Available online at www.sciencedirect.com
ScienceDirect
International Journal of Coal Geology 72 (2007) 124 – 140
International Journal of COAL GEOLOGY
www.elsevier.com/locate/ijcoalgeo

The spontaneous combustion of coal and its by-products in the Witbank and Sasolburg coalfields of South Africa

J. Denis N. Pone[a], Kim A.A. Hein[b,*], Glenn B. Stracher[c], Harold J. Annegarn[d], Robert B. Finkleman[e], Donald R. Blake[f], John K. McCormack[g], Paul Schroeder[h]

[a] Energy and Geo-Environmental Engineering, The Pennsylvania State University, 228 Housler Building, University Park, PA 16802, USA
[b] School of Geosciences, University of the Witwatersrand Johannesburg, P/Bag 3, 2050, WITS, South Africa
[c] Division of Science and Mathematics, East Georgia College, Swainsboro, Georgia 30401, USA
[d] Department of Geography and Environmental Management, University of Johannesburg, P.O. Box 524, Auckland Park, 2006, South Africa
[e] University of Texas at Dallas, Department of Geosciences, Richardson, TX 75083-0688, USA
[f] Department of Chemistry, 570 Rowland Hall, University of California, Irvine, CA 92697-2025, USA
[g] Electron Microbeam Facility, Department of Geological Sciences, MS 172, Mackay School of Mines,
University of Nevada, Reno, Navada 8955-0047, USA
[h] Department of Geology, University of Georgia, 210 Field Street, Athens, GA 30602-2501, USA

Received 27 September 2006; received in revised form 2 January 2007; accepted 9 January 2007
Available online 19 January 2007

Abstract

Spontaneous combustion of coal seams in the Witbank and Sasolburg coalfields, South Africa, was studied in order to determine if toxic chemical elements and compounds are being mobilised into the environment. Samples of the minerals forming on the surface of coal seams, and gases escaping from vents, were analysed to verify the presence of these elements and compounds.

Gas temperature measurements at coal-fire vents range from 34 °C to 630 °C. The coal-fire gas minerals (CFGM) identified included sulphur compounds and salammoniac. X-ray diffraction (XRD) studies of CFGM by-products confirmed the presence of mascagnite ($(NH_4)_2SO_4$), illite ($(Al,Si)_4O_{10}[(OH)_2,H_2O]$) letovicite ($(NH_4)_3H(SO_4)_2$), phlogopite ($KMg_3(AlSi_3)O_{10}(F,OH)_2$), titanium dioxide ($TiO_2$), barite ($BaSO_4$), iron sulphate ($FeSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$) and silicate. An unknown and unclassified sulphur–nitrogen–chlorine CFGM was also identified. The minerals are interpreted to have formed by condensation or sublimation; several may be alteration products. Other heavy elements found in the CFGM's are mercury, arsenic, lead, zinc, and copper. Arsenic and mercury were the major elements of potential environmental significance found accumulating around coal-fire vents.

Relatively high concentrations of toluene, benzene and xylene were found in the gas collected at both Witbank and Sasolburg coalfields. Benzene, toluene and xylenes are known to possess carcinogenic proprieties. Thirty-two aliphatic compounds were detected, as well as halogenated compounds including bromomethane, iodomethane and trichloromethane in low concentrations, and dichloromethane and chloromethane in high concentrations. The highest concentrations of halogenated compounds were measured for gas samples from the Witbank coalfield. High concentrations of carbon monoxide, carbon dioxide, and methane were also detected.

The nature of the risks to human health and the environment of most of the compounds in gas and CFGM by-products of spontaneous combustion at the Witbank and Sasolburg coalfields are unknown and merit investigation. Fires caused by spontaneously combusted coal are pervasive in the coalfields and the health consequences of exposure to hazardous elements are a

---

* Corresponding author. Tel.: +27 11 717 6623; fax: +27 11 717 6579.
E-mail addresses: jnp139@psu.edu (J.D.N. Pone), heink@geosciences.wits.ac.za (K.A.A. Hein), stracher@ega.edu (G.B. Stracher), han@na.rau.ac.za (H.J. Annegarn), rbf@usgs.gov (R.B. Finkleman), dblake@orion.oac.uci.edu (D.R. Blake), mccormac@mines.unr.edu (J.K. McCormack), schroe@gly.uga.edu (P. Schroeder).

doi:10.1016/j.coal.2007.01.001

serious risk. It would be prudent to undertake an environmental impact assessment of these elements in order to determine the extent of their impact on mine workers and the environment in the Witbank and Sasolburg coalfields.

Keywords: Spontaneous combustion; South Africa; Coal; Coal fire; Environmental impact

1. Introduction

One of the consequences of coal mining is the exposure of the coal to air and moisture resulting in the ignition of the coal through the processes of chemisorption, oxidation, and spontaneous combustion. The ignition of coal is a global concern and burning coal may cause significant environmental problems (Bell et al., 2001; Heffern and Coates, 2004; Nolter and Vice, 2004; Stracher, 2004; Stracher and Taylor, 2004; Whitehouse and Mulyana, 2004; Sheail, 2005; Chatterjee, 2006; and others). Although the analyses of coal-fire gas in China, United States, and India reveal the presence of toxins harmful to humans, including arsenic and fluorine (Finkelman et al., 1999, 2001, 2002, Finkelman, 2004; Stracher and Taylor, 2004), the impacts on human health have received little attention by the scientific community.

This study describes and documents the coal-fire gas minerals (CFGM) that form as a reaction product of gas produced by burning coal at the Witbank and Sasolburg coalfields, South Africa. Chemical compounds associated with burning coal fires are characterised, along with the trace-elements released from coal and associated sediment during ignition. The primary objectives of the research were to collect and analyse gas and solid combustion by-products associated with hot fumaroles and to recognise potentially toxic spontaneous combustion by-products and their possible effects on human health.

2. Regional setting

The Witbank coalfield, South Africa, is situated on the northern margin of the Karoo Basin, south of the township of Witbank (Emalahleni), and about 20 km due east of the city of Johannesburg (Fig. 1). The Sasolburg coalfield is situated 40 km south of Johannesburg. The Witbank coalfield extends from the town of Springs in the west to Belfast in the east, and hosts five major coal seams. The Sasolburg coalfield extends from the town of Vereeniging in the north to Telkom in the south, and hosts three major coal seams. In 2001, these coalfields accounted for about 53% of South Africa's coal production, which is used in generating 41% of the country's electricity (Uludag et al., 2001). Total coal production in South Africa for 2001 exceeded 220 Mt and in 2005 rose to 245 Mt, with a growth rate of 1.9% per annum, the larger proportion of coal production being derived from the Witbank and Sasolburg coalfields (Roberts, 2005; Anonymous, 2006).

South Africa coals and related carbonaceous rocks were deposited during the Mid- to Late Permian (Falcon, 1989). They are concentrated in the Vryheid Formation of the Ecca Group of the Karoo Sequence, which hosts nineteen coalfields. The coal seams are thick and shallow in depth (Holland et al., 1989). Ninety-six per cent of the coal reserves are less than 200 m below the surface and over half the reserves are contained in seams thicker than 4 m (Cadle et al., 1993). South African coal seams are typically bounded by shale or sandstone units (Cairncross and Cadle, 1988; Falcon, 1989; Holland et al., 1989). The coal seams are mainly flat-lying with average stratigraphic dips of less than 5°. Dips of 12° or more may be encountered over short distances (Holland et al., 1989).

A sedimentological and coal petrography study by Holland et al. (1989) of the Karoo Sequence in the Witbank coalfield established that the coal seams are laterally continuous. Faults are rare, other than those associated with the emplacement of post-depositional dolerite sills and dykes. Displacements are in tens of meters. The dykes and sills are associated with burning or devolatilization of large volumes of coal in the contact aureole of these intrusions.

2.1. Witbank coalfield

The Witbank coalfield has been the subject of studies for nearly two decades (see Falcon, 1986a,b; Cairncross, 1989; Falcon, 1989; Holland et al., 1989; Cairncross, 1990; Cairncross et al., 1990; Cadle et al., 1993; Uludag et al., 2001 and others). The Witbank coal seams are hosted by the Vryheid Formation, which consists of glacio-fluvial outwash braid–plain conglomerate and sandstone units, and minor glacio-lacustrine and glacio-deltaic sequences (Cairncross, 1990). The oldest coal seams lie unconformably on pre-Karoo basement rocks. Coal seams that disconformably overlie glaciogenic

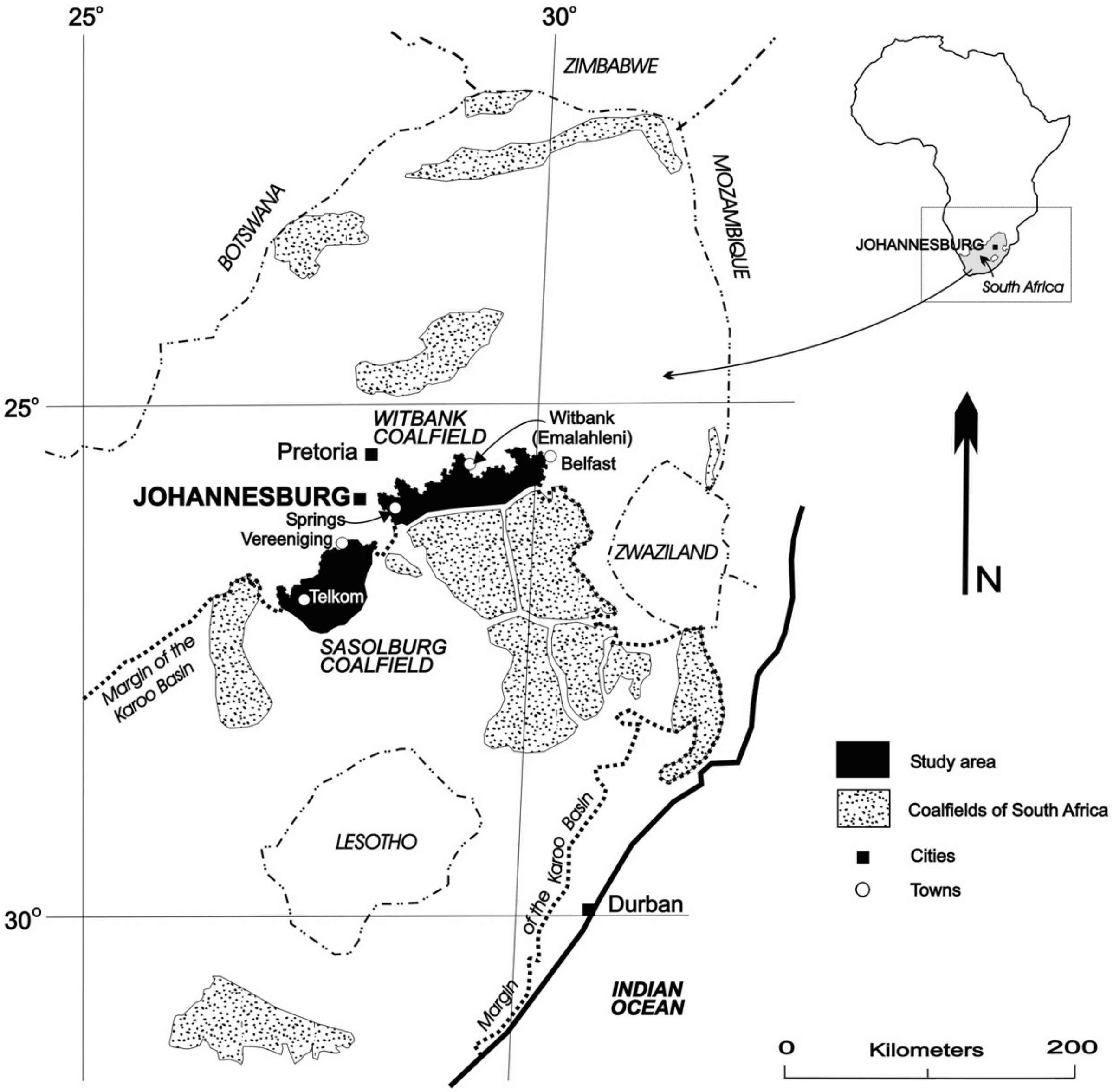

Fig. 1. Location of the Witbank and Sasolburg coalfields in the northeast region of South Africa. The locations of the other 17 principal coalfields are also shown.

strata are interbedded with lobate delta and bed-load fluvial sequences. Fine- to coarse-grained anastomosing channel deposits crosscut some coal seams and deleteriously affect local coal distribution and quality. Coal seams beneath palaeo-channels have been thinned due to channel incision and palaeo-erosion. Hence, palaeo-topography directly controlled sedimentation patterns in the Witbank coalfield. Furthermore, Permo-Carboniferous glaciers scoured valleys into the pre-Karoo basement, and peat beds and sediments of the Vryheid Formation filled glacial valleys (Cadle et al., 1993). Consequently, coal seams thin, pinch and shale-out against relatively steep-sided flanks of palaeo-valleys. Directly above palaeo-topographic highs, coal seams and associated strata attenuate due to compaction, or may be absent.

Stratigraphic studies of the Witbank coalfield by Cairncross and Cadle (1987) identified five main coal seams that are numbered in ascending stratigraphic order 1 to 5. As defined by the South African Department of Mines and Energy these are subdivided into the 1, 2, 3, 4 lower/4 upper/4A and 5 seams (Anonymous, 2006). The No. 2 seam has been extensively mined and remains economically important. Other economic seams include the No. 1, 4 and 5 seams. The thin No. 3 seam (generally less than 0.5 m in thickness) is locally of high quality, where it attains a thickness of approximately 0.8 m and forms an important opencast resource (Uludag et al., 2001).

The No. 1 seam contains less than 11% of the mineable in-situ coal of the Witbank coalfield. Falcon (1989) established that the No. 1 seam formed in a freshwater peat swamp that blanketed an underlying platform of sediment derived from an ancient braided glacial river system. The peat swamp was not subjected to syn-depositional clastic contamination and, as a result, the No. 1 seam produces superior quality coal (i.e., low ash, high calorific value, and high volatile matter, Cairncross, 2001).

The No. 2 seam contains approximately 60% of the coal resources of the Witbank coalfield and contains some of the best quality coal (Uludag et al., 2001). The No. 2 seam is split by a lens of clastic sediment deposited from a braided river system during peat accumulation. The clastic lens deleteriously affect coal thickness and quality (Cairncross and Cadle, 1988). The No. 2 seam is separated from the sub-economic No. 3 seam by mudstone, glauconite mudstone, sandstone, and siltstone units.

The No. 4 seam contributes approximately 26% to the total Witbank coalfield resource. Holland et al. (1989) concluded that the seam accumulated as peat in an upper delta plain environment. Deposition of fine-grained sediment within an embayment, and later, deposition of shale and sandstone during the accumulation of the coal bed, split the No. 4 seam into the No. 4 lower, No. 4 upper, and No. 4A subseams. The No. 4 seam contains numerous shale and sandstone partings. The coal is mainly used as power station feedstock and for domestic steam coal.

The No. 5 seam contributes approximately 3% to the total coal resources of the Witbank coalfield. This seam is approximately 1.5–2.0 m thick and lies about 25 m above the No. 4 coal seam. The No. 5 seam is generally present only above palaeo-topographic highs in the basement (Cairncross, 1990). Laminated sandstone overlies the coal seam leading to weak mine-roof conditions that requires extensive support if mined underground. Usually, the seam is mined by opencast methods.

2.2. Sasolburg coalfield

Of the 19 principal coalfields in South Africa, the Sasolburg coalfield ranks third with respect to production and coal quality (Anonymous, 2006). The New Vaal Colliery and Sigma Mine are the only two operating mines in the coalfield and both exploit bituminous coal. The coalfield hosts three major coal seams: the Bottom seam (No. 1 seam), the Middle seam (No. 2A, 2B seams), and the Top seam (No. 3 seam). They are shallow in depth in the northern and northwestern part of the coalfield, and crop out in some areas (Falcon, 1989). Toward the south, the depth to the top of the coal seams increases to more than 300 m (Braker, 1985). The coal seams are mined by opencast methods using strip mining by dragline, although at the Sigma mine, continuous mining for pillar extraction, and bord and pillar (room and pillar) mining are also used (Anonymous, 2006).

The Bottom (No. 1) seam is developed in the deeper part of the coal basin as a single seam, but in some areas is split into three discrete coal units by interbedded sediment (up to 3.5 m in thickness). The Middle seam is divided into two seams (Nos. 2A and 2B) by a mudstone unit that is 1.5 m in thickness. The total thickness of the Middle seam may be greater than 10 m. The Top seam (No. 3) also reaches a total thickness of 10 m, but because of extremely poor roof conditions, considerable variation in coal quality, and devolatilization associated with an overlying dolerite sill, mining of the seam is limited.

2.3. Coal mining history in the Witbank and Sasolburg coalfields

Coal mining commenced in the 1890's in the Witbank coalfield with small surface mines producing 500 kilotons (kt) of coal per annum. By 1889, at least four collieries were operating in the Middelburg-Witbank district and coal mining commenced in the Salsolburg coalfield at Vereeniging, with the bulk of supply going to the newly discovered goldfields at Johannesburg. Coal production and export increased sharply in 1907 with development of a rail-port system in South Africa, and from 1907 to 1970 coal demand and production increased slowly. In the early 1970's, there was a sharp rise in the domestic demand for coal corresponding with an increase in demand for electricity (Lang, 1995). During this time, mergers within the coal mining industry created the opportunity to expand mining operations and open new mines. By the end of the 1970s, coal production had risen to 74 Mt/a (Moolman, 2004) and walking draglines operating on large surface strip mines had been introduced. The run-of-mine (ROM) coal from these surfaces operations reached 109 Mt, or 44.5% of the coal mined in South Africa by 1998. In 2005, South Africa's total coal production reached 245 Mt, with 174 Mt and 71.4 Mt being consumed by local sales and exports, respectively (Roberts, 2005; Anonymous, 2006).

2.4. Spontaneous combustion in the Witbank and Sasolburg coalfields

Collieries in the Witbank coalfield have historically used bord and pillar mining with typically low coal-recovery ratios, leaving a significant amount of coal in pillars, and as floor and roof coal. When old workings were reopened, ingress of air into galleries resulted in chemisorption and oxidation of coal leading to spontaneous combustion in some collieries. Bell et al. (2001) detailed the environmental impacts associated with spontaneous combustion of coal at the Middelburg colliery in the Witbank coalfield: spontaneous combustion was first noticed during decommissioning of the mine in 1947. Other collieries also reported incidents of spontaneous combustion and coal production was negatively affected.

Spontaneous combustion and burning of coal in the Sasolburg Coalfield was first recorded in 1985 in unmined coal in the New Vaal colliery. As old workings in the Middle seam were exposed, large fires erupted. These were dealt with using a cladding and dozing technique, i.e., sand dumped onto the burning coal seam to choke the fire. However, by February 1990 the fires had spread, and cladding and dozing operations were no longer able to handle the coal fire safely. In 1990 sand was dumped directly over the highwall, closing off the old workings as quickly as possible after they had been exposed. The sand used for this operation formed part of the dragline extended bench and, as it had to be pre-stripped as part of the normal operation, little additional work was required. However, this procedure never extinguished the fires completely (Moolman, 2004).

3. Spontaneous combustion

The mechanisms of spontaneous combustion of coal have been described and discussed by several authors including Kaymakci and Didari (2002), Stracher and Taylor (2004), Stracher et al. (2004), Myles and Glasser (2005a,b) and Chatterjee (2006), and is summarised here. The percolation of air through organic materials, including coal, results in a measurable rise in temperature. This phenomenon is also observed in crushed sulphide ore and is caused by a progressive series of adsorptive, absorptive, and chemical processes (Hudak, 2002). The heat generated, if greater than that dissipated, gives rise to an increase in the temperature of the coal. As the temperature of the coal rises, the rate of coal oxidation increases (Stracher et al., 2004). These reactions cause the self-heating of coal, and if conditions are favourable, spontaneous combustion can result. If the rate of heat generated by percolating air is equal to the rate of heat removed, equilibrium will be reached.

Materials susceptible to spontaneous combustion are characterised by a critical temperature of self-heating (SHT), known as the minimum temperature at which the materials burn spontaneously (Banerjee, 1985). The SHT is the lowest temperature that will produce a sustained exothermic reaction. If the temperature reaches the SHT before thermal equilibrium is attained then the oxidation process will accelerate. As a consequence, the temperature will escalate rapidly, generating higher rates of oxidation until combustion occurs. At this stage, smoke and gaseous combustion products appear.

Glasser and Bradshaw (1990) stated that three factors play a crucial role in the process of spontaneous combustion of coal:

1. The reaction between the coal and the gaseous reactants causing self-heating.
2. The transport of the gaseous reactant into the bed.
3. The rate of heat energy dissipation from the bed.

The heterogeneous character of coal seams and waste dumps contribute significantly to the realization of these three factors. The process of self-heating of coal is exacerbated during open-cast mining when coal seams are more or less open to the uncontrollable influences of climate. Identifying the processes that affect the above three factors is necessary in order to understand the nature of spontaneous combustion and coal seam fires.

3.1. Interaction of coal with water

The interaction of coal with water (deposition of water molecules on coal) and the relationship between moisture content and spontaneous combustion of coal, is dependent on adsorption, absorption, and desorption processes and the physico-chemical characteristics of the coal (Ceglarska-Stefanska et al., 1998). Coal generally has a fairly high capacity for moisture, where more than 20% by weight can be moisture (Itay et al., 1989). The coal matrix swells and shrinks as water vapour is first adsorbed then desorbed (Reucroft and Sethuraman, 1987). The process causes disintegration of the coal structure and creates new surfaces. Cleat width and porosity is increased with decreased water content, thus leading to a high rate of oxidation and consequently self-heating.

The chemical thermodynamics that describe coal–water interaction have been documented by Glasser and Itay (1988), Itay et al. (1989), Rosema et al. (2001), and Myles and Glasser (2005a,b). In summary, the interaction of coal with water may be described by two opposing processes. In the first process, the moisture content of coal is driven off by evaporation during the early stages of heating. Hence, some of the heat is removed in water vapour as latent heat of evaporation. The second process involves adsorption of water vapour from air by coal. The heat of adsorption produces an increase in the temperature of the material. The net effect depends on which of the two processes dominates.

3.2. Coal oxidation

The low temperature reaction leading to spontaneous combustion of coal is the process of absorption of oxygen to form oxycoal. The reaction has been studied by Itay et al. (1989), Rosema et al. (2001), Wang et al. (2003), Falcon (2004), Myles and Glasser (2005a,b), and is generally expressed as,

$$\text{Coal} + \text{Oxygen} \Rightarrow \text{Oxycoal} + \text{HEAT} \Rightarrow \text{Gas products.} \tag{1}$$

Experimental studies of coal by Banerjee (1985) established that the oxidation process occurs in four stages. These include:

1. Physical adsorption of oxygen commenced at about −80 °C, which is reversible, but rapidly diminished to become negligible beyond 30 °C to 50 °C. The process of adsorption produces heat as a by-product of the modified surface energy of the material. This causes an initial rise in temperature.
2. Chemical absorption (known also as chemisorption or activated sorption) becomes significant at about 50 °C. Chemisorption progressively causes the formation of unstable compounds of hydrocarbons and oxygen known as peroxy-complexes.
3. At a point known as the self-heating temperature (SHT) of the coal, the peroxy-complexes decompose at an accelerating rate to provide additional oxygen for the further stages of oxidation. This happens within a range of approximately 50 °C to 120 °C, but most typically at 70 °C. At higher temperatures, the peroxy-complexes decompose at a rate greater than they form (Wang et al., 2003) and the gaseous products of chemical reaction are liberated. In particular, carbon monoxide, carbon dioxide, water vapour, and the oxalic acids, aromatic acids, and unsaturated hydrocarbons that gives the characteristic odour of gobstink (Lu et al., 2004).
4. When the temperature exceeds approximately 150 °C, the combustion process accelerates rapidly. Incineration of the coal occurs with escalating emissions of the gaseous products of combustion (Rosema et al., 2001; Wang et al., 2003; Lu et al., 2004).

The rate at which oxygen is consumed varies both with time and the phase of oxidation. Oxygen is consumed rapidly in the earlier stages of chemisorption and as pyroxy-complexes are formed. Consumption reduces with time because coal particles become oxidized and weathered, and the reaction approaches equilibrium. If the SHT is reached, then both the rate of oxygen consumption and the temperature escalate rapidly.

3.3. Dealing with spontaneous combustion

Spontaneous combustion is a phenomenon that occurs during coal mining (underground and opencast), storage (stockpiles, silos), waste disposal (waste dumps, back-filling) and transportation. To manage and mitigate spontaneous combustion it is useful to understand the environmental factors and thermodynamic conditions that control the phenomenon. In a comprehensive study of the self-heating of coal stockpiles, Brooks and Glasser (1986) and Brooks et al. (1988) developed a simplified one-dimensional model consisting of three differential equations describing the variations in a coal bed of the oxygen concentration ($y(x)$), the energy ($T(x)$), and pressure ($P(x)$). It was assumed that a coal bed consisted of (1) nonporous coal particles; (2) the reaction occurred effectively only on the external surface of the particles; (3) and the rate of oxidation was temperature dependent. The monitoring and eventual prevention of spontaneous combustion could be achieved using the gradual evolution of the rate of oxidation as a function of the temperature. Fig. 2 illustrates graphically on the same graph the heat generated and the heat removed as a function of temperature. The removal of heat can be written as:

$$\text{Heat removed} = \alpha{*}\text{temperature} + \beta\text{, where } \alpha, \beta \epsilon \text{R and } \beta \text{ are constants.} \tag{2}$$

In Fig. 2, the heat generated as a function of temperature is represented by the curve C1, while the heat removed is represented by the curves C2, C3, and C4. The latter three correspond to different scenarios that could occur during spontaneous combustion.

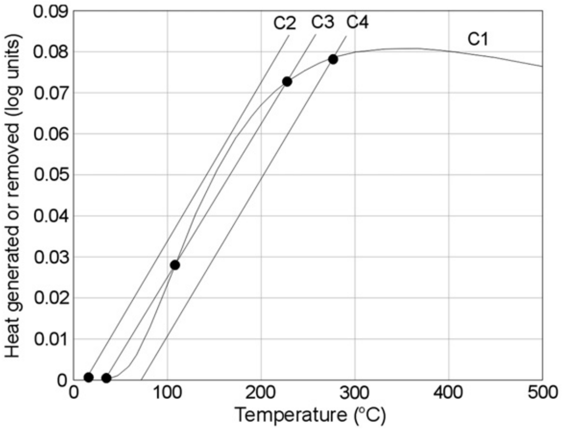

Fig. 2. Plot of heat generated versus temperature, after Brooks and Glasser (1986). The heat generated as a function of temperature is represented by the curve C1, while the heat removed is represented by the curves C2, C3, and C4 corresponding to different situations that could occur during the process of spontaneous combustion.

The intersection of two curves indicates steady state conditions.

1. The intersection between C1 and C2 occurs at low temperature indicates no combustion and coal material is safe.
2. Curves C1 and C3 have three points of intersection. The lower and higher intersection points are stable state where no combustion occurs at the lowest and combustion at the highest. The middle point is an unstable state meaning that the material is considered conditionally safe. The temperature at the intersection (≈100 °C) is relatively high and additional effects (e.g. wind) can trigger or accelerate the combustion process.
3. The intersection between C1 and C4 occurs at high temperature and indicates that combustion is likely.

4. Methodology

4.1. CFGMs sampling technique

A principal objective of this research was to collect coal-fire gas minerals (CFGM) and gas samples from fumaroles associated with an actively burning coal fire. The samples were collected during site visits made in 2005 to selected mines in both the Witbank and Sasolburg coalfields (Fig. 1). Fifteen CFGM's were collected from vents or fissures associated with coal fires by carefully scraping CFGM off rock and soil. Each sample was placed into a plastic vial and labelled. An Etrex® geographical positioning system unit (GPS) was used to record geographical coordinates (latitude/longitude) of the sampling points.

4.2. Gas sampling technique

Eight gas samples were collected from the Witbank coalfield and five from the Sasolburg coalfield using a hand-operated pump with Teflon inlet and exhaust tube. The gas was pumped into an inert and impermeable container for storage and transported to the laboratory for analysis. Despite its effectiveness, the method showed some limitations because the tube melted at high temperatures. To avoid melting of the tube, the hand-operated pump apparatus was replaced by vacuum stainless steel canisters. The vent temperature was measured using a digital thermocouple connected to a 1.0 m platinum thermoprobe.

4.3. Analytical methods

Each of the samples in this study was investigated using a combination of approaches. X-ray powder diffraction (XRD) studies in combination with scanning electron microscopy (SEM) analyses were conducted to identify the mineral phases collected from gas vents. The scanning electron microscope was equipped with an energy-dispersive X-ray spectrometer (SEM-EDX). Mineral identifications in the SEM were made on the basis of morphology and grain composition using both secondary electron and back-scattered electron modes. Both SEM and XRD analyses were conducted at the United States Geological Survey, Reston, VA and at the Mackay School of Mines, University of Nevada, Reno, NV. XRD measurements were conducted with a Scintag XDS-2000 X-ray diffractometer. Instrumental conditions were CoKα radiation (generated at 40 kV and 40 mA), a 250-mm goniometer radius, 1°/2° primary/scattering slits, 0.5°/0.3° scattering/receiving slits, primary and receiving Soller slits, and a liquid N_2-cooled germanium solid-state detector. XRD data were collected using a scan rate of 0.5° 2θ per minute, with a step increment of 0.01° 2θ. Diffractograms were processed using an external National Institute of Standards and Technology (NIST), USA, reference silicon powder, SRM640a, and peak shapes were analysed using profile-fitting software. Peak positions were best matched with patterns from the USA International Centre for Diffractions Data–Powder Diffraction File (ICDD-PDF). Digital SEM images were acquired using operating conditions of 10–15 kV and 1–30 nA. Electron microprobe analyses of individual mineral

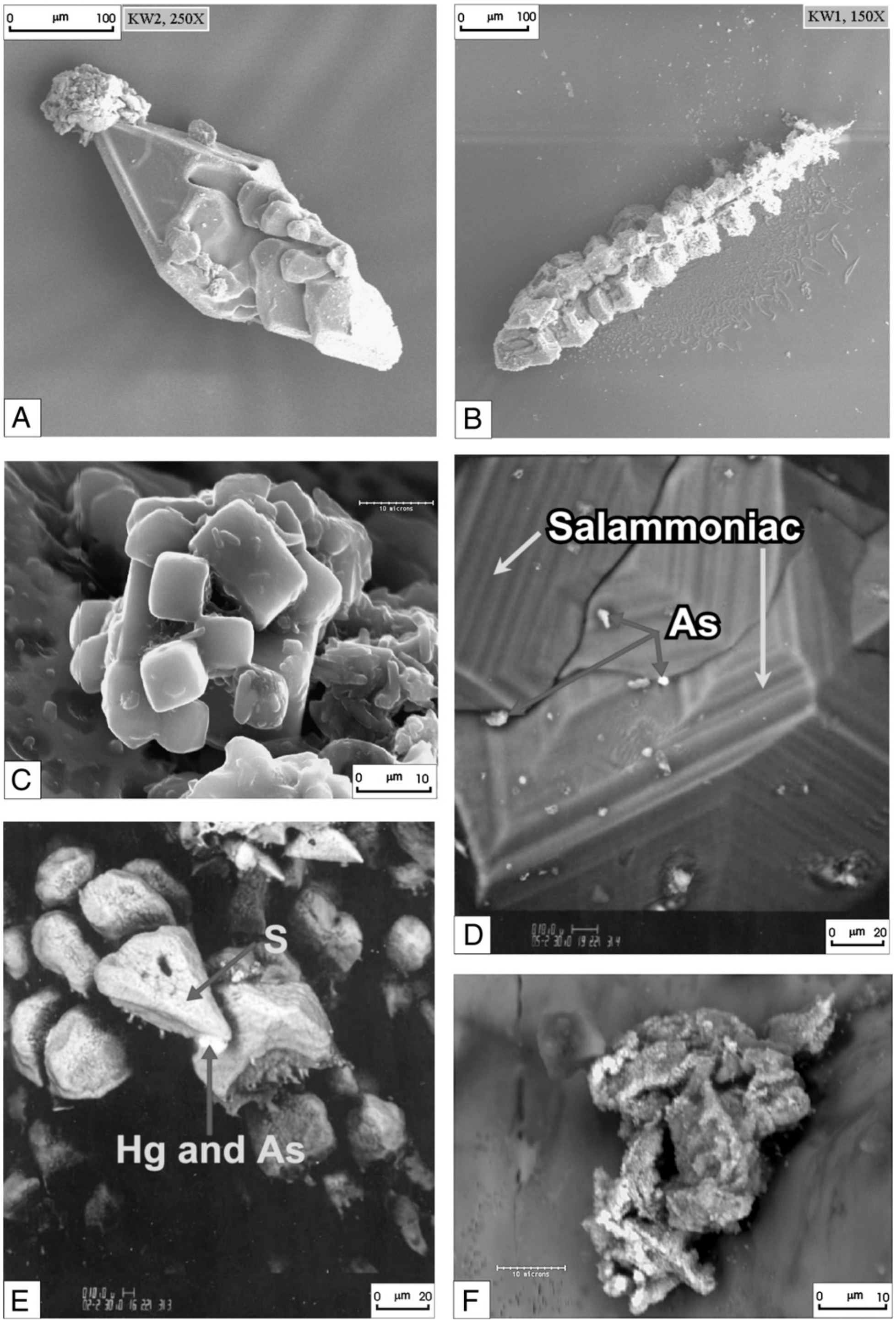

Fig. 3. Scanning-electron photomicrographs of CFM (coal-fire minerals). A. Hexagonal sulphur crystal from Witbank Coalfield. B. Skeletal to dendritic sulphur crystal from Witbank Coalfield. C. Cubic salammoniac crystal from Sasolburg Coalfield. D. Salammoniac-bearing arsenic compound from Witbank Coalfield. E. Sulphur bearing mercury–arsenic compound from Witbank Coalfield. F. Skeletal aggregate of sulphur, lead, zinc, copper, iron and germanium from Sasolburg Coalfield.

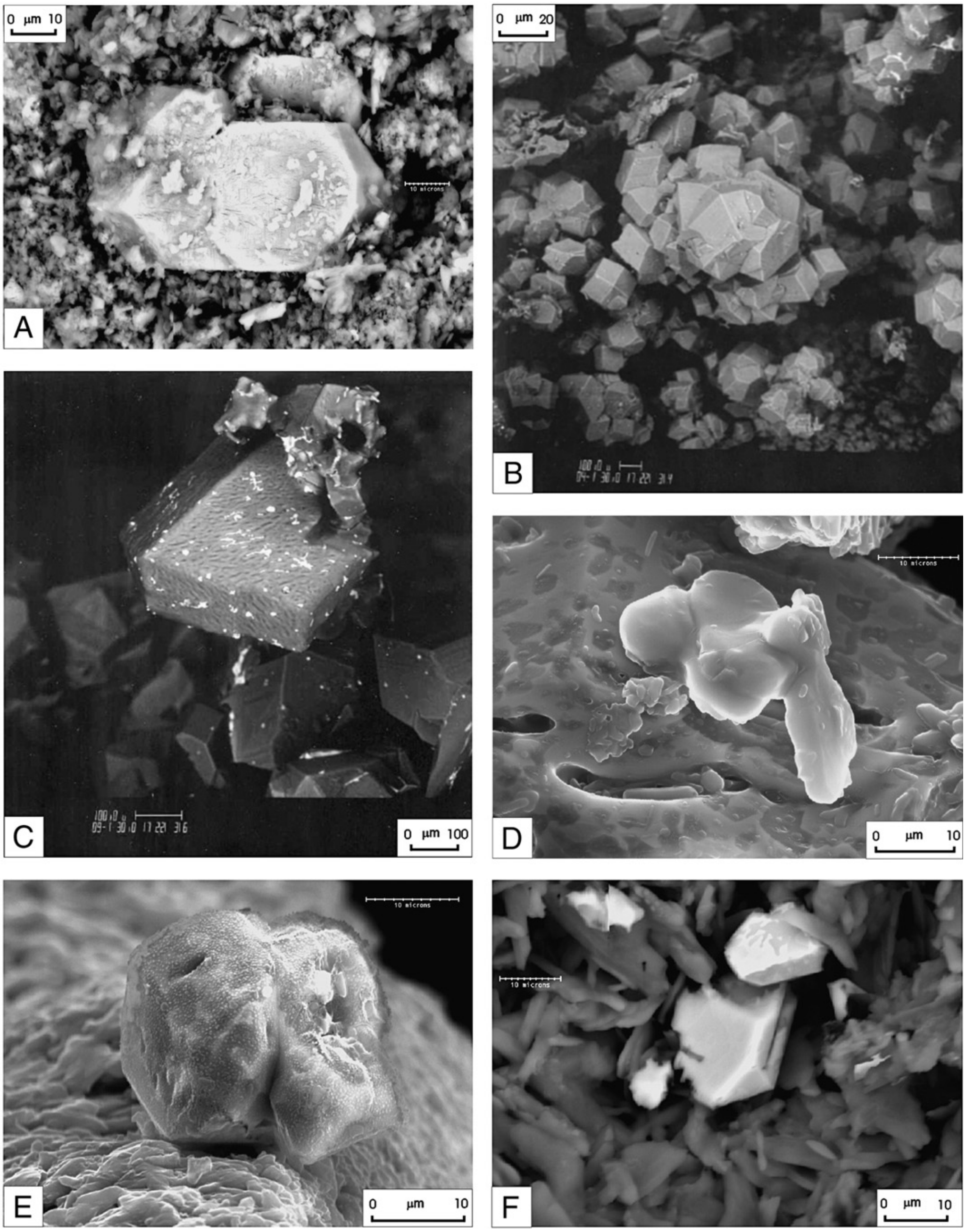

Fig. 4. Scanning-electron photomicrographs of CFM (coal-fire minerals). A. Crystals composed of sulphur, nitrogen and chlorine. B. Crystals composed of chlorine and bromine. C. Crystals composed of chlorine and iodine. D. Crystal composed of sulphur and nitrogen. E. Crystal composed of sulphur, nitrogen and oxygen. F. Crystals composed of sulphur, hydrogen and chlorine.

phases were not possible because the samples deteriorated during polishing of thin sections.

Gas chromatographic analyses of the sample were performed at the University of California, Irvine Department of Chemistry Laboratory, using the method presented by Colman et al. (2001) and Barletta et al. (2002). The analytical techniques involved the cryogenic pre-concentration of the air sample with liquid nitrogen (−196 °C). The pre-concentrated gas was subsequently vapourised using a hot water bath and split into five different detectors connected to three separate Hewlett–Packard (HP) 6890 gas chromatographs (GC). Two electron capture detectors (ECD), a mass spectrometer detector (MSD), and two flame ionization detectors (FID) were all used to analyse hydrocarbons, halocarbons and a variety of halogenated compounds. Carbon monoxide and methane analyses were carried out using a GC (HP5890) equipped with FID. For CO_2 analyses, an HP 5890 gas chromatograph equipped with a thermal conductivity detector was used. N_2, O_2, and sulphur oxides, detectable in the field (Stracher and Taylor, 2004) were not quantifiable due to the laboratory analytical setup. H_2O was not quantified because of its tendency to condense in the canister and its known variability in coal-fire gas.

5. Results

5.1. Mineralogy and temperature at the gas vents

XRD and SEM analyses established that condensation by-products were mostly sulphur (Fig. 3A, B) and sulphur-bearing minerals. Salammoniac (NH_4Cl) was the dominant mineral phase found as CFGM. Heavy metals such as arsenic (Fig. 3C, D) were detected. A grain of pure mercury was also found (Fig. 3E) and an aggregate of zinc, copper, lead, iron, and germanium (Fig. 3F) was detected. XRD diffractograms confirmed the presence of mascagnite ($(NH_4)_2SO_4$), illite ($(Al,Si)_4O_{10}[(OH)_2,H_2O]$), letovicite ($(NH_4)_3H(SO_4)_2$), and phlogopite ($KMg_3(AlSi_3)O_{10}(F,OH)_2$). The compounds titanium dioxide (TiO_2), barite ($BaSO_4$), iron sulphate ($FeSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$) and silicate were also identified. An unknown and unclassified CFGM composed of sulphur, nitrogen and chlorine (Fig. 4A) is reported herein for the first time. Other minerals detected during SEM analysis were composed of chlorine and bromine (Fig. 4B), chlorine and iodine (Fig. 4C), sulphur and nitrogen (Fig. 4D), sulphur, nitrogen, and oxygen (Fig. 4E), and sulphur and chlorine (Fig. 4F). The minerals detected at the Witbank and Sasolburg coalfields are similar to minerals and compounds derived from burning anthracite seams in Pennsylvania (Finkelman et al., 1974a). The minerals are interpreted to have formed during gas exhalation and condensation, and by interaction of gases and CFGMs with surface water, atmospheric gases, and surrounding rocks.

Table 1
Temperature in °C recorded at coal-fire vents and fissures in the Witbank and Sasolburg coalfield using a digital thermocouple and 1.0 m long platinum thermoprobe

Location	Temperature (°C)	Latitude, longitude
Sasolburg Coalfield		
Sample no. 1	390	S26°57.661 E27°57.838
Sample no. 2	276	S26°43.189 E27°55.833
Sample no. 3	465	S26°43.197 E27°55.833
Sample no. 4	82	S26°40.162 E27°55.846
Sample no. 5	320	S26°42.070 E27°56.240
Witbank Coalfield		
Sample no. 1	630	N/A
Sample no. 2	473	N/A
Sample no. 3	386	N/A
Sample no. 4	213	N/A
Sample no. 5	155	S26°00.010 E29°14.520
Sample no. 6	330	S26°00.050 E29°14.341″
Sample no. 7	67	S26°00.012′ E29°14.440′
Sample no. 8	34	S26°00.080′ E29°13.330′

(N/A): Not available — the GPS was not working.

Table 2
Average Volatile Organic Compounds (VOC) from Witbank and Sasolburg coalfields, South Africa

Volatile Organic Compounds (VOC)		
Compounds	Witbank (ppm)	Sasolburg (ppm)
Benzene	6.6	49.8
Toluene	5.2	397.4
Ethylbenzene	0.1	2.1
m/*p*-Xylene	0.2	5.9
o-Xylene	0.1	1.7
Isopropylbenzene	0.0	0.1
Propylbenzene	0.0	0.1
3-Ethlytoluene	0.0	0.3
4-Ethyltoluene	0.0	0.1
1,3,5-Trimethylbenzene	0.0	0.3
2-Ethyltoluene	0.0	0.2
1,2,4-Trimethylbenzene	0.0	0.2

Temperatures measured using a digital thermocouple revealed that gases escaping from vents in both the Witbank and Sasolburg coalfields range from 34 °C to 630 °C (Table 1).

5.2. Compounds from gas analyses

Gases emitted from coal-fire vents in the Witbank and Sasolburg coalfields consist of a complex mixture of hydrocarbons, halocarbons, greenhouse gases, and toxic concentration of CO, benzene, xylene and toluene. Four principal groups of chemicals were identified during analyses. These include (1) aromatic compounds, (2) aliphatic hydrocarbons, (3) halogenated hydrocarbons and, (4) greenhouse and other gases. Average values for all gases analysed are presented in Tables 2–5.

Benzene, toluene, ethylbenzene, xylenes, ethyltoluene, and trimethylbenzene were the main aromatic compounds present in gaseous effluents, and their concentrations varied (Table 2). Samples from the Sasolburg coalfield had the highest concentration for each aromatic compound (~398 ppm–0.2 ppm) and Witbank coalfield had the lowest (~7 ppm–0.005 ppm).

Table 3
Aliphatic hydrocarbon from Witbank and Sasolburg coalfields, South Africa

Aliphatic hydrocarbon		
Compounds	Witbank (ppm)	Sasolburg (ppm)
Ethane	116.8	714.6
Ethene	14.5	67.7
Ethyne	0.1	0.1
Propane	21.8	186.9
Propene	4.5	49.7
i-Butane	1.9	19.4
n-Butane	5.0	45.8
1-Butene	0.5	8.8
i-Butene	0.6	9.9
Trans-2-butene	0.5	11.7
Cis-2-butene	0.4	8.6
i-Pentane	1.1	9.0
n-Pentane	2.3	24.2
1,3-Butadiene	0.1	0.1
1-Pentene	0.2	4.8
Isoprene	0.0	0.0
Trans-2-pentene	0.3	7.6
Cis-2-pentene	0.1	3.7
Cyclopentane	0.4	3.6
2,3-Dimethylbutane	0.1	0.5
2-Methylpentane	0.8	5.8
3-Methylpentane	0.2	1.5
n-Hexane	1.3	16.4
n-Heptane	0.8	11.4
n-Octane	0.4	5.9
n-Nonane	0.1	2.3
n-Decane	0.1	0.6
3-Methyl-1-butene	0.0	0.8
2-Methyl-1-butene	0.1	2.2
2-Methyl-2-butene	0.3	6.4
2-Methyl-1-Pentene	0.0	0.5
4-Methyl-1-pentene	0.3	3.2

This is consistent with studies that suggest that coals of lower rank in general are characterised by a complex mixture of trapped saturated hydrocarbons and alkylated aromatic compounds (Puttmann et al., 1991). However, the analyses of proximal coal from Witbank and Sasolburg (Table 6) show that the percentage volatile content in Witbank coal is higher than that in Sasolburg coal (for the samples analysed).

Toluene, benzene, xylene, and ethylbenzene were the major VOC's emitted from both Witbank and Sasolburg coalfields. Benzene contribution was 53.7%, and toluene was 42.9% of overall VOC emitted. The difference in VOC concentrations revealed that coal quality analyses could not be used to accurately predict the volume of gases generated during coal seam fires. It would be necessary to determine the ability of VOC to transfer into the gaseous phase when spontaneously burning to establish hazardous VOC concentrations. Isopropylbenzene and propylbenzene exhibited variable behaviour with concentrations below the limit of detection.

Table 4
Halogenated hydrocarbons from Witbank and Sasolburg coalfields, South Africa

Halogenated hydrocarbon		
Compounds	Witbank (ppm)	Sasolburg (ppm)
Trichloromethane	0.000	0.000
Dichloromethane	0.072	0.015
Trichloroethylene	0.002	0.002
Tetrachloroethylene	0.006	0.007
Methyl chloride	0.019	0.002
Methyl bromide	0.000	0.000
Methyl iodide	0.000	0.000

Thirty-two aliphatic compounds were analysed (Table 3). The concentrations of these compounds were more regular than that of aromatic compounds. Ethane, followed by propane and butane, showed the highest concentration in both coalfields. Ethane contribution was 67%, pentane 12%, propene 8% and ethyne 3% of the overall aliphatic hydrocarbons produced during spontaneous combustion.

The results for halogenated hydrocarbons indicate very low concentrations when compared to those observed in other three groups of compounds (aromatic, aliphatic, and greenhouse) (Table 4). Some compounds, such as bromomethane, iodomethane, and trichloromethane occurred in very low concentrations. Other compounds such as dichloromethane and chloromethane occurred in high concentrations. Dichloromethane concentrations of 0.072 ppm at Witbank coalfield and 0.015 ppm at Sasolburg Coalfield, were detected which is significant because dichloromethane is a known human health hazard at ppm concentrations (David et al., 2006). The highest

Table 5
Greenhouse and other gases from Witbank and Sasolburg coalfields, South Africa

Greenhouse gases and others		
Compounds	Witbank (ppm)	Sasolburg (ppm)
Methane	1793.0	11710.0
Carbon monoxide	641.0	27500.0
Carbon dioxide	31925.0	89612.0
Cysteinesulfonic acid	6.3	6.1
Dimethyl sulfoxide	0.0	0.0
Carbon bisulfide	0.4	2.2
Methyl nitrate	0.0	0.0
Ethyl nitrate	0.0	0.0
Alkyl nitrate (i-$PrONO_2$)	0.0	0.0
Alkyl nitrate (n-$PrONO_2$)	0.0	0.0
Alkyl nitrate (2-$BuONO_2$)	0.0	0.0

Table 6
Witbank and Sasolburg coal proximate analyses

Air-dry-basis							
Coalfield	Calorific value MJ/kg	Moisture %	Ash %	Volatile matter %	Fixed carbon %	Total sulphur %	Rank designation (VR)
Witbank (Kleinkopje)	27.63	2.8	15.4	24.0	57.8	0.69	Medium-rank C
Sasolburg (New Vaal)	15.56	5.9	40.2	22.3	31.6	0.55	Medium-rank D

concentrations of halogenated compounds were measured for gas samples from the Witbank coalfield. These compounds are interpreted to have formed during the combustion process.

Finally, analyses of greenhouse and other gases (Table 5) revealed the presence of toxic concentrations of methane (1793 ppm in the Witbank Coalfield and 11,710 ppm at Sasolburg), carbon dioxide (31,925 ppm in the Witbank Coalfield and 89,612 ppm at Sasolburg) and carbon monoxide (641 ppm in the Witbank Coalfield and 27,500 ppm at Sasolburg).

6. Discussion

CFGM that result from the burning of coal seams or coal waste-dumps have been found in various parts of Pennsylvania (USA), Inner Mongolia (Northern China), and Indonesia, and have been detailed by Finkelman et al. (1974a,b), Finkelman and Mrose (1977), Finkelman (1978), Lapham et al. (1980), Dunn et al. (1986), Stracher (1995), Stracher et al. (2004) and Stracher et al. (2005). Mineral assemblages similar to those reported from these coal-fire sites also occur in the Witbank and Sasolburg coalfields. Most of these minerals form by condensation from the vapour phase and occur as minute, euhedral hexagonal or orthorhombic crystals (Figs. 3, 4), often in a complex of interlocking grain. Some mineralisation has resulted from the interaction of gases and CFGM along with surface water and surroundings rocks.

The gases released from gas vents at the Witbank and Sasolburg coalfields consist of a complex mixture of hydrocarbons, halocarbons and greenhouse gases (Tables 2–5) that are associated with negative effects on environment and on human health (Terblanche et al., 1992, 1994; Finkelman, 2004). These toxic compounds are carbon monoxide, carbon dioxide, methane, benzenes, toluenes, and xylenes. The presence of these products in the gas samples may be explained by the thermal degradation during spontaneous combustion of biopolymers buried in the coal seams (Puttmann et al., 1991). Stracher et al. (2005) stated that the exchange reaction between the gas, rocks, and solutions influenced the chemistry of gas *en route* to the surface. The high concentration of carbon monoxide and carbon dioxide detected in the samples are above the recommended World Health Organisation (WHO) guidelines and South African national guidelines, but sometimes occur in the Vaal Triangle (Annegarn et al., 1996a,b).

Puttmann et al. (1991) suggested that the concentration of benzenes, toluenes and xylenes (BTX) transferred from the geosphere to the atmosphere/hydrosphere can be estimated to be about 45 g/t overburden for coals of the Witbank and Sasolburg rank, which is based on the approximation that about 10% of the material in spoil piles is coal. This rate is higher when the material is subjected to self-heating and spontaneous combustion. In addition, Heffern and Coates (2004) stated that for complete oxidation of sub-bituminous coal in the Powder River Basin of the U.S.A. during combustion, 1.75 t CO_2 per/t of coal was produced. This represents huge volumes of CO_2 released into the environment every year simply from the natural burning of coal through wildfires and spontaneous combustion. According to Lloyd (2002), some 170 Mt of CO_2 is emitted from the natural burning of coal annually, while the amount of CO_2 emitted from the use of coal is around 112 Mt. The greenhouse effect of ever increasing global CO_2 emissions is by now largely accepted. The Kyoto Protocol may have far-reaching implications for those countries relying on coal and is of particular concern for South Africa because coal mining and production is predicted to grow over the next few decades (Anonymous, 2006). Unfortunately, no CO_2 sequestration research projects have yet been undertaken in South Africa, and no companies in South Africa are actively involved in global collaborative research on this topic (Falcon and Keyser, 2001).

The effect on human health of the many compounds reported in the gas and CFGM from the Witbank and Sasolburg coalfield are unknown and merit investigation. However, the effects of sulphur and sulphur compounds, salammoniac, arsenic, mercury, lead, benzene, toluene, xylene, dichloromethane, and greenhouse gases are known (Dean, 1985; Juberg et al., 1997; Gupta, 1999; Zheng et al., 1999; Mandal and Suzuki, 2002; Gorman et al., 2003; Finkelman, 2004; Eastmond et al., 2005; Zahir et al., 2005; David et al., 2006).

Sulphur and sulphur compounds are interpreted to have been sourced from mineral and organic sulphur in the coal. Sulphur in coal can be divided into three categories: pyritic sulphur, sulphur in sulphate minerals and organic sulphur (Alvarez et al., 1997). During combustion, pyritic sulphur is released as an oxide at about 500 °C (Chinchon et al., 1994). The sulphates do not release as sulphur dioxide until 1060 °C, a temperature at which 13.7% of the initial sulphur still remains (Alvarez et al., 1997). Sulphur oxides, primarily sulphur dioxide (SO_2), are released as gas into the atmosphere during coal seam fires. The sulphur oxides react with ions in the fluid phase (e.g. water, rain, water particles in the atmosphere, etc.) and precipitate sulphur-bearing minerals during condensation. These solid sulphur compounds may, in part, be dissolved into the surface water and transported in streams and waterways.

Salammoniac (NH_4Cl) occurs as a sublimation product of coal-fire gas and fumes from volcanic vents. It is therefore not surprising that it occurs as a CFGM at the Witbank and Sasolburg coalfields. According to Lapham et al. (1980), the minimum time for the sublimation of salammoniac at the Kehley's Run Anthracite Mine fire (eastern Pennsylvania, U.S.A.) was less than 24 h. Encrustations of salammoniac on volcanic rocks such as those on Mount Vesuvius, Italy, and Paricutin Volcano, Mexico, are also common (Gaines et al., 1997). The mineral has been identified as a condensation by-product around fumaroles associated with burning oil shale near Kimmeridge Bay on the Dorset Coast of England (Cole, 1975). Although the environmental impacts of this compound are not known, the considerable quantity generated in the Witbank and Sasolburg coalfields would make an environmental and health impact assessment useful in the near future.

Arsenic was detected in both coalfields. Arsenic (As) and related volatile compounds are mobilised during coal combustion and enter the environment as gas or as solid phases depending on the burning conditions (Yudovich and Ketris, 2005). Thermodynamic modelling by Bel'kova et al. (2000) showed that during the combustion of coal at low temperatures, arsenic is released as solid phases. Yan et al. (2001) stated that the dominant solid arsenate released during low-temperature combustion of coal is thallium arsenate ($TlAsO_4$). When the temperature of combustion exceeds ~600 °C (873 K), arsenic passes into the gaseous phase in the form of As_2, As_3, and/or AsS. Given that the temperature measured during this study was generally higher than 600 °C, it is interpreted that most of the arsenic escaping from coal-fire vents at Witbank and Sasolburg coalfields is in the gas phase, probably as AsO and As_2O_3 because they are the dominant gas species released at the temperature around 1000 °C (Yudovich and Ketris, 2005).

The environmental and human health impacts of arsenic are well known from studies by Finkelman (2004), Gupta (1999), Zheng et al. (1999), and Mandal and Suzuki (2002). Although symptoms of arsenic poisoning have not yet been reported by workers in the Witbank and Sasolburg coalfield, an assessment of the environmental impact of arsenic compounds in those regions may prevent a possible disaster in the future.

Mercury, detected as a CFGM by-product, is the most volatile trace element released during the combustion of coal. Furimsky (2000) stated that between ~1527 °C and 927 °C, more than 99% of mercury present in coal is vapourised in the form of elemental mercury. He stated that mercury compounds, which appeared in the solid phase at about 327 °C, consisted of $HgCl_2$ and $HgSO_4$. The detection of a pure grain of mercury during CFGM analyses provides limited evidence that mercury is also emitted into the atmosphere as a solid-phase pollutant. Although there is no direct evidence of health problems caused by mercury from coal combustion (Finkelman, 2004), the proportion of anthropogenic mercury in the environment is a matter of concern for the Witbank and Sasolburg area, given its toxicity even at low doses (Zahir et al., 2005).

Lead, detected as a CFGM by-product in the assemblage zinc–copper–lead–iron–germanium, is generally associated with minerals such as galena (PbS), clausthalite (PbSe) (Hower and Robertson, 2003), pyrite (Diehl et al., 2004), aluminosilicates, and carbonates (Finkelman, 1994; Goodarzi, 2002). The release of lead during coal combustion is dependent on its mode of occurrence and the combustion conditions (Lapham et al., 1980). Regardless, lead is readily absorbed into the bloodstream and stored in bone where it is returned to the blood stream during aging. Given sufficient exposure, lead can produce severe and chronic health effects (Juberg et al., 1997; Gupta, 1999).

Benzene, toluene, and xylenes were detected in gaseous effluents from both coalfields. Benzene is an established carcinogen in humans and animals (Dean, 1985; Eastmond et al., 2005), and an increased incidence of leukemia (cancer of the tissues that form white blood cells) has been observed in humans occupationally exposed to benzene (Eastmond et al., 2005). In contrast, toluene vapour and xylenes are inhibitors of the central nervous system (CNS). Symptoms are related to exposure concentration and the effects are irreversible. However, unlike benzene, toluene and xylene isomers are not mutagenic and may inhibit the carcinogenic effect of benzene (Dean, 1985).

Dichloromethane was detected during spontaneous combustion of coal with the concentration of 0.072 ppm at Witbank and 0.015 ppm at Sasolburg coalfields (Table 4). Dichloromethane (methylene chloride) metabolises to CO in humans and animals, and increases the risk of liver and lung cancer (David et al., 2006). There is also evidence that exposure can result in haemolytic anaemia especially among those individuals with erythrocytes deficient in glucose-6-phosphate dehydrogenase (Davidson et al., 1985). The observed cardiotoxic properties include cardio-depression and cardiosensitisation.

The gas analyses from the Witbank and Sasolburg coalfields also revealed the presence of toxic concentrations of CO with concentrations of 641 ppm and 27500 ppm from samples collected at Witbank and Sasolburg coalfields, respectively (Table 5).

7. Conclusion

The Inter-Governmental Panel for Climate Change (IPCC) has recognised spontaneous combustion of coal as a potential source of greenhouse gas emissions. The analysis of chemical elements mobilised by spontaneous combustion in Witbank and Sasolburg coalfields, South Africa, have demonstrated that this phenomenon may contribute not only to the degradation of the global ecosystem as suggested by IPCC, but has the potential to affect the health of mine workers and communities living near the coalfields.

This study has identified that during spontaneous combustion of coal in Witbank and Sasolburg coalfields, burning coal released high concentrations of toxic gases including benzene, toluene, xylene, ethylbenzene, methane, and carbon oxides. Thirty-two aliphatic compounds were detected. Halogenated compounds included bromomethane, iodomethane and trichloromethane in low concentrations, and dichloromethane and chloromethane in high concentrations. Different CFGM such as salammoniac and mascagnite were detected. Heavy metals such as mercury, arsenic, lead, zinc, and copper were also found.

The considerable quantity of salammoniac generated by spontaneous combustion in the Witbank and Sasolburg coalfields would make an environmental and health impact assessment important in the near future. Solid sulphur compounds which are, in part, dissolved into surface water and transported in streams and waterways, have the potential to contribute to the deterioration of the local hydrology. The environmental and human health impacts of arsenic, mercury and lead are known and an environmental impact assessment of these elements in Witbank and Sasolburg coalfields will be necessary in the future to assess the health risk to local communities. Benzene, toluene and xylenes are known to possess carcinogenic proprieties. Dichloromethane and carbon monoxide are a recognised human health hazard if they occur in toxic concentrations.

However, the nature of the risks to human health and the environment of most of the compounds in gas and CFGM by-products of spontaneous combustion at the Witbank and Sasolburg coalfields are unknown and merit investigation, particularly given the high concentration of polyaromatic hydrocarbons detected with carcinogenic and mutagenic effects. Establishing criteria for toxicity and limits on toxic emission from uncontrolled fires in coal will be necessary for development of environmental regulations in the future and for assessment of the impacts on air and water quality, and human health.

Acknowledgements

This research work was supported during the period 2004–2005 by Prof. H.J. Annegarn Research Grant. AngloCoal, South Africa provided access to opencast pits, and H. Lodewijks and mine staffs at AngloCoal collieries assisted during sample collection. My sincere thanks go to J. L. Stracher and J. Finkelman for the support during my research visit at the USA. The USGS are acknowledged for their help with this study. E. Heffern is thanked for the careful review of the final version.

References

Alvarez, R., Clemente, C., Gomez-Limon, D., 1997. Reduction of thermal coals environmental impact by nitric precombustion desulfurization. Environmental Science and Technology 31, 3148–3153.

Annegarn, H.J., Turner, C.R., Helas, G., Tosen, G.R., Rorich, R.P., 1996a. Gasesous pollutants. In: Held, G., Gore, B.J., Surridge, A.D., Tosen, G.R., Turner, C.R., Walmsley, R.D. (Eds.), Air Pollution and its Impacts on the South African Highveld. Environmental Scientific Association, Cleveland, pp. 25–33.

Annegarn, H.J., Terblanche, A.P.S., Sithole, J.S., Rorich, R.P., Turner, C.R., 1996b. Residential air pollution. In: Held, G., Gore, B.J., Surridge, A.D., Tosen, G.R., Turner, C.R., Walmsley, R.D. (Eds.), Air Pollution and its Impacts on the South African Highveld. Cleveland Environmental Scientific Association, pp. 47–57.

Anonymous, 2005. Operating and developing coal mines in the Republic of South Africa. Department of Minerals and Energy Report R50/2005, Pretoria, Republic of South Africa. 66 pp.

Banerjee, S.C., 1985. Spontaneous Combustion of Coal and Mine Fires. Balkema, Rotterdam, p. 18.

Barletta, B., Meinardi, S., Simpson, I.J., Khwaja, H.A., Blake, D.R., Rowland, F.S., 2002. Mixing ratios of volatile organic compounds (VOCS) in the atmosphere of Karachi, Pakistan. Atmospheric Environment 36, 3429–3443.

Bel'kova, V.A., Bychinsky, I.M. Tshadov, Kotel'nikov, N.V., 2000. The behaviour of trace elements at the Cheremkhovo coal combustion. Ugol' [Coal] 5, 43–47.

Bell, F.G., Bullock, S.E.T., Halbich, T.F.J., Lindsay, P., 2001. Environmental impacts associated with an abandoned mine in the Witbank Coalfied, South Africa. International Journal of Coal Geology 45, 195–216.

Braker, J., 1985. South African coalfields study. Boulder BXG, Inc., Johannesburg.

Brooks, K., Glasser, D., 1986. A simplified model of spontaneous combustion in coal stockpiles. Fuel 65, 1035–1042.

Brooks, K., Svanas, N., Glasser, D., 1988. Evaluating the risk of spontaneous combustion in coal stockpiles. Fuel 27, 651–656.

Cadle, A.B., Cairncross, B., Christie, A.D.M., Roberts, D.L., 1993. The Karoo Basin of South Africa: type basin for the coal-bearing deposits of southern Africa. International Journal of Coal Geology 23, 117–157.

Cairncross, B., 1989. Paleodepositional environments and tectono-sedimentary controls of the postglacial Permian coals, Karoo Basin, South Africa. International Journal of Coal Geology 12, 365–380.

Cairncross, B., 1990. Tectono-sedimentary settings and controls of the Karoo Basin Permian coals, South Africa. International Journal of Coal Geology 16, 175–178.

Cairncross, B., 2001. An overview of the Permian (Karoo) coal deposits of southern Africa. Journal of African Earth Sciences 33, 529–562.

Cairncross, B., Cadle, A.B., 1987. A genetic stratigraphy for the Permian coal-bearing Vryheid Formation in the East-Witbank Coalfield, South Africa. South African Journal of Geology 90, 219–230.

Cairncross, B., Cadle, A.B., 1988. Palaeoenvironmental control on coal formation, distribution and quality in the Permian Vryheid Formation, East Witbank Coalfield, South Africa. International Journal of Coal Geology 9, 343–370.

Cairncross, B., Hart, R.J., Willis, J.P., 1990. Geochemistry and sedimentology of coal seams from the Permian Witbank Coalfield, South Africa; a means of identification. International Journal of Coal Geology 16, 309–325.

Ceglarska-Stefanska, G., Brzóska, K., Winnicki, J., 1998. Sorption of water vapour on exinite concentrations. Chemistry and Materials Science 4, 313–319.

Chatterjee, R.S., 2006. Coal fire mapping from satellite thermal IR data — a case example in Jharia Coalfield, Jharkhand, India. ISPRS Journal of Photogrammetry and Remote Sensing 60, 113–128.

Chinchon, J.S., Querol, X., Fernandez-Turiel, J.L., 1994. Environmental impact of mineral transformations undergone during coal combustion. Environmental Geology and Water Sciences 18, 11–15.

Cole, D.I., 1975. Observations on a burning cliff. Proceedings of the Dorset Natural History and Archaeological Society for 1974, Dorchester, Dorset, UK, vol. 96, pp. 16–19.

Colman, J.J., Swanson, A.L., Meinardi, S., Sive, B.C., Blake, D.R., Rowland, F.S., 2001. Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B. Analytical Chemistry 73, 3723–3731.

David, R.M., Clewell, H.J., Gentry, P.R., Covington, T.R., Morgott, D.A., Marino, D.J., 2006. Revised assessment of cancer risk to dichloromethane II. Application of probabilistic methods to cancer risk determinations. Regulatory Toxicology and Pharmacology 45, 55–65.

Davidson, I., Egle Jr., J., Greenberg, M., Parker, J., 1985. Health assessment document for dichloromethane (methylene chloride). U.S. Environmental Protection Agency, Washington, D.C., EPA/600/8-82/004 (NTIS PB86123742).

Dean, B.J., 1985. Recent findings on the genetic toxicology of benzene, toluene, xylenes and phenols. Mutation Research 154, 153–181.

Diehl, S.F., Goldhaber, M.B., Hatch, J.R., 2004. Modes of occurrence of mercury and other trace elements in coals from the Warrior Field, Black Warrior Basin, northwestern Alabama. International Journal of Coal Geology 59, 193–208.

Dunn, P.J., Peacor, D.R., Criddle, A.J., Finkelman, R.B., 1986. Laphamite, an arsenic selenide analogue of orpiment, from burning anthracite deposits in Pennsylvania. Mineralogical Magazine 50, 279–282.

Eastmond, D.A., Mondrala, S.T., Hasegawa, L., 2005. Topoismerase II inhibition by myeloperoxidase-activated hydroquinone: a potential mechanism underlying the genotoxic and carcinogenic effects of benzene. Chemico–Biological Interactions 153–154, 207–216.

Falcon, R.M.S., 1986a. Classification of coals in southern Africa. In: Anhauesser, C.R., Maske, S. (Eds.), Mineral Deposits of Southern Africa, vol. II. Geological Society of Southern Africa, pp. 1899–1921.

Falcon, R.M.S., 1986b. A brief review of the origin, formation, and distribution of coal in Southern Africa. In: Anhauesser, C.R., Maske, S. (Eds.), Mineral Deposits of Southern Africa, vol. II. Geological Society of Southern Africa, pp. 1879–1898.

Falcon, R.M.S., 1989. Macro-and micro-factors affecting coal-seam quality and distribution in Southern Africa with particular reference to the No. 2 seam, Witbank Coalfield, South Africa. International Journal of Coal Geology 12, 681–731.

Falcon, R.M.S., 2004. The constitution of coal and its inherent capacity to self-heat — as applied to an integrated spontaneous combustion risk. Final Proceedings of the International Conference on Spontaneous Combustion. Fossil Fuel Foundation and SABS, Johannesburg, pp. 8–9.

Falcon, R.M.S., Keyser, M.J., 2001. The status of coal in South Africa: production, utilization, characterization. Final Proceedings of the International Conference on Coal Quality: Global Priority. US Geological Survey Circular 1272, Reston, VA, CD.

Finkelman, R.B., 1978. Release of trace elements from a burning bituminous culm bank. USGS Open-file Report, vol. 78-864.

Finkelman, R.B., 1994. Modes of occurrence of potentially hazardous elements in coal: levels of confidence. Fuel Processing Technology 39, 21–34.

Finkelman, R.B., 2004. Potential health impacts of burning coal beds and waste banks. International Journal of Coal Geology 51, 19–24.

Finkelman, R.B., Mrose, M.E., 1977. Downeynite, the first verified natural occurrence of SeO_2. American Mineralogist 62, 316–320.

Finkelman, R.B., Lapham, D.M., Barnes, J.M., Harrisburg, P., Downey, W.F., 1974a. Observations on minerals from burning anthracite seams and culm in Pennsylvania. Geological Society of America, Abstracts with Programs 5 (No. 1), 27–28.

Finkelman, R.B., Larson, R.R., Dwornik, E.J., 1974b. Naturally occurring vapor–liquid–solid (VLS) whisker growth of germanium sulfide. Journal of Crystal Growth 22, 159–160.

Finkelman, R.B., Belkin, H.E., Zheng, B., 1999. Health Impacts of Domestic Coal use in China: Proceedings of the National Academy of Science, USA, vol. 46, pp. 3427–3431.

Finkelman, R.B., Skinner, H.C., Plumlee, G.S., Bunnell, J.E., 2001. Medical Geology Geotimes 46 (11), 21–23.

Finkelman, R.B., Orem, W., Castranova, V., Tatu, C.A., Belkin, H.E., Zheng, B., Lerch, H.E., Marharaj, S.V., Bates, A.L., 2002. Health impacts of coal and coal use: possible solutions. International Journal of Coal Geology 50, 435–443.

Furimsky, E., 2000. Characterization of trace element emissions from coal combustion by equilibrium calculations. Fuel Processing Technology 63, 29–44.

Gaines, R.V., Skinner, H.C., Foord, E.E., Mason, B., Rosenzweig, A., 1997. Dana's New Mineralogy, edition 8. John Wiley and Sons, Inc., New York, p. 1819.

Glasser, D., Bradshaw, S.M., 1990. Spontaneous combustion in beds of coal. In: Cheremisin Off, N. (Ed.), Handbook of Heat and Mass Transfer: 4 Advances in Reactor Design and Combustion Science, Chapter 26, NJ Gulf, p. 1071.

Glasser, D., Itay, M., 1988. The low temperature oxidation of coal taken from near a dolorite intrusion. Fuel Processing Technology 18, 201–208.

Goodarzi, F., 2002. Mineralogy, elemental composition and modes of occurrence of elements in Canadian feed-coals. Fuel 81, 1199–1213.

Gorman, D., Drewry, A., Huang, Yi Lin, Sames, C., 2003. The clinical toxicology of carbon monoxide. Toxicology 187, 25–38.

Gupta, D.C., 1999. Environmental aspects of selected trace elements associated with coal and natural waters of Pench Valley coalfield of India and their impact on human health. International Journal of Coal Geology 40, 133–149.

Heffern, E.L., Coates, D.A., 2004. Geologic history of natural coal-bed fires, Powder River basin, USA. International Journal of Coal Geology 59, 25–47.

Holland, M.J., Cadle, A.B., Pinheiro, R., Falcon, R.M.S., 1989. Depositional environments and coal petrography of the Permian Karoo Sequence: Witbank Coalfield, South Africa. International Journal of Coal Geology 11 (2), 143–169.

Hower, J., Robertson, J.D., 2003. Clausthalite in coal. International Journal of Coal Geology 53, 219–225.

Hudak, P.F., 2002. Spontaneous combustion of shale spoils at a sanitary landfill. Waste Management 22, 687–688.

Itay, M., Hill, C.R., Glasser, D., 1989. A study of the low temperature oxidation of coal. Fuel Processing Technology 21, 81–97.

Juberg, D.R., Kleiman, C.F., Kwon, S.C., 1997. Position paper of the American Council on Science and Lead and Human Health. Ecotoxicology and Environmental Safety 38, 162–180.

Kaymakci, E., Didari, V., 2002. Relations between coal properties and spontaneous combustion parameters. Turkish Journal of Engineering and Environmental Science 26, 59–64.

Lang, J., 1995. Coal Mining in the Life of South Africa: Power Base. Jonathan Ball Publishers, Johannesburg, p. 231.

Lapham, D.M., Barnes, J.H., Downey Jr., W.F., Finkelman, R.B., 1980. Mineralogy associated with burning anthracite deposits of eastern Pennsylvania. United States Geological Survey, 4th Series, Mineral Resource Report, vol. 78. 82 pp.

Lloyd, P.J., 2002. Coal mining and the environment. Final Proceedings of the International Conference on Coal and Environment IBA Durban, South Africa, pp. 8–9.

Lu, P., Liao, G.X., Sun, J.H., Li, P.D., 2004. Experimental research on index gas of the coal spontaneous at low-temperature stage. Journal of Loss Prevention in the Process Industries 17, 243–247.

Mandal, B.K., Suzuki, K.T., 2002. Arsenic round the world: a review. Talanta 58, 201–235.

Moolman, C., 2004. The spontaneous combustion challenges in mining old coal pillar workings from surface. Final Proceedings of the International Conference on Spontaneous Combustion. Fossil Fuel Foundation and SABS, Johannesburg, South Africa, pp. 11–18.

Myles, A.S., Glasser, D., 2005a. Spontaneous combustion of carbonaceous stockpiles. Part I. The relative importance of various intrinsic coal properties and properties of the reaction system. Fuel 84, 1151–1160.

Myles, A.S., Glasser, D., 2005b. Spontaneous combustion of carbonaceous stockpiles. Part II. Factors affecting the rate of the low-temperature oxidation reaction. Fuel 84, 1161–1170.

Nolter, A.M., Vice, D.H., 2004. Looking back at the Centralia coal fire: a synopsis of its present status. International Journal of Coal Geology 59, 99–106.

Puttmann, W., Steffens, K., Gobel, W., 1991. Analysis of aromatic hydrocarbons in overburden from coal mines: assessment of the environmental impact. In: Peters, D.C. (Ed.), Geology in Coal Resource Utilization. TechBooks, Fairfax, VA, pp. 483–498.

Roberts, M., 2005. South Africa's mineral production and sales 1985–2004. Department of Minerals and Energy Report R50/2005, Pretoria, Republic of South Africa. 20 pp.

Rosema, A., Guan, H., Veld, H., 2001. Simulation of spontaneous combustion, to study the causes of coal fires in the Rujigou Basin. Fuel 80, 7–16.

Reucroft, C.F., Sethuraman, A.R., 1987. Effect of pressure on carbon dioxide induced coal swelling. Energy Fuels 1, 72–75.

Sheail, J., 2005. 'Burning bings': a study of pollution management in mid-twentieth century Britain. Journal of Historical Geography 31, 134–148.

Stracher, G.B., 1995. The anthracite smokers of Eastern Pennsylvania: Ps2(g)-T stability diagram by TL analysis. Mathematical Geology 27, 499–511.

Stracher, G.B., 2004. Coal fires burning around the world: a global catastrophe. International Journal of Coal Geology 59, 1–6.

Stracher, G.B., Taylor, T.P., 2004. Coal fires burning out of control around the world: thermodynamic recipe for environmental catastrophe. International Journal of Coal Geology 59, 7–17.

Stracher, G.B., Taylor, T.P., Nolter, M., Vice, D.H., Blake, D.R., Cerpovicz, P., 2004. Centralia mine fire collecting extravaganza with National Geographic. Geological Society of America Abstracts with Programs 36 (5), 42.

Stracher, G.B., Prakash, A., Schroeder, P., McCormack, J., Zhang, X., Dijk, P.V., Blake, D., 2005. New mineral occurrences and mineralization processes: Wuda coal-fire gas vents of Inner Mongolia. American Mineralogist 90, 1729–1739.

Terblanche, A.P.S., Opperman, L., Nel, C.M.E., Reinach, S.G., Tosen, G., Cadman, A., 1992. Preliminary results of exposure measurements and health effects of the Vaal Triangle air pollution health study. South African Medical Journal 81, 550–556.

Terblanche, A.P.S., Nel, R., Golding, T., 1994. Household energy sources in South Africa: an overview of the impact of air pollution on human health. CSIR Environmental Services, Department of Mineral and Energy Affairs and EMSA, Pretoria, South Africa.

Uludag, S., Phillips, H.R., Eroglu, H.N., 2001. Assessing Spontaneous Combustion Risk In South African Coal Mining by Using a GIS Tool, 17th International Mining Conference and Exhibition, Turkey.

Wang, H., Dlugogorski, B.Z., Kennedy, E.M., 2003. Coal oxidation at low temperatures: oxygen consumption, oxidation products, reaction mechanism and kinetic modelling. Progress in Energy and Combustion Science 29, 487–513.

Whitehouse, A.E., Mulyana, A.A.S., 2004. Coal fires in Indonesia. International Journal of Coal Geology 59, 91–97.

Yan, R., Gauthier, D., Flamant, G., 2001. Partitioning of trace elements in the flue gas from coal combustion. Combustion and Flame 125, 942–954.

Yudovich, Y.E., Ketris, M.P., 2005. Arsenic in coal: a review. International Journal of Coal Geology 61, 141–196.

Zahir, F., Rizwi, S., Haqb, S.K., Khanb, R.H., 2005. Low dose mercury toxicity and human health. Environmental Toxicology and Pharmacology 20, 351–360.

Zheng, B., Ding, Z., Huang, R., Zhu, J., Yu, X., Wang, A., Zhou, D., Mao, D., Su, H., 1999. Issues of health and disease relating to coal use in southwestern China. International Journal of Coal Geology 40, 119–132.