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Gaseous compounds and efflorescences generated in self-heating coal-waste dumps — A case study from the Upper and Lower Silesian Coal Basins (Poland)

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ABSTRACT

Gases emitted in coal waste self-heating and efflorescences blooming around fissures of coal waste dumps of the Upper and Lower Silesian Coal Basins were investigated. Gas chromatography (GC-FID) and charcoal tubes were applied for gas emissions, gas chromatography–mass spectrometry (GC–MS) for organic fraction of blooms, and X-ray diffraction and scanning electron microscopy for inorganic efflorescences. The results show that coal waste dump gases contain a wide range of inorganic and organic compounds that are highly variable in their occurrence and concentrations, even in samples from the same dumps or the same coal basin. Chemical composition of self-heating products is related to source organic matter characteristics, composition and amount of coal waste material deposited on individual dumps, time and temperature range of the self-heating, composition and temperature of gas jets and condition variations at different depths. Carbon dioxide and carbon monoxide dominate in all gases, with additional components such as carbonyl sulphide, carbon disulphide, methane, light *n*-alkanes, *n*-alkenes, *iso*-alkanes, cyclic alkanes, chloroform, and benzene and its alkyl derivatives. Efflorescences blooming at vents and fissures at all sampling sites differ greatly in their phases, amounts, and chemical compositions, with organic blooms including phenanthrene (ravatite), phthalimide (kladnoite), and 9,10-antraquinone (hoelite) found only in one of the dumps. They are accompanied by salammoniac and native sulphur which are ubiquitous at a newly formed vents as in coal waste dumps with long time range of self-heating. Self-heating leads to the synthesis of new components such as unsaturated hydrocarbons, sulphides, chloroform, and phthalimide (kladnoite), for which formation mechanism is proposed in the paper.

1. Introduction

In Poland, 0.3–0.6 t of coal wastes is generated during the mining of 1 t of coal. The wastes, stored in coal waste dumps, may undergo self-heating connected with the alteration of both organic and mineral matters. This is a common occurrence in both the Upper and Lower Silesian Coal Basins. A wide variety of gases are emitted during these processes.

1.1. The self-heating process

Self-heating in coal waste dumps and coal beds can be generalized as a multistage diffusive combustion and/or smoldering process (Sokol et al., 2005). Alterations of coal wastes occur during weathering and self-heating processes. The latter can lead to self-combustion. It takes place only when three factors occur at the same time, namely, the presence of organic matter, access of air into the dump, and the possibility of heat accumulation within the dump (Brooks et al., 1988; Kaymakçi and Didari, 2002; Pone et al., 2007; Szafer et al., 1994; Urbański, 1983). The heating spots are usually located 1.5–2.5 m below the dump surface (Urbański, 1983; Walker, 1999). The process occurs randomly in discrete spots within coal waste dumps and temperatures in these spots fluctuate with time (e.g., Misz-Kennan, 2010; Misz-Kennan and Tabor, 2013). At the initial (incubation) stage the temperature rises slowly with organic and mineral matter oxidated. Self-ignition occurs in 60–80 °C, with temperature of self-ignition strongly rank-related, being higher, the higher the rank of the organic matter present in the wastes. The temperature of self-heating is ca. 150 °C for subbituminous coals, ca. 200 °C for bituminous coals, and ca. 300 °C for anthracites (Sokol et al., 2005). The

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self-heating involves many factors influencing the process such as the maceral composition of any organic matter, its rank and its mineral composition, the shape of a dump, its height, level of air access, and atmospheric precipitation (e.g., Krishnaswamy et al., 1996; Misz-Kennan et al., 2013; Misz-Kennan and Tabor, 2013; Pan et al., 2009, 2010; Pone et al., 2007; Urbański, 1983; Walker, 1999).

The decomposition of organic-matter macromolecules with rising temperature is associated with the release of gaseous compounds. This happens in combustion (free access of oxygen) or in oxygen-depleted conditions such as in pyrolysis or coking. These industrial processes which are carried out in a controlled environment can be used to assess the conditions and mechanisms of self-heating. The term self-combustion is commonly used for the high-temperature processes taking place in the wastes. Misz-Kennan (2010) has shown that self-heating occurs where air access is limited, commonly in the presence of moisture, probably from atmospheric precipitation and the decomposition of organic compounds. On this basis, the terms pyrolysis or hydropyrolysis can be applied to them. The gas–liquid products (pyrolysate) and solid products (coke) formed compare to those formed during industrial or laboratory coal pyrolysis; however, the heating of gangue rocks in the waste give, in addition, products such as fluorine and water (Sokol et al., 2002; Yurkevich and Rosinskiy, 1973).

Liquid products (pyrolysate) of coal concentrate heavier compounds such as saturated and unsaturated aliphatic hydrocarbons; aromatic hydrocarbons such as benzene, naphthalene, anthracene, and fluorene and their derivatives; heterocyclic hydrocarbons such as carbazole, pyridine, quinoline, tiophene, and other sulphur compounds; and functional oxygen compounds such as phenol and cresoles. Coking gas contains, on average, about 58–62% H_2, 24–26% CH_4, 5–6.5% CO, 2–3.5% N_2, 2–2.5% 1.6–3% CO_2, and 0.4–0.8% O_2. In lower amounts there are aliphatic hydrocarbons, benzene derivatives; NH_3, HCN, H_2O, HCl, sulphur compounds (SO_2, SO_3, H_2S, CS_2, COS, CNS, and C_4H_4S), and metaloorganic compounds (Babcock and Wilcox Co., 2005; Yurkevich and Rosinskiy, 1973). Coal distillation and pyrolysis are processes carried out under strictly-controlled conditions. Self-heating, in contrast, is a chaotic process involving many ill-defined variables.

1.2. Petrography and mineralogy of self-heated coal wastes

Endogenic fires caused by self-heating and self-ignition generate changes in the wastes — changes due to pyrometamorphism and combustion metamorphism. The products include paralavas (parabasalts, pseudobasalts) interpreted as completely melted, partially recrystallized sedimentary substrate, and metapelites (metaargilites) usually formed as a result of partial annealing of the protolith. Other lithological types, namely slags, metacarbonate slags, and ashes, are distinguished in some cases (Ciesielczuk and Paszkowski, 2009; Kruszewski, 2006, 2008; Panov et al., 1999; Sokol et al., 2005).

Self-combustion of coal waste dumps causes their intensive reconstruction due to diverse fire-triggered mineralogenic processes. The oxidation of coal and disseminated sulphide minerals leads to the formation of local fire centers. These centers emit hot gaseous jets that contribute to heat convection and the ignition of the overlying zones. Inward migration of the fire centers is also possible. These phenomena have been described in detail by e.g., Chesnokov et al. (1998), Panov et al. (1999), and Sokol et al. (2005). The exhalative activity on self-heating coal-waste dumps leads to the appearance of mineral efflorescences. The mineralogenic processes are dependent on the composition and temperature of the gaseous jets (Chesnokov et al., 1998; Engle et al., 2012; Kruszewski, 2008; Silva et al., 2011). The redox potential of gas is clearly dependent on temperature and of the reactions occurring within the C–O–H system. The temperature of the gaseous jets, which is also dependent on coal ash content, may reach 1200 °C, even 2000 °C in the combustion zone (Sokol et al., 2005).

1.3. Gaseous products of self-heating

Most of the research carried out indicates that CO_2 is the main gas product expelled from self-heating coal wastes. It is accompanied by CO and lighter organic compounds, partly from gaseous compounds trapped in organic matter pores and partly due to organic-matter pyrolysis in the oxygen-depleted conditions of dump interiors. The decomposition of clay minerals may contribute fluorine compounds and additional amounts of H_2O (Sokol, 2005; Sokol et al., 2002). Some sulphur compounds may also derive from the decomposition of coal disseminated sulphides as does CO_2 from the decarbonisation of carbonate rocks.

Liu et al. (1998) estimate that 1 t of coal-mine waste can generate 0.84 kg of SO_2, 0.61 kg of H_2S, 0.03 kg of NO_x, 99.7 kg of CO, and 0.45 kg of smoke (no assessment about CO_2 was given by the authors). The exact composition of the gas depends on the temperature range, the fixed carbon concentration, and oxygen availability (Davidi et al., 1995; Kim, 2007; Querol et al., 2008; Younger, 2004). It is extremely difficult to quantify whole-dump emissions of CO_2 and CH_4, the main greenhouse gases from self-heating due to such measurement problems as representative sampling, variability of gas emission with time, the diffuse nature of the emissions, the large scale of measurement sites, and the influence of varying weather conditions. For example, methane desorption from coal increases with temperature by ca 0.001% per 1 °C (Kim, 2007). Emission fluxes of CO_2 and CH_4 from spoil piles and waste dumps at 11 coal mines in Australia show great variability with CO_2 emission from 1 m^2 ranging from ca. 12 kg CO_2/year to 8200 kg/year (Carras et al., 2009).

Volatile organic compounds (VOCs) emitted during coal or coal-waste self combustion comprise aliphatic and aromatic hydrocarbons and halocarbons. Aliphatic hydrocarbons, in some cases found in concentrations lower than aromatic hydrocarbons (except CH_4), include light saturated and unsaturated compounds (C_1–C_4), with methane present in the highest concentrations and ethane as the second compound according to concentrations. Small amounts of higher *n*-alkanes ($>C_5$) up to *n*-dodecane were found in emissions from burning coal wastes by Ribeiro et al. (2010). Among aromatic compounds, benzene, toluene, ethylbenzene, xylenes, ethyltoluene, and trimethylbenzene comprise more than half of the VOCs emitted. However, the amounts and concentrations of particular compounds tend to vary strongly depend on site, temperature, and coalification. Halogenated hydrocarbons such as bromomethane, iodomethane, and trichloromethane occur in the lowest concentrations of all VOCs (Davidi et al., 1995; Pone et al., 2007). Heterocyclic oxygen compounds such as furane derivatives, sulphur (thiophene derivatives), and nitrogen heterocyclics (e.g., pyridine and pyrazine) have also been identified (Ribeiro et al., 2010).

In Poland, apart from routinely monitoring of CO_2, CO and CH_4 expelled from coal waste dumps, it is very little known about the types and quantities of gaseous compounds generated in self-heating. In the world, most examples published concerns rather gas products of coal-fires (e.g. Hower et al., 2009; O'Keefe et al., 2011). Thus the aim of the work presented here is:

- for the first time to establish the composition of the gaseous products of self-heating coal-waste dumps from the Upper and Lower Silesia Coal Basins (Poland);
- to define the mineral and chemical composition of efflorescences blooming in and around fissures on self-heating coal-waste dumps;
- to propose formation pathway(s) for new compounds found in dump gases and efflorescences.

2. Geological setting

The Upper Silesian Coal Basin (USCB) is located in southern Poland. It covers an area of 7400 km^2, of which 5800 km^2 lies within Poland. Numerous coal seams of various thicknesses (0.4–24 m) occur in the Carboniferous profile of the basin (Jureczka and Kotas,