitors and coal surface as well as interactions between oxygen and coals impregnated by inhibiting agents. Three samples of bituminous coals and one sample of subbituminous coal were investigated (*see* Table 3 for the coal characteristics). Aqueous solutions of 15 different chemical substances were applied at 10% wt concentrations as possible inhibitors. These are listed in Table 4. The nature of the interactions between the coal and the inhibitors was studied with DSC. As a quantitative parameter, the heat of the coal immersion in the inhibitor solution Q was determined. Heat of the immersion of the coal in de-ionised water was used for comparison. In order to evaluate the effectiveness of the individual additive, oxidation heats were measured for coal samples pre-treated by the inhibitor solutions (Taraba, 1997). Oxidation heat for a coal sample pre-treated with the pure water served as the comparative basis. The relative effectiveness of the inhibitor was then assessed as the ratio between the value of the oxidation heat for the inhibitor-treated coal and that for the water-treated sample (%). The basic temperature for the calorimetric measurements was 30ºC. The basic calorimetric data are summarised in Table 4.

Based on the data in Table 4, Taraba and Peter (2003) consider that most of the additives exhibit immersion heat Q quite comparable with the heat accompanying the immersion of coal in pure water. Thus, they conclude that hydrogen bonding between water molecules and functional groups on the coal surface can be denoted as the main type of mutual interaction in such systems. Slight increase in Q values for solution of the inorganic salts could then be ascribed to the heat effects connected with ion exchange and/or complex reactions of the cations. According to Taraba and Peter (2003), this is supported by the increase in values of Q for $NaCl = KCl < NH_4Cl < CaCl_2$, which corresponds to the increase in ion-exchange capability of these cations. In general, interactions of these additives with the coals does not lead to irreversible changes on coal surfaces. Thus, their action can be denoted as physical in character. However, sodium sulphite and phenol are different to the other additives in that their immersion heat Q values markedly exceed the level of Q for pure water. This indicates that these additives affect the coal chemically, causing irreversible changes in its surface.

In Table 5, Taraba and Peter (2003) summarise the results of oxidation heats determined for coals pre-treated with additives. The relative effectiveness of the additives was used (that is, ratio between the value of oxidation heat from the coal treated with an additive and that for coal treated with water) as a quantitative parameter. The data show that the promoting effect of sodium sulphite on coal (chemically) with an increase of more than one order in coal oxy-reactivity (sample $HN_2$) makes it unattractive as an inhibitor of spontaneous heating of coal. On the other hand, the addition of phenol to coal causes practically no change in coal oxy-reactivity. The influence of urea and/or thiourea on coal oxy-reactivity is a somewhat higher immersion heat for inorganic salts, not as high as values of Q for sodium sulphite and/or phenol (*see* Table 5). However their effect on coal oxy-reactivity is quite different. While urea inhibits the coal oxidation process, thiourea increases it. A certain decrease in oxidation heats was observed for inorganic salts with a reduction in oxy-reactivity by 5–45%. Among these, the effect of calcium chloride is the most pronounced. The inhibiting effect of the salts may be explained by hindered access of oxygen to the coal surface when coated by these additives (Taraba and Peter, 2003).

**Table 5 Relative effectiveness, %, of additives in the oxidation of coal samples (values of W correspond to the coal moisture content during the calorimetric testing)** (Taraba and Peter, 2003)

| Additive | Sample PV1 (W=11%) | Sample HN2 (W=16%) | Sample C4 (W=1%) |
|---|---|---|---|
| Calcium chloride, $CaCl_2$ | 55 | 80 | 85 |
| Sodium chloride, NaCl | 60 | - | 90 |
| Ammonium chloride, $NH_4Cl$ | 60 | - | - |
| Urea, $(NH_2)_2CO$ | 60 | 75 | 90 |
| EDTA | 100 | 85 | 95 |
| Phenol, $C_6H_5$-OH | 95 | 100 | 100 |
| **Deionised water, $H_2O$** | 100 | 100 | 100 |
| Sodium sulphite, $Na_2SO_3$ | 200 | 1200 | 130 |
| Thiourea, $(NH_2)_2CS$ | 780 | 170 | – |

## 3.5 Isothermal methods

In isothermal techniques, a coal sample is heated in a bath or furnace at a constant temperature with oxygen or air passing through it at a predetermined rate. The oxidation rate is thus established. This can be used as an indicator of the coal's potential for self-heating (Jain, 2009).

Wang and others (2002) examined $CO_2$, CO and $H_2O$ formation during low temperature oxidation of a bituminous coal in an isothermal flow reactor. The authors consider that the following reactions play important roles in coal oxidation at low temperature:

- chemisorption of oxygen in coal pores and the formation of unstable intermediates;
- decomposition of the unstable intermediates to gaseous products and stable solid oxygenated complexes;
- degradation of the stable complexes and generation of new active sites for coal oxidation following the decomposition of the solid complexes.

Thus, the products of coal oxidation at low temperatures are present both in gas and solid phases. Gaseous products primarily consist of $CO_2$, CO and $H_2O$. The products in the solid phase consist of species containing phenolic -OH, OH, -COOH and -C=O groups in coal aliphatic or aromatic structures. For in depth chemical and physical analysis of coal, aliphatic and aromatic structures *see* Deno and others (1978); Herod and others (1981); and Yun and others (1987).

Experimental testing and careful measuring techniques of $CO_2$, CO and $H_2O$ production, $O_2$ consumption and the change in mass of the coal sample was demonstrated in an isothermal flow reactor to evaluate the mass balance for low temperature oxidation of coal. Wang and others (2002) found that the mass of coal sample usually increased during an experiment, reflecting the accumulation of solid oxygenated complexes in the coal matrix. At temperatures of 60–90ºC, the most important carbon containing gaseous product of oxidation was $CO_2$ while CO is released in smaller amounts, with a molar ratio of $CO_2/CO$ production of about 3. The authors concluded that a significant amount of water vapour is produced during low temperature oxidation of coal and that the amount is proportional to the amount of generated CO, with a molar ratio between them of about 21. The molar ratio of CO production to $O_2$ consumption was found to depend on temperature. Wang and others (2002) consider that this ratio can be taken as an indicator for the onset of coal self-heating and can also serve as an index for the assessment of the propensity of coal to self-heat or combust spontaneously, especially for coals that have already undergone initial oxidation.

## 3.6 Crossing point temperature (CPT)

Crossing point temperature is determined by laboratory techniques and means the temperature at which coal ignites spontaneously. In this method, coal is heated to a specific temperature, which is kept constant. The temperature increase is compared with the temperature increase of an inert material. The point at which the coal temperature exceeds that of the inert material is called crossing point temperature (CPT). The higher the CPT the less prone the coal is to self-heating. This is, internationally, a popular method to determine coal self-heating propensity (Uludag, 2007).

Nugroho and others (2000) reported on the low-temperature oxidation of single and blended coals under self-heating conditions using the CPT method in a cubical wire mesh basket. Four Indonesian coals ranging from lignite, subbituminous and bituminous coals were used in the project. The criteria for the selection of these coals were that they represented low range sulphur coals (<1%) and that the rank should span from low to high rank coals with different self-heating behaviours. The properties of the coals used are listed in Table 6. Following CPT testing, Nugroho and others (2000) state that there are two distinct trends, for lower and higher rank coals, with regard to the physical structure of the coal. For the lower rank coals (South Bangko/Tanjung Enim), there was no change in surface area with particle size. This is due to the porous structure of these coals consisting mainly of mesopores and macropores. There were, however, completely different trends for the higher rank coals (Prima/Pinang). As these hard coals have only a few open pores, for a reduction of particle sizes the surface area increases substantially (almost five fold for Prima coal).

With reference to the self-heating phenomenon, the authors found evidence suggesting that in self-heating conditions, the coal ignition starts from the centre of the bed involving the low temperature, slow oxidation reaction as the main reaction. However, the situation differs under highly supercritical conditions, where the flat temperature profile does not develop, and the central temperature is continuously below the other local temperatures. Subcritical conditions are defined as those where no ignition occurs whilst supercritical conditions are those that lead to ignition. The critical ambient temperature for spontaneous ignition to occur is defined sharply by these marked changes in subcritical and supercritical behaviour which is obtained from the central temperature-time observations.

Nugroho and others (2000) concluded that particle size has considerable influence on the self-heating character of coal. A smaller particle reduces the critical ambient temperature for spontaneous ignition to occur. A typical critical ambient temperature is about 400 K for all coals at an average particle diameter of 0.06 mm. The change of the critical ambient temperature with particle size was found to be almost negligible for porous coals (South Bangko and Tanjung Enim) but significant for hard coals (Pinang and Prima). It was noted that finely crushed (pulverised) bituminous coals exhibit a strong tendency to spontaneous combustion similar to those

**Table 6 Properties of the coal samples tested for low-temperature oxidation of blended coals** (Nugroho and others, 2000)

| Properties | South Bangko coal (Sumatra) | Tanjung Enim coal (Sumatra) | Prima coal (Kalimantan) | Pinang coal (Kalimantan) |
|---|---|---|---|---|
| **Proximate analysis, % wt** | | | | |
| Moisture | 14.2 | 17.5 | 5.2 | 8.8 |
| Volatile matter | 43.7 | 39.7 | 46.8 | 39.2 |
| Fixed carbon | 37.5 | 39.1 | 49.1 | 47.5 |
| Ash | 4.6 | 3.7 | 2.9 | 4.5 |
| **Ultimate analysis, daf % wt** | | | | |
| Nitrogen | 1.25 | 1.05 | 1.76 | 1.55 |
| Carbon | 62.54 | 65.36 | 76.78 | 72.02 |
| Hydrogen | 4.20 | 4.51 | 5.50 | 4.99 |
| Oxygen (by difference) | 32.01 | 29.08 | 15.96 | 21.44 |
| Calorific value, MJ/kg | 23.0 | 28.70 | 31.90 | 29.00 |
| Thermal conductivity, W/m.K | 0.13 | 0.14 | 0.11 | 0.11 |
| Specific heat, J/kg | 1480 | 1440 | 1240 | 1310 |
| Packing density, kg/m$^3$ | 635 ± 4 | 620 ± 5 | 725 ± 6 | 720 ± 6 |

of low ranks coals. Furthermore, a coal bed with a variety of coal sizes is much more vulnerable than one with segregated sizes – that is, it only needs a small amount of pulverised particles and/or strongly reactive coal to have a marked effect on the critical ambient temperature. This means that particle size distribution must be considered carefully to judge the spontaneous ignition behaviour of the coal. Thus, the implications are serious with regard to coal blending (Nugroho and others, 2000).

## 3.7 Differential thermal analysis (DTA)

According to Jain (2009), DTA may be defined formally as a technique for recording the difference in temperature between a substance and a reference material against either time or temperature as two specimens are subjected to identical temperature regimes in an environment that is heated or cooled at a controlled rate. The differential temperature is then plotted against time or against temperature. Changes in a sample which lead to absorption of evolution of heat can be detected relative to the inert reference matter. Differential temperatures can also arise between two inert samples when their response to the applied heat treatment is not identical. DTA can thus be used to study thermal properties and phase changes which do not lead to a change in enthalpy. Jain (2009) discussed in detail how to determine the susceptibility of 14 coal samples from Indian coal mines to self-heating and spontaneous combustion by using DTA.

Pis and others (1996) studied the self-heating of fresh and oxidised coals by DTA. They observed self-heating temperatures between 180ºC and 270ºC for coals ranging from high rank bituminous to semi-anthracite. The lowest temperature corresponded to the lower rank coals. They concluded that coal oxidation gives rise to an important modification both in the characteristic temperatures (self-heating and end of combustion temperatures) and in the heat flow rate. The characteristics of the volatiles released up to about 425ºC seemed to be mainly responsible for the loss in calorific value of the coals as a consequence of oxidation. Uludag (2007) discusses the finding of Pis and others (1996).

## 3.8 Adiabatic methods

Adiabatic is a condition under which heat produced by a reaction is retained rather than emitted. A coal sample is placed in an insulated bath or oven chamber that is designed to maintain the coal at a constant temperature. The temperature is then raised to a pre-selected value (starting temperature) in a stream of flowing nitrogen. Once the system has attained thermal equilibrium, the apparatus is put into an automatic control mode in which the nitrogen is shut off and the sample is exposed to a stream of preheated oxygen or air (dry or moist) until the coal temperature is above that of its surroundings. The temperature of the bath or the oven chamber rises automatically to coincide with the coal temperature. Testing is run over a period of several hours depending on the starting temperature and the oxygen concentration until ignition occurs. This is determined as the minimum temperature at which there is a steep rise in the temperature on the temperature-time curve. Coals may also be characterised by their 'adiabatic self-heating time', which is the time interval between the start of the test and ignition of the sample. By incorporating an automatic oxygen feed regulating system, oxidation rate/adiabatic self-heating time curves can be drawn (Jain, 2009).

Beamish and others (2001, 2003) discussed the kinetic parameters associated with self-heating of New Zealand coals under adiabatic conditions. The adiabatic self-heating tests were carried out on five coal samples ranging in rank from lignite to high-volatile bituminous. The results of the study showed that the coals were extremely reactive to oxygen and have a high propensity for self-heating. The subbituminous coals tested had the lowest activation energies and the highest initial self-heating rates. They were therefore deemed extremely prone to self-heating. The activation energies increased for the oxidation reaction for lignite and for the high-volatile bituminous coal tested. Beamish and others (2003) concluded that coal that had been stored or pre-oxidised to some extent through interaction with air in the atmosphere showed a significant increase in activation energy and pre-exponential factor.

The findings supported previous work by researchers that questioned the validity of an assumed activation energy for assessing the self-heating of coals. According to Beamish and others (2003), the test results showed that the adiabatic method is capable of producing kinetic parameters of coal oxidation, which correlate well with other measures of coal reactivity. In a previous study, Beamish and others (2000) established that New Zealand subbituminous coal share self-heating rate index values of 14.91–17.23ºC/h, determined also by testing in an adiabatic oven. They concluded that there is a strong relationship between self-heating rate and coal rank. As coal rank decreases the self-heating rate increases. The authors found that in contrast, Australian subbituminous coal has a self-heating rate index ranging between 3.16ºC/h and 6.16ºC/h. They considered that these values are lower due to the higher inertinite contents of the Australian coal, which tends to inhibit the self-heating process (Beamish and others, 2000).

Beamish and others (2005) reported on the **$R_{70}$ test** to evaluate the propensity of coals to self-heat. The coals ranged from subbituminous to medium volatile bituminous and covered a wide range of ash content from 0.7–63.9%, dry basis. The $R_{70}$ testing procedure essentially involved drying a 150 g sample of <212 mm crushed coal at 110ºC under nitrogen for approximately 16 hours. Whilst still under nitrogen, the coal was cooled to 40ºC before being transferred to an adiabatic oven. Once the coal temperature had equilibrated at 40ºC under a nitrogen flow in the adiabatic oven, oxygen was passed through the sample at 50 m/min. A data logger recorded the temperature rise due to the self-heating of the coal. The average rate that the coal temperature rises between 40ºC and 70ºC was the self-heating rate index ($R_{70}$), which is in units of ºC/h and is a good indicator of the intrinsic coal reactivity towards oxygen. Beamish and Blazak (2005) discuss in detail the relationship

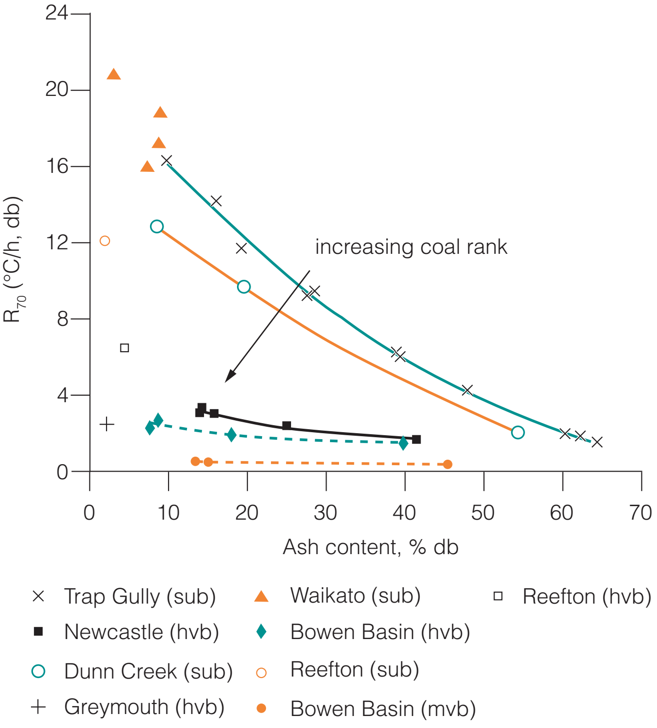


**Figure 16 Relationship between coal ash content, rank and $R_{70}$ self-heating rate** (Beamish and others, 2005)

between ash content and $R_{70}$ self-heating rate of Callide coal while Beamish and Hamilton (2005) present the effect of moisture content on the $R_{70}$ self-heating rate of Callide coal.

According to Beamish and others (2005), as the $R_{70}$ value is obtained on a dry basis, the best way to represent the data, graphically, is to plot it against the ash content (on a dry basis) (*see* Figure 16), which is a standard analytical determination for coal. The ash content is closely related to the mineral matter in the coal. This is composed of the inorganic constituents of the coal that modify its behaviour in many combustion processes. In the case of the coal self-heating the mineral matter acts as a diluent. Figure 16 shows that subbituminous coals have the highest $R_{70}$ values for any given ash content. There also appears to be no major difference between two subbituminous coals from different mines, despite there being a substantial difference in the maceral composition between the two. One coal contains very little inertinite, where the other contains a significant amount of inertinite. The authors find this somewhat surprising and consider that it may be an artefact of the type of sample tested. One was preserved in its original state while the other was from a sample bank and may have undergone some oxidation prior to the testing. According to Beamish and others (2005), the rank and ash relationship shown in Figure 16 makes it possible to infer a reasonable value for $R_{70}$ based on coal quality in areas where no test information is available. However, it should be noted that subtle differences in coal reactivity can occur due to the different types of mineral matter that are present.

**Table 7 Calculated $T_{ad}$ values by NSW (Australia) coalfields** (Sargeant and others, 2009)

| Location | $T_{ad}$ (days) | $R_{70}$ | Ash, % (dry basis) |
|---|---|---|---|
| Southern coalfield | 57.15 | 0.35 | 9.7 |
| Hunter coalfield 1 | 13.03 | 1.28 | 10.1 |
| Newcastle coalfield | 5.24 | 2.62 | 9.3 |
| Hunter coalfield 2 | 2.27 | 4.75 | 10.9 |
| Hunter coalfield 3 | 1.03 | 7.91 | 11.8 |
| Gunnedah coalfield | 0.92 | 9.52 | 8.1 |
| Newcastle coalfield 1 | 4.63 | 2.79 | 11.6 |

Sargeant and others (2009) discussed the '**time to ignition**' theory which has had limited use in the coal industry and virtually no use within Australia. The theory was first applied to Scottish coals to assess their spontaneous combustion propensity during transport in a 3 x 3 m shipping hold. The authors selected adiabatic self-heating data from a laboratory database for analysis. The data consisted of seven samples from four NSW (Australia) coalfields with ash contents in the range 8–12%. The original time to ignition concept was derived in the early 1980s with the purpose of providing an analytical treatment for systems with distributed temperatures in which heat-transport is controlled by conduction. More recently, the concept was used in the calculation of coal transport ignition times. The equation shows the expression used to calculate the times to ignition ($T_{ad}$):

$$T_{ad} = \frac{RT_R^2}{E}\frac{c}{QA}exp\left[\frac{E}{RT_R}\right]$$

where the time to ignition, $T_{ad}$ is in seconds (s) of a reactant of specification A (pre-exponential factor) and E (activation energy) at initial temperature $T_R$, c is the specific heat, Q is the heat of reaction and R is the universal gas constant. The expression c/QA can be obtained directly from the test data. Both $T_{ad}$ and $R_{70}$ values were calculated for the data (*see* Table 7) and plotted in Figure 17. The graph shows a strong non-linear relationship between $T_{ad}$ and $R_{70}$ self-heating rate. Sargeant and others (2009) found this somewhat surprising as the $T_{ad}$ calculations were based on a portion of the adiabatic self-heating curve above 70ºC and the $R_{70}$ value was obtained from 40–70ºC of the curve. The authors noted that the $T_{ad}$ start temperature has a large impact on the resulting time to ignition (*see* Figure 18). The value of 25ºC used for NSW conditions was compared to 40ºC, to replicate Queensland conditions and outline the difference a simple change in temperature has on $T_{ad}$. The southern coalfield sample $T_{ad}$ value reduced from 57 days to 17 days making it clear that a coal mined in NSW may not create a spontaneous combustion issue, but the same coal mined in Queensland could create a problem. The authors concluded that generally, high rank coking coals have the highest $T_{ad}$ values and lower rank steaming coals have the lowest $T_{ad}$ values due to the significant difference in activation energy required for the oxidation reaction to take place in each of these coal types (Sargeant and others, 2009).

Modelling the spontaneous combustion of coal by the adiabatic testing procedure was the subject of a detailed study by Zarrouk and others (2006). The work was part of a project aimed at developing a general-purpose simulator for

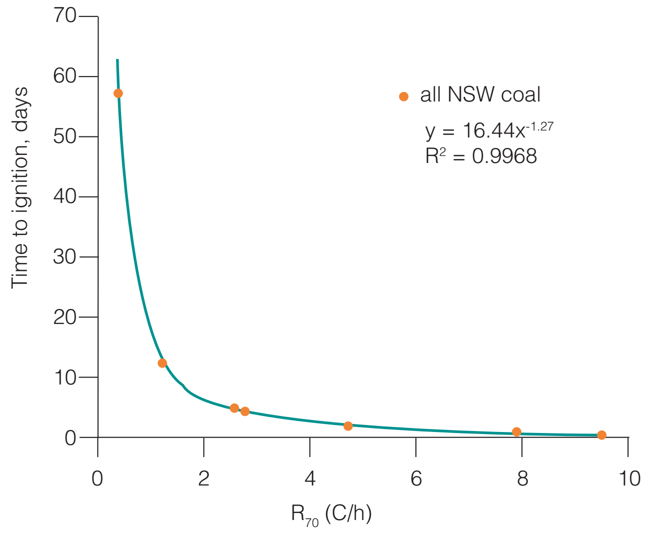


**Figure 17 Relationship between $T_{ad}$ and $R_{70}$ self-heating rate** (Sargeant and others, 2009)

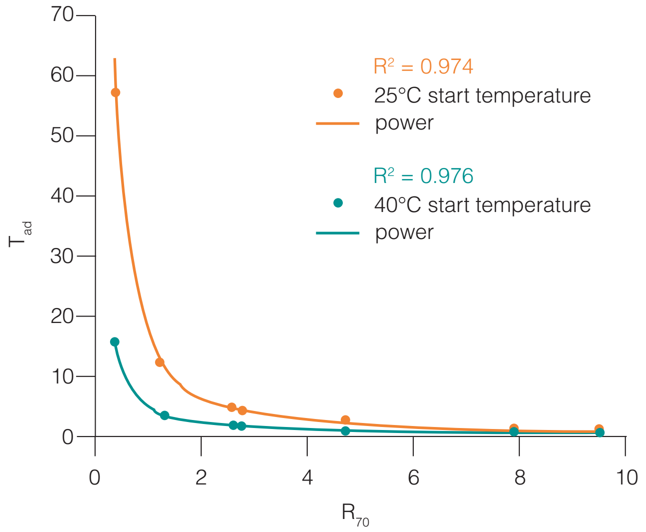


**Figure 18 Comparison of start temperature effect on $T_{ad}$ values** (Sargeant and others, 2009)

modelling heat and mass transfer as well as chemical reactions in coal. The simulator applications included not only the spontaneous combustion of coal but also coal gasification, extraction of coalbed methane and enhanced coalbed methane extraction with re-injection of $CO_2$. The authors concluded that the simulations produced a good match to several experimental results from the adiabatic testing procedure. Zarrouk and others (2006) considered that the simulator enables the modelling of general problems related to the storage and self-heating of coal.

According to Uludag (2007), adiabatic testing is difficult to achieve and the instruments used for this purpose are complex and expensive. They are however, more effective than instruments used for DTA analysis.

## 3.9 Hot storage and heat rate release methods

The hot storage test is also known as the basket test, the F-K (Frank-Kamenetskii) method, the steady-state approach, the oven-heating test and the wire-mesh basket test. It has been widely used to study the self-heating characteristics of solid materials including coal. According to Nelson and Chen (2007), in the hot storage test, coal particles are placed into a gauze container of a known size, which is then suspended in a fan-assisted oven of given ambient temperature. The temperature at the centre of the container is measured using a thermocouple. It is then easy to decide from the maximum temperature increase if the system is subcritical or supercritical. Subcritical conditions are defined as those where no ignition occurs whilst supercritical conditions are those that lead to ignition. The experimental setup must enforce two conditions which are: that there must be purely conductive heat transfer within the coal undergoing self-heating and there should be good convective heat transfer within the oven so that the surface temperature of the sample is maintained at ambient temperature. The hot storage test is based on the theoretical model of F-K. Nelson and Chen (2007) discuss the F-K method as well as the hot storage test application in detail.

The advantage of the hot storage method is that it is relatively small scale and since enough data points can be determined to obtain a straight line fit, it can be used to estimate the critical ambient temperature for self-ignition of large quantities of coal. The disadvantage of the test is that it is very time consuming because an iterative procedure is required to determine the critical ambient temperature for a given sample container. Thus, several experiments are required to obtain one data point. The process is then repeated to obtain data points for sample containers of different sizes. Measuring the critical ambient temperature for five container sizes requires a week or more of experimental work. According to Nelson and Chen (2007), this is the reason that the hot storage test has not been directly used as the basis for determining if self-heating material can be stored safely during transport.

The heat release rate method (HRRM) was developed in the mid-1990s. The test method assumes that there is no heat transfer at the geometric centre of a sample when the temperature there is equal to the oven temperature. According to Nelson and Chen (2007), the advantage of the HRRM method, over the hot storage method, is that one experiment leads to one data point on the kinetic plot, as opposed to the hot storage test, where several experiments are required to obtain one data point. Furthermore, all data points can be obtained using one container size, whereas several container sizes are required in the hot storage test. The HRRM is therefore time-effective compared to the hot storage test. In the HRRM test, as in the hot storage method, a gauze container is loaded with 'cold' coal particles and is placed in a fan assisted 'warm' oven of a given ambient temperature. A cubical container with 10 cm sides is typically used. Where the HRRM method differs from the hot storage test is how the data are analysed. The HRRM test can be applied to estimate the activation energy from a single criticality data point obtained using the hot storage test. For detailed analysis of the HRRM test, see Nelson and Chen (2007).

A large amount of experimental work has been undertaken on self-heating and spontaneous combustion of coal. According to Nelson and Chen (2007), the Frank-Kamenetskii (F-K) steady-state model for the self-heating of bulk solids is the simplest model for the spontaneous combustion of a coal stockpile. The method underpins experimental tests that are used to explore the safety of transporting hazardous material. There is limited experimental work carried out on large stockpiles, due to the expense and time-consuming nature of such work.

In summary, there are numerous methods currently in use and some under development to evaluate, monitor and detect coal-fires in stockpiles, silos and bunkers. Three of the major, widely used techniques are based on carbon monoxide (CO) monitoring, thermal monitoring and infrared scanning. The methods used to evaluate, monitor and detect coal self-heating discussed in this chapter included mathematical modelling, chemical kinetics, infrared/Fourier transform infrared (FTIR) spectroscopy, Differential scanning calorimetry (DSC), isothermal methods, Crossing point temperature (CPT) technique, Differential thermal analysis (DTA), adiabatic methods and hot storage and heat rate release methods.

# 4 Coal fire prevention and control

Whilst in storage, coal continually oxidises and generates heat and unless methods are used to monitor and identify the area of coal self-heating, a fire may start which unless controlled/suppressed, can result in not only the loss of income due to plant shut-down but also can be costly in human life. In February 2009, The Business Journal of Milwaukee (USA), reported an explosion at We Energies' Oak Creek coal-fired power plant complex which left five workers injured, 4 of them critically. They had been working in a large coal dust collector hopper. Another example is the fire which occurred in an underground coal stockpile in Finland in October 2009, as a result of coal self-heating and spontaneous combustion (Reuters, 2009). On 4 June 2009, firefighters were required at stockpiles of coal inside the Aurora Energy Downtown power plant. One individual was injured due to the fire (Delbridge, 2009).

The primary cause of self-heating, as discussed in Chapter 2, is the exothermic oxidation of coal at low temperatures. Below 40ºC, the rate of oxidation is slow, but accelerates by a factor 1.8 thereafter. The critical temperature above which the oxidation and self-heating process becomes self-sustaining is about 50ºC for lignites and 70–80ºC for bituminous coals. In general, the oxidation increases at 10 times its usual rate as the temperature rises from 30 to 100ºC. This self-heating can only occur where there is sufficient oxygen, the coal is dry and the heat balance is in favour of heat retention in a pile. The critical (intrinsic and extrinsic) factors that affect coal self-heating are shown in Table 8 (Nijhof, 2006). Cliff (2009) discusses spontaneous combustion management and linking experiments with reality.

Douberly (2003) discussed fire protection guidelines for handling and storing Powder River Basin (PRB) coal which has a greater propensity to ignite in bunkers, silos and hoppers compared to other US coals. The PRB Coal Users' Group (USA) has devised a set of recommended practices for safely preventing, detecting and extinguishing coal fires at power plants. The guidelines are not equipment specific because the physical layout of coal-handling facilities varies significantly between plants and because all fires are unique. Douberly (2003) advises that the guidelines are not comprehensive and that their purpose is to recommend general practices that must be adapted for the specific needs of a plant. The guidelines provide information about three areas: fire prevention and detection, fire-fighting equipment and training, and fire-fighting. According to Douberly (2003), operators familiar with the unique requirements of burning PRB coal acknowledge that it is not a case of 'if' but 'when' will there be a fire. The prevention of fires and explosions is the foremost objective for any plant firing PRB coal. Problems and solutions when firing PRB coal are discussed by Javetski (2004). Upgrading of pulverisers and modifying fuel handling systems to cope with PRB coals are discussed by Kmiotek and others (2004).

## 4.1 Identifying areas of self-heating

Predicting the propensity of coal to self-heat is complex and difficult due to the number and variety of variables involved. However, adapting a controlled storage process, avoiding particle segregation and limiting air flow in a pile, can make predictions viable (Nijhof, 2006).

Few large-scale experimental studies have been undertaken into the behaviour of stockpiles of the size found in coal storage yards in power plants due to the expense of running such tests and the length of time it can take to run one experiment. Despite these drawbacks, Nelson and Chen (2007), discuss some experiments that have provided useful data. The larger the stockpile, the greater is the risk of spontaneous combustion. Such stockpiles can undergo subcritical self-heating that reduces both the calorific value and the weight of the stored coal. The changes in coal properties due to subcritical heating is known as weathering or pre-oxidation. According to Nelson and Chen (2007), in addition to self-heating, secondary mechanisms for mass and calorific loss include partial or total coal combustion, removal of small coal particles due to wind and rain (leaching),

**Table 8 Critical factors affecting coal self-heating** (Nijhof, 2006)

| Intrinsic factors that cannot be controlled | Extrinsic factors that can be controlled |
|---|---|
| **Coal properties** | **Storing practices** |
| High volatile matter | Segregation/accumulation of fines |
| High moisture | Maintenance |
| High friability | Oxygen access/air pressure differential |
| High dispersion of pyrite (>2%) | Degree of consolidation |
| High specific particle surface area | Layout of stack/exposed stack surface |
| Pre-stresses/micro-fracturing | Relative moisture content of coal and air |
| Geological disturbances | Reduction of oxygen concentration through emission of gases (purging) |

volatilisation due to pyrolysis and incomplete recovery of the pile during removal. The significance of leaching and dragging is difficult to estimate experimentally. When self-heating reaches a stage where the stockpile needs to be cooled, water may be applied. However, the increase in coal water content reduces its heating value. In addition, when stockpiled coal is exposed to water, whether through rain or the application of water spray, some organic and inorganic matter such as calcium, magnesium and sulphur leach out. Not only can this cause a small decrease in the calorific and weight value of the coal, but it also produces an environmental hazard. Since self-heating can increase the local temperature inside a stockpile to above 100ºC, the application of a water spray to reduce localised self-heating may result in hot water running through the stockpile thus increasing leaching.

In addition to the possibility of spontaneous combustion due to the size of the stockpile, variation in the ambient temperature due to solar heating can also induce ignition. If the stockpile ignites, the amount of coal involved, which can be hundreds or even thousands of tonnes, presents major problems in extinguishing the resulting fire. Stockpiles must therefore be continuously monitored as it can take several months before a hot spot appears within a pile. Nelson and Chen (2007), state that mathematical models are required to develop reliable practices that minimise self-heating in large stockpiles.

Infrared thermography may be a suitable technique for measuring radiation emitted from coal at temperatures at around 300 K. However, in a late-1980s study, the method was unsuccessful in detecting self-heating in a coal pile. In a more recent study undertaken in the late 1990s, surface temperatures of a stockpile measured by an infrared thermographic camera were in agreement with those measured by thermocouples. Nelson and Chen (2007) consider that in order to obtain good results, infrared measurements have to be restricted to the hours of the day in which the surface temperature does not change rapidly. Infrared thermography was also deemed efficient at detecting hot spots in the coal. Where hot spots are identified near the surface of a stockpile they can be excavated or are exposed to the atmosphere to permit cooling.

One area of self-heating is a silo/bunker following an unscheduled shut-down. Coal trapped in the silo/bunker can eventually oxidise enough to start burning. The length of time it takes for the coal to reach the burning point is a function of the reactivity of the coal. Some coals can reach this point in a few days. According to Hoover (2005), when coal sits in a silo for a prolonged period of time, such as during a scheduled maintenance outage, it can, and often does, combust spontaneously and by the time the fire is discovered it is extremely difficult to get down into the silo to extinguish the source of the fire. Evaluation, monitoring and detection methods and techniques currently in use and under development were discussed in Chapter 3.

## 4.2 Preventing fires in coal stockpiles

Self-heating in stockpiles must be minimised to reduce economic losses. Carpenter (1999) discusses in detail the management of coal stockpiles in order to minimise such losses. A variety of measures have been tried to reduce self-heating including minimising the angle of the slopes of the stockpile, compaction of the pile, protection of the coal pile by covering it with an inert material, making the atmosphere inert and the use of natural or artificial wind barriers around the perimeter of a stockpile (to reduce air flow through the stockpile). These measures have advantages and disadvantages. Compaction of the pile reduces the pore volume between coal particles, which decreases air ventilation through the stockpile and is an effective method to reduce permeation of air. A loosely-stored pile may have a voidage of 25–30%. Voidage is the volume of the voids in a sample of powdered material divided by its overall volume (that is, the total volume occupied by the voids and the solid material). Voidage may be reduced to 10% by compaction using mechanical means. Compaction also reduces the permeation of water into the pile and changes the thermal conductivity of the pile. Compaction can significantly increase the safety of a stockpile for reactive coals, such as lignites and brown coals. However, it can have the opposite effect for unreactive coals (Nelson and Chen, 2007).

Oberrisser (2008) discusses trends in coal pile design. He considers that an optimal coal pile design takes into account the site-specific, and often conflicting, needs of a new power plant in its early design stages rather than using the land available after the plant layout is finalised. Questions to be addressed include potential coal blending, switching, and delivery, as well as land availability. In general, the answer results in choosing a conventional longitudinal or circular pile layout. Oberrisser (2008) considers that both types have pros and cons. He states that regardless of the pile design chosen, every coal pile must have the flexibility to handle coal of various quality and makeup. Oberrisser (2008) undertook four case studies that highlight pile selection criteria and management. He concluded that a coal pile management system has three main functions, which are buffering, composing and homogenising.

The buffering function ensures that there is enough coal in the plant's coal bunkers for the plant to achieve continuous operation. It prevents brief supply interruptions from becoming an operational problem. The composing function ensures that a completed coal pile has the required composition, that is the correct proportion, by weight, of coals with different chemical and/or physical characteristics. The homogenising function manages the layering of various coal types over the length of the pile. Layering reduces the average deviation of a chemical or physical property over successive pile cross sections, compared to the deviation from average of the characteristic in arriving coals. If the plant served by the pile will be firing coal blends, a stockpile pre-homogenising system would allow a capacity increase simply by extending the length of the rails on which the stacker and reclaimer ride (Oberrisser, 2008).

If there is no air flow through a stockpile, then once the oxygen within the pile is consumed, the oxidation rate is zero. Where there is sufficiently low air circulation, the oxidation rate is limited by the supply of oxygen and only a minor amount of self-heating occurs and therefore the stockpile is safe. This is also the case when there is sufficiently high air circulation in the stockpile. In this case, the heat is removed quicker than it is generated and the temperature of the stockpile approaches the air temperature. This is called a ventilated pile. Between these two states, there are two scenarios. In the first case scenario, self-heating inevitably leads to spontaneous combustion. In the second case, there are two possibilities, either limited self-heating takes place or spontaneous combustion occurs. Which scenario is likely to happen depends on the initial conditions of the problem. This is called a thermal explosion of the 'second kind' (Nelson and Chen, 2007). Thus, one method of reducing self-heating is to control the air flow through the pile. However, this has the danger that if air flow is incorrectly implemented, the risk of spontaneous combustion increases.

In a segregated pile of coal the processes of oxidation and adsorption do not occur uniformly. The rate and direction of air movement and air/coal surface contact area depend upon the geometry of the pile, the permeability of the walls containing the pile, compaction, and the fineness of the coal. Hence, the escalation of temperature that characterises the development of a concealed fire, predominantly in uncovered piles, occurs first at discrete foci (hot-spots). The movement of the heat depends upon the rate and direction of air flow. Appropriate pile configuration that limits the introduction of oxygen in the pile is therefore critical in mitigating spontaneous combustion (Nijhof, 2006).

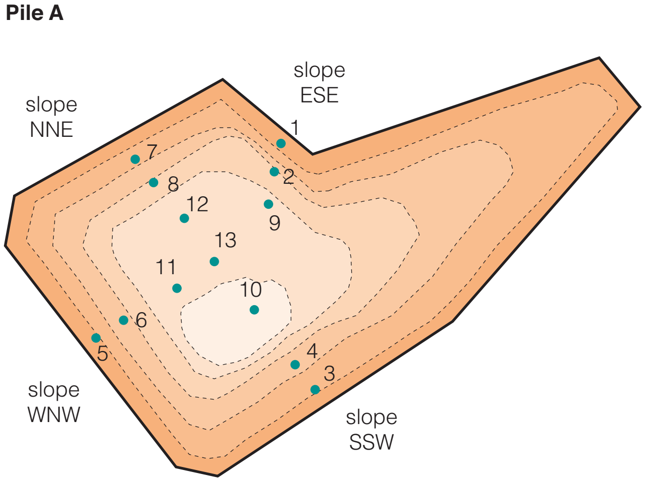
Modelling work on low temperature oxidation of coal and spontaneous combustion in stockpiles began in earnest in the early 1990s. Krishnaswami and others (1996) prepared a series of papers on such modelling work. The authors found that large-scale tests indicated that fires in stockpiles, in general, occur on the windward side of the pile. At a given wind velocity, coal piles with gentler slopes are therefore less susceptible to spontaneous combustion. Nelson and Chen (2007), state that the wind velocity through the pile (ventilation) and the porosity of the pile (voidage) have been identified in modelling work as being key parameters for controlling self-heating in stockpiles. Voidage was found to be the more important parameter because it controls the effects of the wind velocity. The crucial role played by voidage was observed as hot spots did not appear in simulations of stockpiling over 400 days at a voidage of 10%, whereas at a voidage of 25% hot spots appeared in a few hours. It has also been observed that aged and pre-oxidised coals have a higher initial rate of heating in adiabatic tests than fresh coals. This suggests that freshly mined coals should neither be processed nor stored with weathered coals because the more rapid initial heat release from the aged coals may provide sufficient energy to ignite the fresh coal. Nelson and Chen (2007) consider that this mechanism may explain the observation that 'when a new pile of coal is laid on an existing weathered pile, fires occur in the plane of contact between the two piles'.

Furthermore, where two coals have the same mixture of particles sizes, the propensity for spontaneous combustion of the reactive coal may be reduced by blending it with a less reactive coal or by increasing its ash content. However, a coal blend containing a mixture of sizes throughout its volume is more vulnerable to self-heating than coal in which the different sizes of particles are segregated throughout its volume. The effect, however, is non-linear and therefore the presence of a small amount of either a finely crushed coal or a very reactive coal can lead to a large increase in the propensity to self-ignite. Where a stockpile contains coal that has been added at different times, a 'first-in, first-out' policy should be used when coal is removed (Nelson and Chen, 2007).

Ejlali and others (2009) propose a new criterion to design reactive coal stockpiles by using mathematical modelling and computational fluid dynamics (CFD). The authors modelled a triangular stockpile as a porous medium to study the fluid flow, heat transfer, variation of maximum temperature and consequently heat removal phenomena under steady state conditions. Numerical results showed that the maximum temperature of the coal stockpile decreases as air ratio increases. Air ratio enhancement improves the heat removal but it also increases the coal oxidation process. The authors concluded that the intersection between air ratio and maximum temperature curves, when plotted versus air ratio, can be used to find out the safe (design) area for a reactive stockpile (Ejlali and others, 2009).

Krajčiová and others (2004) developed a mathematic model including a detailed radiation balance of coal stockpile surfaces. The aim of the project was to describe the role of the meteorological conditions in temperature changes in more detail even on the oriented slopes of a coal stockpile. Cyclical, and therefore non-constant, energy from the sun has a strong influence on the temperature profile in a coal stockpile. The model has been developed using meteorological input data obtained experimentally and thus evaluation of several parameters for the computation may be omitted. The authors consider that a two-dimensional model is necessary when describing a commonly used heap-like stockpile where the changing boundary conditions must be applied on the topside as well as on both slopes. The periodic boundary conditions applied on the oriented slopes differs from that applied on a horizontal surface. The slope angles as well as the cardinal points, according to Krajčiová and others (2004), play their role in simulations. This is because there is a difference in the global radiation on an oriented slope facing west and east (south and north). Thus, the temperature profiles for a heaplike stockpile are not symmetric.

Krajčiová and others (2004) included four types of coal with different reactivities in their studies. The influence of several factors were observed on the temperature profile in two types of coal stockpiles. Factors observed included coal reactivity, coal matrix porosity, meteorological conditions as well as coal reactivity (two-dimensional model) and coal matrix porosity (two-dimensional model). The authors concluded that coal reactivity has a strong influence on the maximum temperature in the stockpile. The same can be said of stockpile porosity – that is, by decreasing the stockpile porosity, even a runaway can be prevented. The simulations of a heap-like stockpile showed that the temperature profile is not symmetric and that the hot spot occurs mostly on one side. According to Krajčiová and others (2004), this is due to different solar radiation exposure on two differently oriented slopes. The



| probe, m | levels, m | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| 3.00 | 1.00 | 2.00 | 3.00 |
| 1.50 | 0.50 | 1.00 | 1.50 |
| 0.60 | 0.20 | 0.40 | 0.60 |

**Figure 19 Topographic map of Pile A with probe locations and probe levels** (Fierro and others, 1999a)

authors also observed that more solar radiation reaches the horizontal surface than the slopes. In addition, they found that the slope orientation to the cardinal points is not negligible. Their final observation was that the slope angle influences the temperature within the stockpile.

Nijhof (2006) reported the computational investigation of oxygen penetration in coal storage. The author states that since the surfaces of the stacks/piles are frequently exposed to the surrounding atmosphere (air), the configuration of the pile is of importance with regard to self-heating. Nijhof (2006) considered four types of storage and their exposed surface area. Irregular dispersal of the coal particle sizes (segregation) in the stack accommodates self-heating in that the coarse particles allow the air to enter the pile at one location, travel and react with the high surface area fine particles in another location. According to Nijhof (2006), introducing a controlled method of stacking and reclamation (that is, layer by layer) results in no segregation and therefore a reduced risk of self-heating.

**Table 9 Properties of coal selected for experimentation** (Fierro and others, 1999)

| Analysis | |
|---|---|
| Volatiles, % | 33.0 |
| Ash, % | 31.0 |
| Fixed carbon, % | 36.0 |
| Pyritic sulphur, % | 3.60 |
| Sulphate sulphur, % | 0.39 |
| Higher calorific value, kcal/kg | 4711 |
| Peroxide number (eq peroxide/g coal) | $7.7 \times 10^{-5}$ |
| Thermal conductivity, W/mK, 20°C | 0.113 |
| Heat generation rate, mW/kg, 40°C | 600 |

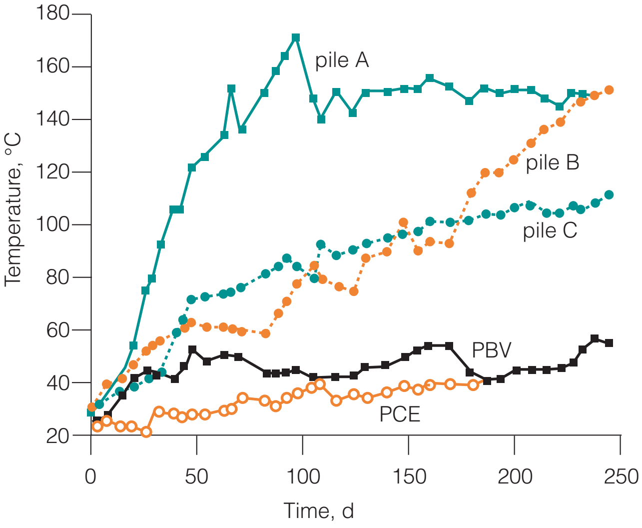


**Figure 20 Variation in average temperature over time for five coal stockpiles** (Fierro and others, 1999a)

Fierro and others (2000 and 1999a) reported their experimental results for the prevention of spontaneous combustion in five coal stockpiles (weighing between 2000 and 3000 t). As an example, Figure 19 gives a topographic map of Pile A with probe locations and probe levels. The experimental piles were erected to allow the testing of the efficiency of periodic compaction, use of a low angle slope in the prevailing wind direction, pile protection by artificial barriers or covering the pile with an inert layer to prevent self-heating and spontaneous combustion. Table 9 shows the properties of the coal selected for the experiments. The authors note that the coal's high ash, pyritic sulphur and sulphate content is evidence of previous weathering. The high concentration of peroxide combined with the high value of heat generation rate and the above mentioned pyritic content, indicate that the coal is highly susceptible to spontaneous combustion. In order to obtain a better characterisation of the coal, bulk density, water density, particle size distribution, specific surface area, infrared and Mössbauer spectroscopy as well as other calorimetric tests were carried out. The results showed that the most interesting phase in the evolution of coal piles is the first 50 days. Fierro and others (1999a) found that during this period significant roles are played by the characteristics of the coal (for example: reactivity, particle size distribution and moisture content), characteristics of the pile (for example: geometry, shape and porosity) and meteorological conditions (for example: direction and intensity of wind, temperature fluctuation and humidity). Studying the average temperatures in the piles highlighted the important differences of the temperature that may be reached. The average temperatures for the five coal piles are shown in Figure 20. Pile A, used as the reference, appears very active in the first 100 days. Temperatures as high as >500º were detected, however, later the average temperature became approximately constant as shown in Figure 20. Fierro and others (1999a) consider this to be due to a certain balance of heat produced in the pile and the heat loss caused by natural convection because of the low compaction of the slopes, which allows the air to enter in and results in heat loss in hot spots. The authors explain that the high activity of the reference pile A could be due to the high slope angle (>45º), which allows the wind to enter the pile easily and thus increasing, significantly, natural and forced convection. When removing the pile, ash layers of 0.40–0.50 m thick were found on the external part of the slopes.

According to Fierro and others (1999a), smaller porosity of the pile reduces its tendency toward spontaneous heating, thus periodical compaction was applied to pile B. The compaction of the slopes reduced oxygen access to the pile but the formation of hot spots in zones of lower compaction could have lead to a general heating of the pile. Although pile B had a lower cooling effect than pile A, the authors noted that it could have had a similar danger of self-heating if it had been studied for a longer period of time. The slope in pile C was considered one of the most important considerations in safe stockpiling. The pile was built with a low angle slope oriented to the prevailing wind. Although evidence of self-heating was observed in the pile (*see* Figure 20), the low angle slope section reached only a maximum temperature of 67ºC. Pile PVB, which was protected with a wind barrier, did not show signals of self-heating or potential for spontaneous combustion during the experimental period. The effect of covering the coal stockpile with an inert layer of fly ash-water slurry mix was a smooth and constant increase in temperature reaching 88.5ºC at the highest point. However, the total average temperature of the PCB pile was 41ºC. This pile was considered by the authors a ‘cold pile’. The fly ash-water slurry layer withstood rain, wind and temperature variations. In order to sustain the adequate moisture content, the layer was irrigated periodically and carefully. During the experimental period, loss in the layer due to rain, wind and other factors was <5% of the total protected surface.

Fierro and others (1999b) discussed in detail the use of infrared thermography for the evaluation of heat losses during coal storage. Fierro and others (1999a) concluded that the high (19.5%) total losses in pile A could have been caused by the high angle (>45ºC) of the slopes. The application of one low angle slope in pile C was considered effective despite the high total losses in the pile due to the remaining high angled slopes. Periodic compaction of the coal stockpile was found to be effective in reducing losses (from 19.5% to 7.1%) at a cost half of that required for wind screens as in the PVB pile. The PCB pile, covered in fly ash-water slurry mix obtained from the power plant where the experiments were carried out, was found to be the most effective and efficient measure with the lowest coefficient of total losses (3%) combined with a moderate application cost. Although the wind screen PVB pile had a low coefficient of total losses, at 6%, it is more costly (Fierro and others, 1999a).

## 4.3 Preventing fires in coal silos and bunkers

Coal storage is a subject that is being reconsidered and examined more closely according to Ruijgrok (2009). The main criteria in deciding whether to use silo storage include space and capacity considerations, environmental considerations, safety and fire issues and a high degree of automation.

Space and capacity considerations are necessary particularly for restricted areas, as the volume to area storage factor is of great importance. Silos are compact in comparison to covered stockpiles, whether circular or rectangular. Their environmental impact is smaller as they result in, for example, less dust emissions and water percolation. The configuration of a silo can minimise the intrusion of oxygen in the stored coal mass and the tight packing can reduce the potential for possible fires. Where self-heating is discovered, by using for example a CO-detection system, measures may be taken to stop a fire starting, for instance by making the silo fully inert by nitrogen purging. Silos with a mechanical filling and reclamation system can be controlled remotely. In addition, an online blending facility may be included through controlled reclamation from two or more silos simultaneously (Ruijgrok, 2009).

Periodical cleaning as well as proper filling procedures can prevent a fire starting in a silo/bunker due to coal self-heating. Housekeeping involves controlling dust and preventing spills. For example, float dust must be contained within transfer points and spillage from belts must be minimised. The accumulation of PRB coal below a conveyor or on conveyor parts can contribute to spontaneous combustion. Float dust either in the air or settled on beams, pipes, conduits, equipment and fixtures provide fuel for explosions. A manual, daily wash-down with a hose is beneficial but generally is not totally effective in removing the coal debris from under conveyors or from overheads. According to Douberly (2003), fixed wash-down systems designed for 100% coverage are commercially available, greatly reduce labour cost and significantly improve housekeeping over manual wash-down. Plants that have installed such systems report being satisfied with their performance.

In planned outages, operators should ensure that all idle bunkers and silos are completely empty and verify that by visual checks. Bunkers and silos should be thoroughly cleaned by washing down their interior walls and any interior structural members, but not their horizontal surfaces. Idle bunkers and silos that contain coals such as PRB should be monitored frequently for signs of spontaneous combustion by using CO monitors, infrared scanning or temperature scanning. These were discussed in Chapter 3. Douberly (2003) states that some plants make bunkers or silos inert with carbon dioxide when they are expected to be idle. In order for this practice to be effective, Douberly (2003) emphasises that the enclosure must be completely sealed, especially the bottom cone, because carbon dioxide is 1.5 times heavier than air. The amount of $CO_2$ needed to effectively render an enclosure inert is 3.3 $lb/ft^3$ (~53 $kg/m^3$), so for a silo measuring 22 feet (~6.7 m) in diameter and 55 feet (~16.8 m) high would require 3.2 tons (2.9 t) of $CO_2$. A bulk supply of $CO_2$ and an extensive piping system for bunkers and silos may be necessary to implement such a system.

Typically, fire under normal operating conditions is not experienced in an active bunker or silo. If a fire occurs while a bunker is actively moving coal, it may be a result of design irregularities that contribute to coal bridging or some kind of stoppage. For example, according to Douberly (2003), PRB coal is notorious for lodging within cracked weld joints and spontaneously combusting. Although the construction of bunkers and silos differs from plant to plant, they share one function that is independent of age and design which is managing/maintaining the mass flow of coal. When raw coal is loaded into a bunker or silo, size segregation begins to take place. Large pieces of coal tend to roll out to the periphery of the bin, while smaller pieces and fines stay in the centre. This size segregation facilitates air migration up along the sides of the bunker or silo. It also presents a practical fire fighting challenge when applying water from above as water tends to 'rathole' through voids and can bypass the seat of the fire. Design changes in older plants may be required, such as eliminating flat bottoms in bunkers and obtaining free flow through bottom cones. Where mass flow conditions are not available it is recommended that an evaluation of the cone's lining is performed (Douberly, 2003).

According to Khambekar and others (2009), many coal-fired power plants built before 1980 were constructed using bins, bunkers and silos designed for relatively easy-handling lump coal. The more recent trend towards firing lower rank, processed coals and added coal preparation steps has resulted in harder-to-handle coal and a greater potential for silo flow problems. Coal in parts of these storage systems can remain unrecoverable leading to a loss of capacity and stoppage of flow or in extreme cases spontaneous combustion and fires. Khambekar and others (2009) discuss modifications carried out to silo design at three units in a large coal-fired power plant in order to achieve more reliable operation and avoid mass flow and potential self-heating problems.

Hoover (2005) presented a case study of using thermography technology to aid in the detection and fire fighting efforts of an electric utility coal silo fire. During an outage at the OG&E Electric Services (USA) Muskogee (unit 5) coal-fired power plant, a fire erupted in the coal silos. Pyrotechnic expertise was used to extinguish the fire using an oxygen reduction chemical. In this case, it was not possible to determine the exact location of the fire in the silo. Staff were able to direct the extinguishing agent to the fire using thermal imaging (that is thermography technology) of the silo. An infrared camera was used in the process. In addition to finding the location of the fire, it was important to determine the level of involvement of the fire as this information determined the amount of chemical needed to extinguish it. As the chemicals are applied, using the thermography technique makes it possible to survey the entire surface of the silo and monitor the results of the figure fighting effort. Hoover (2005), states that it is important to note that wind speed could affect the temperature reading on the silo casing as could solar reflection. However, in this case the silos were inside the boiler enclosure area, thus they were protected from external influences. This made it easier to determine the hot areas as well as the integrity of the fire fighting efforts. Hoover (2005) concluded that thermography is an effective technology in determining thermal problems in rotating equipment and electrical devices.

## 4.4 Controlling self-heating/fires

Inerting with $CO_2$ vapour is a widely used technique to prevent suspected fires in silos/bunkers. If liquid $CO_2$ is discharged to atmospheric pressures, dry ice particles are formed which could block the gas flow. Chemetron Fire Systems (2000) describe inerting with $CO_2$ vapour technique based on technology developed in 1953 and refined over decades. The system involves using $CO_2$ which is stored as a liquid and vaporised by a vaporiser. Flow controls, using throttling valves with pressure gauges and metering orifices, are also used to measure and distribute the $CO_2$ flow properly. The principle of the system is to push $CO_2$ vapour through the coal, reach the level of adsorption, and fill all the void spaces between the coal particles to reduce the oxygen available to the fire to near zero. At some point, the heat generation by oxidation will become less than the heat loss by conduction and the burning mass will cool. Holding this condition long enough will result in extinguishing the fire. According to Chemetron Fire Systems (2000), it is well known that carbon adsorbs $CO_2$ (for example, carbon-based filters) and while coal cannot remove $CO_2$ from a $CO_2$/air mixture, it will adsorb $CO_2$ on its surface. The anticipated $CO_2$ use was estimated, if a fire is detected in a silo, following evaluation and quantification. The minimum recommended amount needed for inerting was approximately three gross volumes of the silo, assuming minimal loss out of the bottom of the silo.

While the coal is burning in a storage silo, combustible gases, such as carbon monoxide (CO) and methane ($CH_4$) are produced. These could cause a problem in the air space above the coal. It is common practice to use detection equipment for these gases. Where a high level of CO and $CH_4$ are identified inerting is initiated. It is advisable to inert the space above the coal to a safe level as quickly as possible (Chemetron Fire Systems, 2000).

In the Chemetron inerting with $CO_2$ vapour technique, where a fire is detected (or suspected) the $CO_2$ vapour flow is started by injecting the $CO_2$ above the coal, as well as into the coal at the sloping surface of the silo. The bottom of a silo is sloped to 70º or more to ensure a smooth coal flow. Ventilation in the air space is shut down and a $CO_2$ concentration of 75% or more is achieved as quickly as is practically possible. Injection of the $CO_2$ vapour above the coal is done gently to reduce turbulence that might unnecessarily stir up coal dust. When the air space above the coal is inert, the $CO_2$ injection rate there is decreased and the rate of $CO_2$ application into the coal at the bottom of the silo is increased until this $CO_2$ vapour starts to come out at the top of the stored coal. When this is achieved, $CO_2$ injection into the bottom of the silo is also reduced to a maintenance rate. The $CO_2$ is held in the silo as long as necessary. Chemetron Fire Systems (2000) emphasise the importance of appropriate sealing at the coal outlet at the bottom of the silo to prevent $CO_2$ vapour leakage and entry of air into the silo.

When a fire breaks out in a bunker or silo, access to the interior of the bunker or silo for firefighting is one of the most important aspects of successful fire suppression and one of the most difficult to achieve. Ease of access is often severely limited and therefore planning how to access hard-to-reach spaces is recommended. Installation of access ports around the bunker or silo and at various levels may be required. Silos that are taller than 50 ft (~15.2 m) should be provided with access ports at various elevations to accommodate the injection of firefighting agents. The specific locations of the ports are determined by analysis of the silo design. Although directly attacking a fire using a piercing rod is most effective, using a rod on a fire in a silo taller than 55 feet (~16.75 m) is extremely difficult. Douberly (2003) advises installing a fixed hazard mitigation system-zoned to apply an agent only at levels expected to be fire-prone. He also recommends using infrared thermography to locate fires and to determine the zone(s) that should be activated. Dealing with a fire inside a bunker or silo is dangerous and must be addressed with the correct equipment and training. Douberly (2003) recommends three methods for fighting a silo or bunker fire: using a fixed system installed inside the enclosure; using a special tool called a piercing rod; or both. Experience indicates that the very best method of attack is to get the extinguishing agent directly to the seat of the fire. Organisation and appropriate planning usually allow the necessary time to deal with the fire. For greater detail in discussing firefighting equipment and training *see* Douberly (2003).

Merritt and Rahm (2000) discussed managing silo, bunker and dust-collector fires. According to the authors, at that time, Western Kentucky Energy (WKE) (USA) found that 'throughout the industry, insufficient information and inadequate education have created serious misconceptions regarding how best to address coal-plant fires'. In April 2000 two unrelated coal fires broke out in a coal-fired power plant operated by WKE. The first was in the conveyor belt system. The second incident occurred in a silo. Merritt and Rahm (2000) consider that two mistakes were made prior to shut-down that contributed to the incident. First, the silo was not emptied in anticipation of the outage. Approximately 300 t of coal remained inside. Second, the reclaimer picked up coal from a hot spot in the stockpile and loaded the hot coal into the silo, just a half hour before the shut-down began. Monitoring of CO levels and temperature was delayed due to misinformation but was undertaken, albeit late, using a probe lowered into the silo through a conduit. On the seventh day of the outage the temperature recorded was 107ºF (~42ºC). By 8:00 am on the ninth day of the outage, the temperature recorded was 154ºF (~68ºC). By 11:00 am, on the same day, the temperature had risen to 171ºF (~77ºC), indicating that the event was at a critical stage. Four corrective actions were considered including purging with nitrogen, which was not readily available; purging with $CO_2$, which was available at a feeder under the bunker; withdrawing the coal using a vacuum truck and hose, which is labour-intensive; and flooding with water, which although the silo is equipped with a water deluge system was considered a messy option.

Purging with $CO_2$ was the first option used. However, due to two concerns the process was terminated. The concerns were that $CO_2$ is not an effective means of putting out the fire and the purging could produce high levels of CO or even explosions. Upon inspection, the latter was found to be the case. The second option used was the withdrawal of the coal using a vacuum truck and hose. The coal was then wetted down with water and slowly removed over the next three days. WKE concluded from their experience with the fire at the plant that (Merritt and Rahm, 2000):

- coal fires at power plants occur far too frequently;
- the potential for disaster is significant;
- more education and training are necessary on how to prevent fires from occurring and how to extinguish them if and when they do.

One method of suppression of a fire is the use of a chemical agent. According to Merritt and Rahm (2000), most power plants are equipped with water-deluge systems in their dust collectors, silos/bunkers and tripper rooms as well as over their conveyors. Wetting and chemical agents can be added to these deluge systems to increase their effectiveness. Prevention of a fire however is the better option and the first prevention measure for a silo or bunker fire is to eliminate stagnant coal. Most silos and bunkers have a 'funnel flow' pattern, which is created when the walls of the hopper section at the bottom of the silo are too shallow or rough for the coal to easily slide along. As a result, according to Merritt and Rahm (2000), the coal flows preferentially through a funnel shaped channel located directly above the outlet while material outside this flow channel remains stagnant. The design results in a 'first-in, last-out' flow pattern, which leaves stagnant coal that is prone to oxidation and subsequently, spontaneous combustion. Funnel flow, which is commonly known as 'rat holing', also reduces the capacity of the silo.

Merritt and Rahm (2000), suggest that a mass-flow design, in contrast, puts all of the coal in motion when any amount is being withdrawn. Oxidation and spontaneous combustion of the coal is thus minimised because of the 'first-in, first-out' flow pattern. The authors also suggest that where a funnel-flow design is in use, the coal should be drawn down the silos and bunkers periodically to remove stagnant coal. The optimum expulsion period can be determined by experience with each type of coal as well as the design of the silos or bunkers. It is recommended that PRB coals should not be left in a rat-holing silo or bunker for more than 14 days, depending on whether the coal is fresh off a train or reclaimed from a stockpile. Merritt and Rahm (2000) also suggest two other measures that can be taken to prevent silo or bunker fires. The first is eliminating hot coal from the stockpile, which when loaded into a silo or bunker, can mix with stagnant coal and quickly cause a fire. The second is avoiding sparks from welding or cutting which can fall into a silo or bunker and start a fire.

When a silo fire is detected, the correct procedure to follow depends on issues such as the type of coal, where the coal came from (stockpile or train), where the fire is located within the silo, how much coal is present, whether there is a mill operating under the outlet nearest the fire, if coal is flowing and the extent of the fire. In each case, a fire-fighting procedure must be developed with careful consideration given to the configuration of the plant's coal storage system, fire-fighting equipment and level of personnel training. Merritt and Rahm (2000) consider that all procedures should include the following steps:

- closing the gate above the mill feeder and shutting off the mill-feeder purge air;

- shutting off all equipment in the area above the silo (or bunker);
- evacuating the area above the silo (or bunker) and barricading the access to that area;
- allowing access only to trained personnel equipped with proper fire-fighting gear;
- locating and determining the extent of the fire using a laser pyrometer or thermal imaging camera;
- washing down the entire area above the silo (or bunker) including walls, ceiling, beams, pipes and light fixtures with the objective of removing all of the coal dust from the area;
- activating the silo (or bunker) deluge fire-suppression system, which removes coal dust from the walls and roof beams and wets the top of the coal. In lieu of a permanent deluge system, a hand watering line with a fog pattern may be used, although access to the coal dust on the beams may be limited;
- after the area has been thoroughly wetted and as much coal dust as possible has been removed, inserting a fire-fighting piercing rod (FFPR) through an opening in the top of the silo (or bunker) directly onto the top of the fire. The FFPR may have to be angled toward the fire depending on the location of access holes in the top of the silo (or bunker);
- once the fire is extinguished, continuing to monitor the area with the laser pyrometer or thermal imaging camera for signs of re-flash. Also continuing the monitoring of CO levels in the silo (or bunker);
- finally, opening drain pipe or pipes location just above the mill feeder gate to decant any water prior to opening the gate.

Many methods have been used to extinguish fires in a silo or bunker. For example, $CO_2$ blanketing is one common method. Merritt and Rahm (2000) discuss a case in which a power plant had an inactive silo on fire that was blanketed with $CO_2$ for a month. The procedure slowed the fire but did not extinguish it. Plant personnel then decided to remove the coal from the silo through the feeder. However, they did not wash down inside the silo or in the area above the silo before starting the coal removal process. When the gate was opened at the bottom of the silo and coal flow was established, a cavern that had been created by the smouldering fire collapsed, igniting coal dust in the silo and producing a primary explosion. The pressure wave and the flame front exited the silo into the conveyor area damaging the building's walls and roof. The pressure wave blew a cloud of dust out of the building, which was immediately ignited by the flame front. No injuries were sustained due to the explosion, however, the damage was estimated to be nearly US$ 1 million.

Another method to extinguish a silo fire is using dry ice. According to Merritt and Rahm (2000), several years previously, a plant brought in 1000 lb (~450 kg) of dry ice to drop through the top of a silo onto burning coal. The first block dropped only served to disturb the fire, causing a fireball to exit the top of the silo into the building above. Foam is another method used to extinguish a silo or bunker fire. The principle is that foam seals off the top of the coal, allowing CO to displace oxygen, which effectively smothers the fire. However, the problem with this technique is the length of time required in order to smother the fire. Water alone is the most commonly used extinguishing agent in silo or bunker fires. However, experience shows that using a fire-fighting chemical agent in addition to water can achieve better results.

Merritt and Rahm (2000) conclude that early detection of silo or bunker fire is essential in order to extinguish it quickly and minimise the damage. To achieve this, they advise that a permanent CO detector should be installed in each silo and several in each bunker, depending on the size of the bunker. The authors consider that setting the detectors to raise an alarm when an upward trend over a given time is detected is the most reliable method.

Predicting the propensity of coal to self-heat is complex and difficult due to the number and variety of variables involved. However, prediction can be viable if a controlled storage process is adopted in which particle segregation is avoided and air flow in a pile is limited. Computational simulation and mathematical modelling have been used to develop stockpile design which minimises the potential of self-heating and spontaneous combustion. Inerting with $CO_2$ vapour is a widely used technique to prevent suspected fires in silos/bunkers. Another method of suppression of a fire is the use of a chemical agent. However, in all cases a fire-fighting procedure must be developed with careful consideration given to the configuration of the plant's coal storage system, fire-fighting equipment and level of personnel training.

# 5 Greenhouse gas emissions

There are numerous studies on greenhouse gas emissions ($CO_2$ and $CH_4$) from low temperature oxidation and spontaneous combustion in coal mines, *see for example* Carras and others (2009). These are not discussed in this review. Studies have also been carried out on emission of greenhouse gases from coal stockpiles. For example, *see* Kozinc and others (2004), Wang and others (2003a) and Grossman and others (1994). In addition, many investigations have been undertaken to evaluate and assess the risk of transporting coal from the mine to a power station. However, in general, the work involves the greenhouse gases emitted due to the use of vehicles, trains, ships or barges to transport the coal. Studies have also investigated the impact of reduced heat value of the coal on final emissions, that is after firing the coal in a boiler. However, the author could not trace work that has been undertaken to evaluate how much $CO_2$, for example, is emitted through the low temperature oxidation of the coal itself during transportation or whilst in a stockpile awaiting use in a power plant.

The use of coatings to prevent dust emissions and leachates from coal stockpiles is the subject of many studies. Coatings can include compositions formed of a filler, such as pulverised coal and a binder consisting of a combination of waxes and plastics, also various latex emulsions, both with and without fillers. The purpose of coating is to seal the surface of the stockpile. This prevents water penetration into the coal. By sealing the surface of the pile, dust losses are prevented and leachate formation is minimised. However, air circulation through the stockpile is also greatly reduced. This yields the added benefits of reduced oxidation of the coal and thus prevention of spontaneous combustion, which in effect reduces greenhouse gas emissions. Cold weather handling characteristics of the coal are also improved. Protective coatings appear to be an effective means of prevention of fugitive emissions from coal stockpiles. The economic benefits from reduced oxidation and improved handling more than off-set the cost of application. Use of coatings on unit trains or barges may also be effective.

## 5.1 During transport

In 1998, Fukuchi and others investigated the amount of methane gas produced from coal, while in storage in the hold of a ship, that may lead to spontaneous combustion. Simulations carried out showed that the gas accumulation in the cargo hold depends on coal properties and characteristics. The authors considered that, depending on the coal type and tendency to generate methane, hold ventilation by itself may not necessarily be an effective method of controlling the methane gas production and as a result spontaneous combustion (Fukuchi and others, 1998).

## 5.2 Coal stockpiles

Kozinc and others (2004) investigated gas emissions of carbon dioxide, methane, dimethylsulphide, carbon monoxide and oxygen from the lignite mined at the Velenje coal mine (Slovenia) and fired at the Šoštanj thermal power plant. Coal reserves of 2–3 months are kept in a stockpile at the mine due to the high coal consumption at the 755 MW facility. The experimental evaluation of gas emissions undertaken was important for two reasons – firstly, planning optimal stockpile size that would suffice in case of low coal supply from the mine and secondly, minimise $CO_2$ emission as well as reduce the calorific value of the coal in the stockpile. The test stockpile size in the experiment was 2000 $m^2$ (10,000 t) while the size of the whole stockpile varied between 100,000 and 200,000 $m^2$. The amount of lignite ranged between 330,000 and 800,000 t. The coal in the piles ranged from a calorific value of between 9,500 to 11,000 kJ/kg, humidity 37–43%, and sulphur content 1.5–1.0%. Gas tight, polycarbonate sampling tents were used in the experiment. Gas samples from the surface of the stockpile were collected in two sampling tents. One was ventilated after sampling every day, the other was closed during the whole sampling period. The gases collected during the sampling periods as well as calibration gases were then analysed under the same conditions. The concentration of gases determined in the ventilated and non-ventilated tents were found to be comparable, *see* Table 10 (Kozinc and others, 2004).

Kozinc and others (2004) expected the temperature to play a major role in the oxidation and desorption processes. Figures 21–25 illustrate that the increase and decrease in CO and $CO_2$ concentrations are linked to temperature fluctuation on a daily basis. The authors state that in general, the results of the analyses indicate higher concentrations of CO and $CO_2$ during spring and summer when the temperatures were high and lower during autumn and winter when the temperatures were lower. Kozinc and others (2004) also found that the concentration of $CO_2$ in the sampling tent was inversely proportional to the $O_2$ concentration due to the oxidation process. The concentration of $CH_4$ was under the quantification limits of 100 ppm most of the time, except in June and July 2001. Kozinc and others (2004) found that the amount of $CO_2$ emitted was 30-times higher during spring and summer than during autumn and winter. The authors consider that the results show that the main source of $CO_2$ is the oxidation process, which is accelerated by higher temperatures. The evaluated emissions of $CH_4$ were higher in June although the average temperature was higher in July. This confirms that the main source of $CH_4$ was the desorption process. Emissions of CO were also highest during the summer period. The authors conclude that the amount of $CO_2$ emitted from the Velenje stockpile is negligible compared to the emissions from the power plant.

## 5.3 Regulatory impact, if any

A 2005 New Zealand government consultation paper on putting a price on greenhouse gas emissions included the stockpiling of coal. In the paper two potential problems in

**Table 10 Evaluation of gas emissions calculated for the whole coal stockpile** (Kozinc and others, 2004)

| 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 m² and stockpile surface ≈121,000 m² during June and July 2001 and ≈107,000 m² during December 2001 and January 2002.

**Evaluation of sampling precision**

| Gas | Concentration | RSD[a], % | RSD[b], % |
|---|---|---|---|
| $CH_4$ | 0.02% | 4 | 17 |
| $CO_2$ | 0.97% | 4 | 12 |
| CO | 56 ppm | 7 | 11 |
| $O_2$ | 19.0% | 1 | 8 |

RSD relative standard deviation
[a] sampling from one tent – three samples in one day
[b] different points from ventilated tents (one sample from each tent, three successive days)

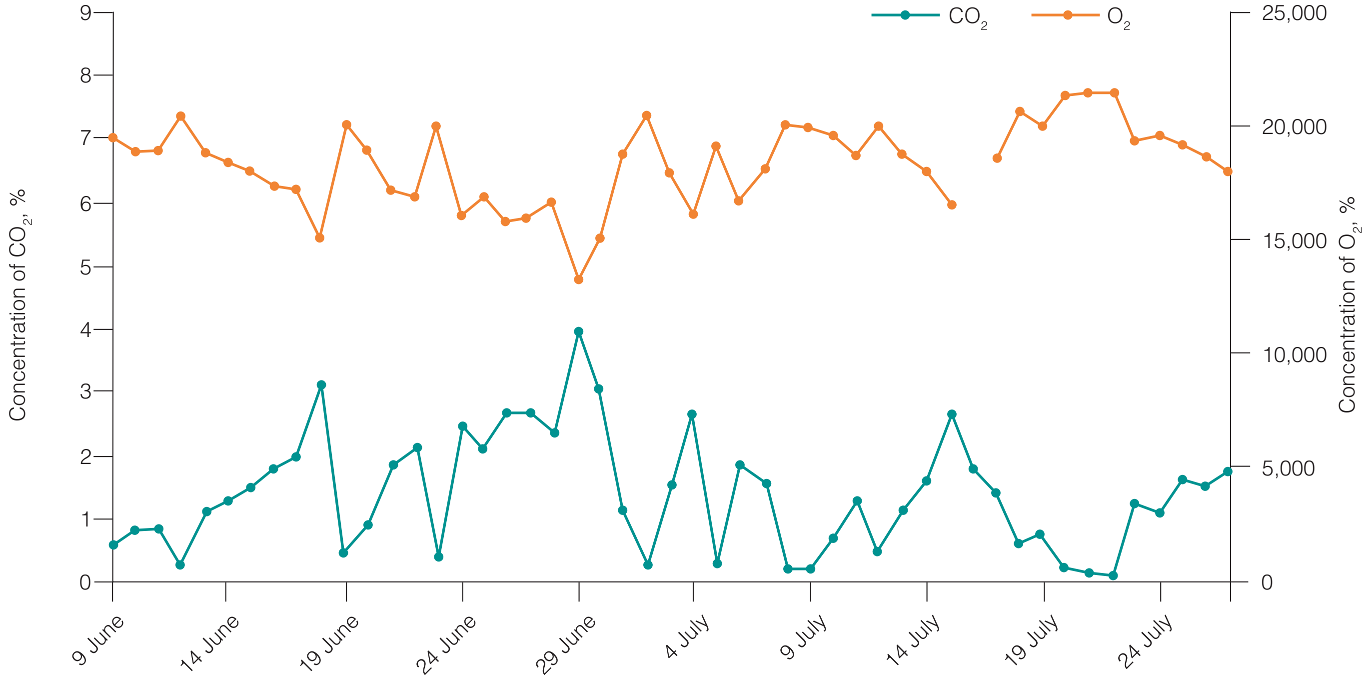


**Figure 21 Concentration of $CO_2$ and $O_2$ in June and July 2001 from ventilated sampling tent** (Kozinc and others, 2004)

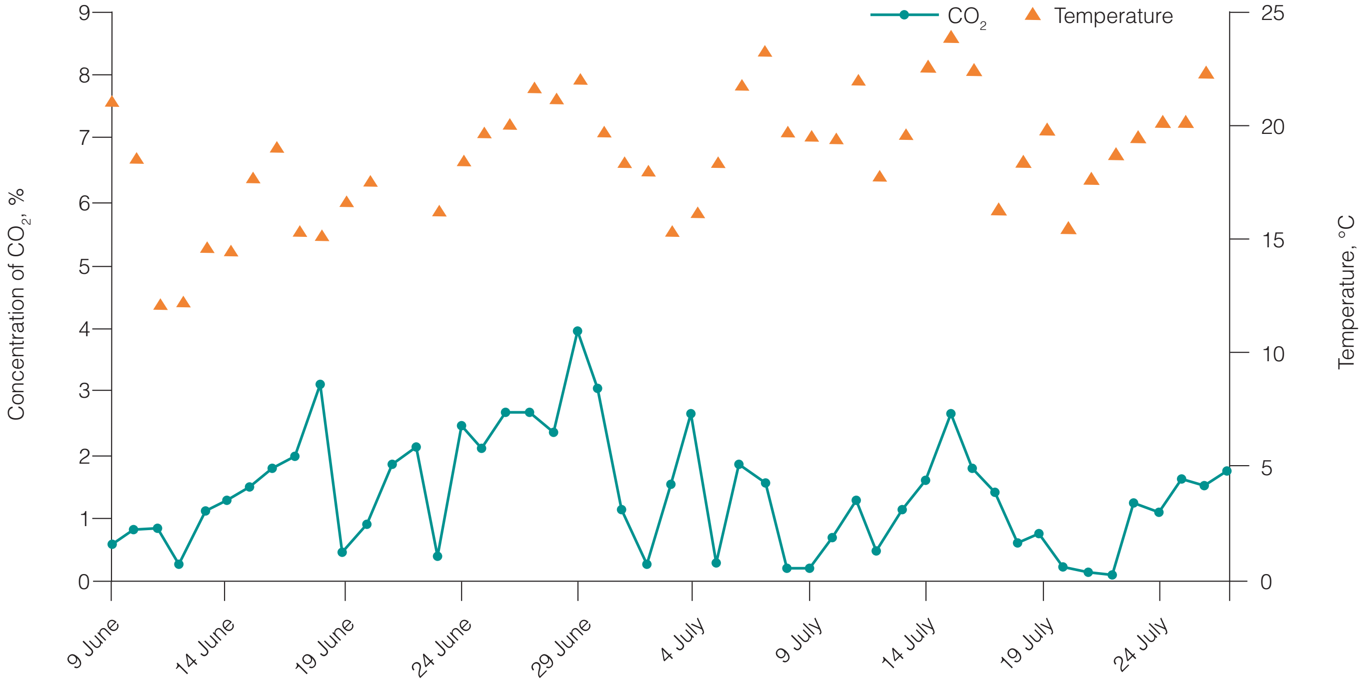


**Figure 22 Concentration of $CO_2$ and temperature in June and July 2001 from ventilated sampling tent** (Kozinc and others, 2004)

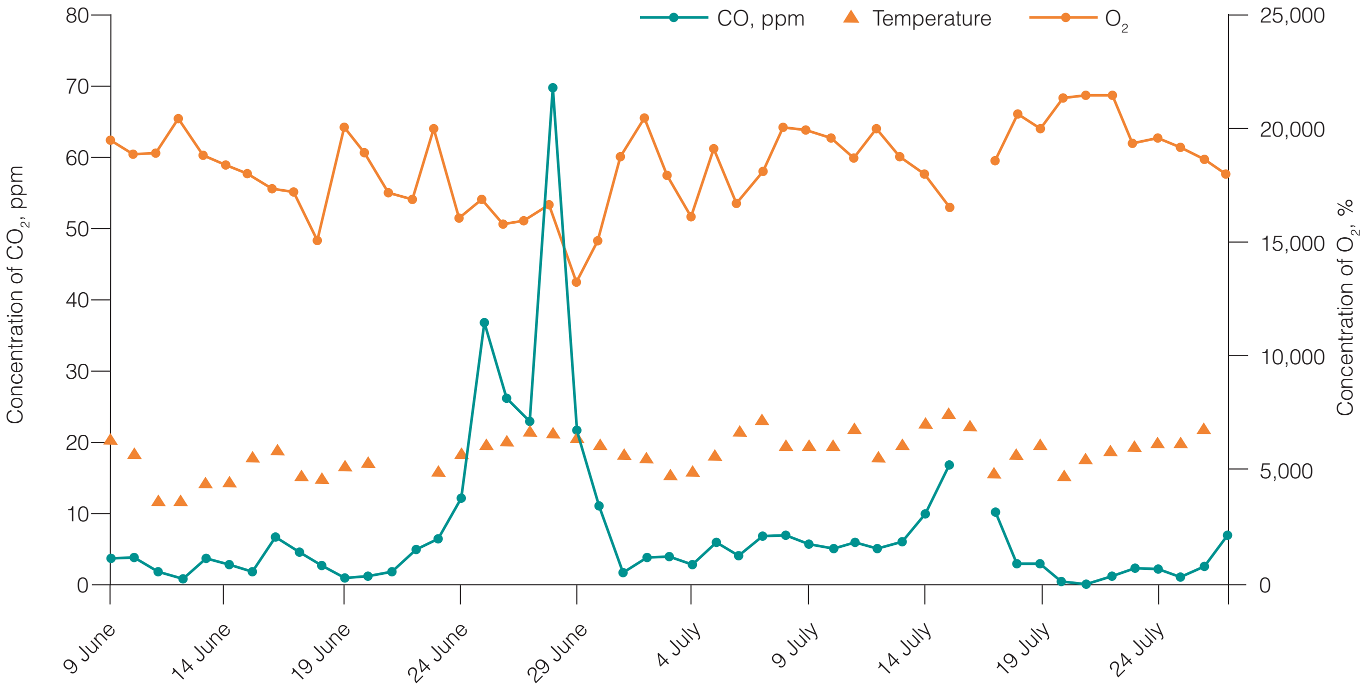


**Figure 23 Concentration of $CO_2$, $O_2$ and temperature in June and July 2001 from ventilated sampling tent** (Kozinc and others, 2004)

applying the carbon tax to stockpiles were presented. One related to the transition on introduction, and the other to the carrying cost of the tax on some of the very large stockpiles that consumers hold (as opposed to producers). With regard to transitional stockpiles, it appeared that some firms, particularly some electricity generators, were able to store large stocks of untaxed coal at the introduction date. Given that the carbon tax was applied from 1 April 2007, and there was a risk of unintended disparities of the initial impact of the tax on the different fuels, it followed that users of coal who would otherwise not be taxed should be taxed on that date. Obviously, there was a question of scale, that is limiting the tax to larger stockpiles. However, a firm raised the question of carrying cost of the carbon tax on its potentially very large stockpile of coal pointing out that '*greenhouse gases would be released only when the stockpile is used*'. For reasons of compliance and administrative simplicity, the tax was levied at the earliest practical point in the supply chain. In the government's view, the mere existence of a stockpile was not sufficient reason to overturn the principle. However, where

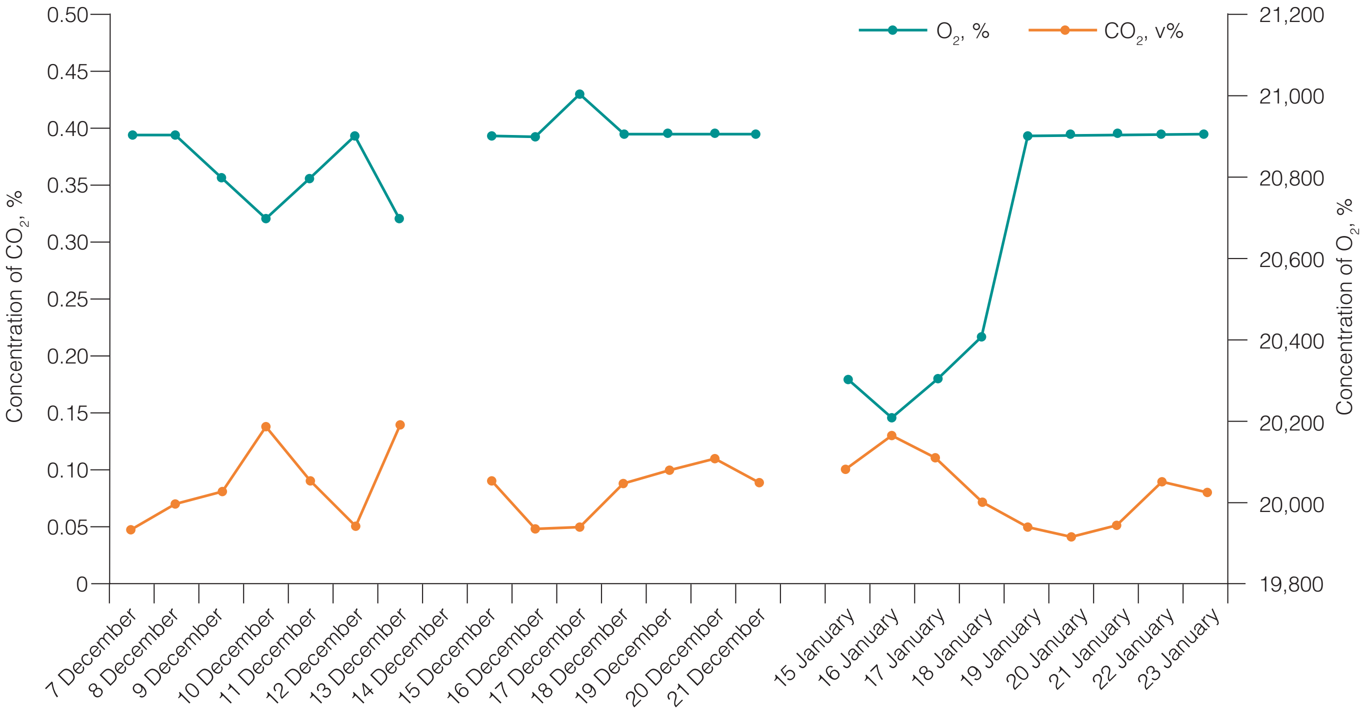


**Figure 24 Concentration of $CO_2$ and $O_2$ in December 2001 and in January 2002 from ventilated sampling tent** (Kozinc and others, 2004)

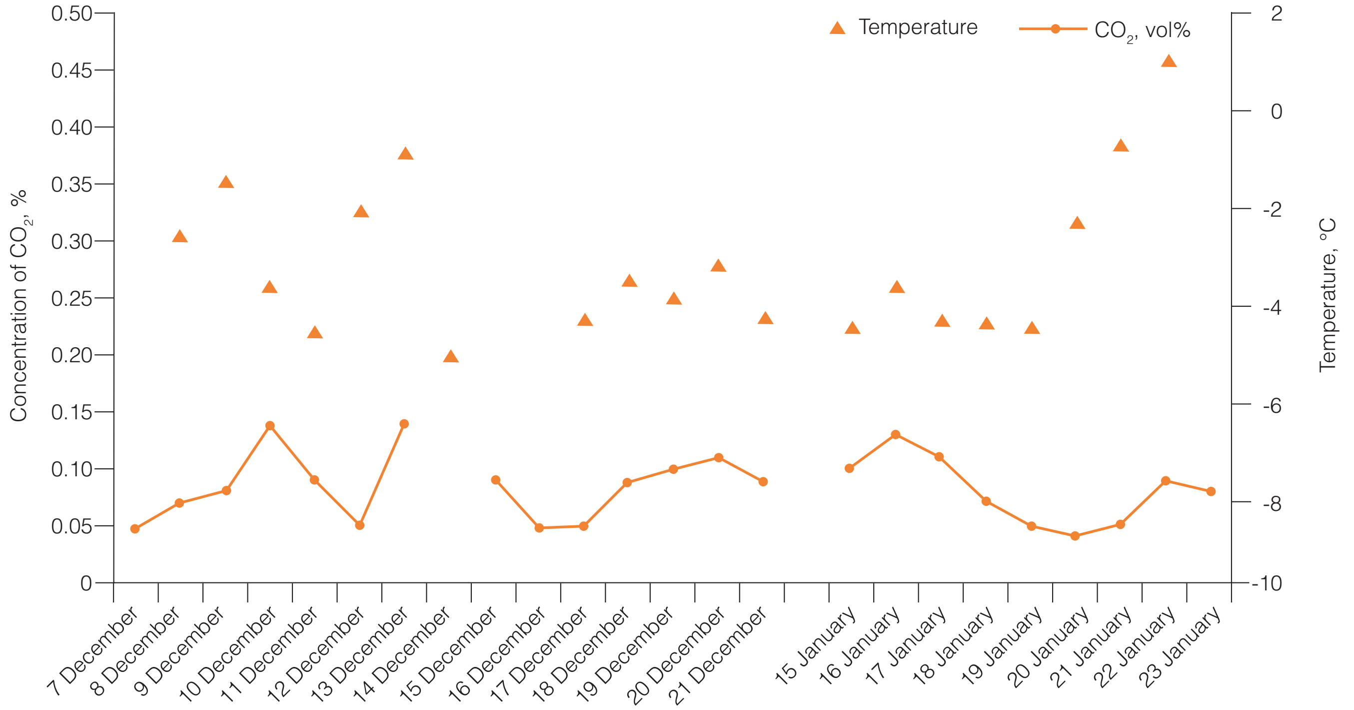


**Figure 25 Concentration of $CO_2$ and temperature in December 2001 and in January 2002 from ventilated sampling tent** (Kozinc and others, 2004)

the stockpile is very large and therefore the carrying cost of the carbon tax is also large, relief could be offered by some form of stock-on-hand adjustment (Cullens and Hodgson, 2005).

Finally, there appears to be little information available in the public domain on actual emissions of $CO_2$ and/or other greenhouse gases from the self-heating process or spontaneous combustion of coal during transport, in stockpiles, in silos/bunkers or in pulverisers/mills. Until such information is quantified and made available, regulation would not be feasible.

# 6 Conclusions

The propensity of some coals to self-heat can result in spontaneous combustion. Spontaneous combustion means an oxidation reaction without any externally applied heat from a spark or a pilot flame, so that the departure of the internal temperature profile from being flat is due entirely to the material's own heat release by reason of chemical reaction.

The results of spontaneous combustion are serious and negative; damaging economic effects, detrimental environmental consequences and unwanted costs in health problems and, in some cases, human life. To prevent these outcomes, the processes that lead to coal self-heating must be understood and precautions must be taken to avoid fires caused by spontaneous combustion. There is general agreement that there is a strong relationship between self-heating rate and coal rank. As coal rank decreases the self-heating rate increases. Thus spontaneous combustion, or self-ignition, is most common in low-rank coals and is a potential problem in storing and transporting coal for extended periods. Major factors involved in spontaneous combustion include volatile content, the size of the coal (smaller sizes are more susceptible) and the moisture content. Heat build-up in stored coal can degrade the quality of coal, cause it to smoulder, and lead to a fire. According to some, throughout the coal-based power generating industry, insufficient information and inadequate education have created serious misconceptions regarding how best to address coal-plant fires.

The chemical reaction between coal and oxygen at low temperature is complex and remains not well understood despite many years of research. The gaseous reaction products, evolved during coal oxidation, are primarily CO, $CO_2$ and $H_2O$. Generally, three types of process are believed to occur including physical adsorption, chemical adsorption (which leads to the formation of coal-oxygen complexes and oxygenated carbon species), and oxidation (in which the coal and oxygen react with the release of gaseous products, typically carbon monoxide, carbon dioxide and water vapour). Oxidation is the most exothermic of these processes. Physical adsorption can begin at ambient temperature where coal is exposed to oxygen. Chemical adsorption takes place from ambient temperature up to 70ºC. Initial release of oxygenated reaction products starts from 70ºC to 150ºC, while more fully oxygenated reaction products occur between 150ºC and 230ºC. Rapid combustion takes places over 230ºC. The start of this rapid temperature rise is also known as thermal runaway. The time it takes to reach a thermal runaway stage is called induction time. The induction time can be used to indicate the potential hazard of coal self-heating. The temperature rise from ambient to 230ºC is a slow process compared to the fast temperature increase after 230ºC, which can lead to major fire hazards and even explosions.

There are numerous methods currently in use and some under development to evaluate, monitor and detect coal fires in stockpiles, silos and bunkers. Three of the major, widely-used techniques are based on carbon monoxide (CO) monitoring, thermal monitoring and infrared scanning. The methods used to evaluate, monitor and detect coal self-heating include mathematical modelling, chemical kinetics, infrared/Fourier transform infrared (FTIR) spectroscopy, Differential scanning calorimetry (DSC), isothermal methods, Crossing point temperature (CPT) technique, Differential thermal analysis (DTA), adiabatic methods and hot storage and heat rate release methods.

Before coal burns openly, in a stockpile, silo or bunker, an unnoticed process of oxidation takes place. In this process oxygen from the air reacts with the carbon in the coal and carbon dioxide is generated. This is an exothermic reaction, where heat is released. Normally, the heat is transported away by circulation of air which causes a cooling effect. For conditions favouring spontaneous combustion the air supply needs to be high enough to support the oxidation, but too small for sufficient cooling. As a result the coal heats up. The temperature rises and at about 80ºC gases such as carbon monoxide, carbon dioxide and water vapour are released. Combustion begins above a certain critical temperature. The grain size and the surface structure of coal may also influence its susceptibility for spontaneous combustion. In the centre of a large fire, temperatures of 1000ºC and higher can be reached. Some factors that influence the spontaneous combustion of coal are:

- air-ventilation in the stockpile, silo/bunker;
- atmospheric conditions;
- coal quality: low carbon content and large amounts of volatile components support combustion;
- coal moisture content;
- particle size: the smaller the particles, the larger the surface area, the higher the risk.

In stockpiles, parametric model analysis indicates that parameters such as pile slope, the availability and movement of air through the pile, material segregation, coal reactivity, particle size, temperature and moisture play important roles in the occurrence of spontaneous combustion. The role of moisture on the self-heating of coal is complex and much work is required before it will be fully understood. Many of the techniques for ranking the propensity of coal to self-heat and combust spontaneously use dried samples. Yet coal in stockpiles may be wet and have differing combustion characteristics. Studies about the self-heating and spontaneous combustion of coal start with fundamental research questions relating to issues such as the kinetics of oxidation and the role of moisture, both as a heat source or a heat sink and as an agent influencing the chemical mechanism. Mathematical models are used to obtain kinetic parameters and to predict the behaviour of large stockpiles.

The significance of the greenhouse gas emissions resulting from the oxidation during transport and/or storage, especially $CO_2$ were investigated. However there appears to be no emphasis in research work or published material specifically quantifying these emissions. Thus, the potential for future regulation to control these emissions by introducing cooler stockpiling environments or specific transport and bunkering modes remains unexplored. There is a large number of experimental and theoretical work on the self-heating and spontaneous combustion of coal. However, there is limited experimental work carried out on large stockpiles, due to the expense and time-consuming nature of such work.

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