



Petrographic and geochemical investigation of coal slurries and of the products resulting from their combustion



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ABSTRACT

Coal slurry is a fine-grained (<1 mm) by-product of coal washing. In the past, coal slurries were deposited in settling ponds as a waste. Currently, with the introduction of fluidized bed boilers in the Polish energy sector, coal slurries are used as a fuel.

Compared to coal, coal slurries (analyzed in the paper) are characterized by a high content of macerals of the inertinite group, with inertodetrinite dominant. Among macerals of the vitrinite and liptinite groups, a high content of detrital macerals also merit attention. The mineral composition of coal slurries is close to that of coal, although coals are characterized by a slightly higher mineral variability.

Unburned organic matter in the ash resulting from burning a mixture of coal and coal slurry is dominated by detritus (<10 μm). The high content of detritus in the ash may partially result from a very high content of detrital macerals in coal slurries. A small share of solid forms and inerdoids in the ash reflect the generally reactive nature of the inertinite present in coal slurries.

X-ray diffraction and scanning electron microscopy of ash samples reveal quartz, anhydrite, mica, hematite, feldspar, calcite and portlandite in the ash. Metakaolinite, hydrophilite, dolomite, iron oxides, calcium oxide and aluminosilicates occur in smaller quantities.

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1. Introduction

An essential part of the preparation of coal for sale and its further use in the energy sector is mechanical cleaning. The process makes use of the differences in the specific gravities of clean coal, rocks and minerals. The aim of coal processing is to improve and standardize the quality of the coal, mainly in terms of the reduction of ash- and sulfur contents (pyrite separation).

The raw coal is initially subjected to a preliminary classification aimed at separating the coal into two grain-size classes: coarse fractions (>20 mm) and fine fractions (0–20 mm). Coarse fractions are subjected to processing with heavy liquids (dense-medium baths, dense-medium cyclones). Meanwhile, fine fractions are subjected to washing, usually hydrocyclone washing (Laskowski, 2001; Wills and Napier-Munn, 2006). As a result of the dehydration of the washed coal, considerable amounts of water containing material with a grain size of <1 mm are obtained. The water is introduced into Dorr thickeners, where the separation and concentration of the suspension, coal slurry (by-product), takes place (Fig. 1). In the past, it was the main method for disposal

of coal slurries in Poland. Currently, coal slurries are treated as a full-value product, and used as a fuel in power generation (Blaschke and Blaschke, 2005). After further dehydration or agglomeration, coal slurries are used as a component of coal blends for power generation or used directly as coal-water slurries (CWS). Coal slurries are, to a limited extent, subjected to flotation processes to separate coal with a grain size of <1 mm (Barraza et al., 2013). Increased demand in Poland is the reason behind the massive use of coal slurries, previously deposited in thickeners, as a fuel. The major use of coal slurries in power generation in Poland was enabled by the development of fluidized bed boilers.

During the process of combustion, coal macerals are subjected to pyrolysis, resulting in the loss of volatile components and the formation of char (Alonso et al., 2001; Wu et al., 2006). In a final stage of the pyrolysis, the char is burned and subjected to fragmentation. The effectiveness of the combustion of the char is determined by the parameters of the boiler, the rank of the coal and of the maceral from which it originated. Char in the ash is the result of incompletely-burnt microlithotypes, primarily vitrinite and inertinite-rich microlithotypes (Alonso et al., 2001; Jelonek, 2003). With the former, the resulting forms of coke breeze are characterized by high (>50%) porosity. With the latter, the combustion processes are dependent on the reactivity of the inertinite (Crelling et al., 1988; Nandi et al., 1977; Suárez-Ruiz and Crelling, 2008; Tsai and Scaroni, 1987; Valentim et al., 2013). Under optimal conditions, reactive macerals from the inertinite group should be completely burned. Non-reactive macerals from the inertinite group

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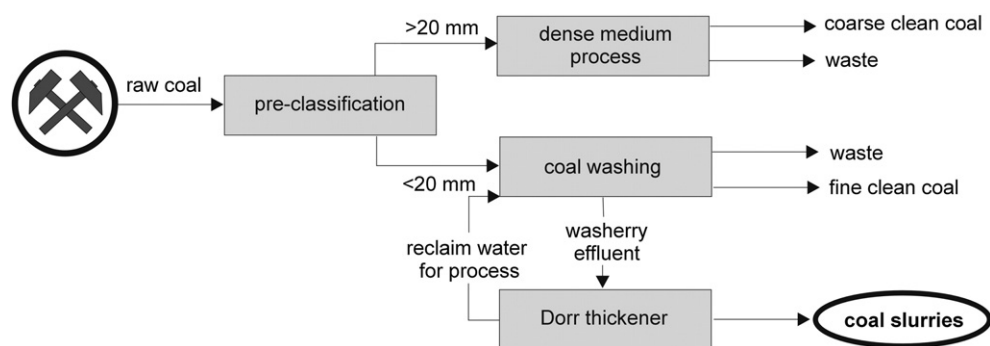


Fig. 1. Flow diagram of coal preparation (own work based on unpublished studies).

are resistant to the pyrolysis processes and convert to ash in form of solids and inertoids. Morphological studies of unburned particles of organic matter mainly focus on wall thickness, pore size and distribution and on particle diameter (Alvarez et al., 1997; Bailey et al., 1990; Cloke et al., 2003; Jones et al., 1985; Shibaoka, 1985; Taylor et al., 1998; Tsai and Scaroni, 1987). These morphological features have been used to create a classification of forms of unburnt organic matter (Lester et al., 2010; Misz, 2002; Tsai and Scaroni, 1987). Numerous publications provide valuable information on the formation and morphological characteristics of unburnt organic matter present in ashes from fluidized-bed boilers (e.g., Bowling and Waters, 1970; Sadhukhan et al., 2009; Valentim et al., 2006; Vleeskens et al., 1988).

Mineral matter in coal is primarily crystalline matter in the form of crystals, grains and aggregates, with lesser contents of amorphous- or fluid matter (Suárez-Ruiz and Crelling, 2008; Vassilev and Vassileva, 1996). The most common minerals include quartz, clay minerals (especially kaolinite and illite), carbonates, feldspars, mica and pyrite (Palmer and Lyons, 1996). Oxides, hydroxy-oxides, sulfates and phosphates occur in smaller quantities (Vassilev and Vassileva, 1996). In addition, numerous accessory- and trace minerals occur (Dai et al., 2012).

During coal combustion, high temperatures cause chemical- and structural transformations of mineral matter (Falcone and Schobert, 1986; Rodrigues et al., 2012). The most significant changes are a reflection of combustion temperature, which depends on the type of boiler. The highest temperatures, <1700 °C, are reached during the combustion of coal in pulverized boilers. In contrast, the combustion of coal in fluidized-bed boilers takes place at much lower (<800–900 °C) temperatures. The mineral transformations involve the loss of CO₂ from carbonates, S from sulfides and of OH or H₂O from clay minerals and sulfates. High temperatures may also result in the formation of new mineral phases and amorphous mineral matter (Rodrigues et al., 2012; Vassilev and Vassileva, 2005). One of the most characteristic changes is the formation of amorphous metakaolin due to the loss of OH from kaolinite at ca 450 °C, followed by conversion to mullite at a temperature of >950 °C. Above 1200 °C, all clay minerals fuse to form glass (Mitchell and Gluskoter, 1976; Ward, 2002). Lime (CaO), and periclase (MgO) are formed as a result of calcite and dolomite

decomposition. During ash quenching, lime interacts with water to form portlandite (Ca(OH)₂). Calcium can also decompose to form aluminosilicate minerals such as gehlenite (CaAl₂Si₂O₇) and anorthite (CaAl₂Si₂O₈), or merge with sulfur oxides to form anhydrite. Hematite, maghemite, magnetite and other spinels result from the decomposition of pyrite and siderite (Taylor et al., 1998; Ward, 2002).

In the literature, there are few petrographic studies of coal slurry or of ash resulting from its combustion. In Poland, though coal slurries have been described, petrographic- and mineralogical studies are lacking. For this reason, the authors of this article began their research.

2. Samples and analytical procedures

2.1. Samples

Samples of coal slurry and of coal were collected from coal mines in the Upper Silesian Coal Basin and at two power plants of the Tauron Group (Tauron Wytwarzanie S.A.). Samples of coal slurries were collected directly from the pipelines supplying the slurries to the boilers. Coal samples were collected manually from conveyor belts or automatically from boiler feeders. Some samples of coal slurries were collected from slurry thickeners, where coal slurries had been deposited in the past. Samples of bottom ash were collected from the push-plate conveyors under the boilers and fly ash samples were derived from the first rows of the electrostatic precipitators.

The samples of coal slurry (6 samples), coal (2 samples) and ash (8 samples) were then used to prepare pellets using epoxy resin (ISO 7404-2:2005). Once hardened, the pellets were ground and polished.

2.2. Analytical procedures

Petrographic analyses of the feed coal and of the ash samples were carried out in reflected white light using a Zeiss Axio Imager.M2m microscope combined with an automated Swift stage point counter. Maceral analysis and vitrinite reflectance were completed on the coal samples in accordance with ISO (ISO 7404-3:2009; ISO 7404-5:2009).

Table 1

Result of the determination of maceral composition (mmf, vol, %) of coal (C1–C2), coal slurries (S1–S6) and vitrinite reflectance (%).

Sample no.	V	Cd	Ct	Cg	T	G	Vd	L	Al	Cu	Ex	Sp	Re	Ld	I	F	Fu	Ma	Mi	Sf	Id	R _o mean
S1	45.3	7.2	13.9	0.6	0.4	2.8	20.4	3.0	0.0	0.2	0.0	1.7	0.0	1.1	51.7	0.0	0.8	0.0	3.6	7.9	39.4	0.42
S2	39.4	8.3	6.7	0.0	0.2	0.0	24.2	5.0	0.0	0.0	0.0	2.7	0.0	2.3	55.6	0.2	0.6	0.0	2.9	4.2	42.7	0.44
S3	37.0	7.3	4.4	0.4	0.2	2.3	22.4	5.4	0.0	0.2	0.2	2.1	0.0	2.9	57.6	0.0	0.4	0.0	0.0	8.1	49.1	0.55
S4	42.5	10.6	2.6	0.0	0.2	1.6	27.5	5.5	0.0	0.0	0.2	2.4	0.0	2.6	52.1	0.8	1.0	0.0	0.0	10.1	40.2	0.36
S5	41.8	12.1	2.7	0.5	0.5	0.9	25.1	3.6	0.0	0.0	0.4	1.4	0.0	1.8	54.6	2.1	0.6	0.0	3.8	7.0	41.1	0.43
S6	57.5	18.4	5.6	0.8	0.0	0.0	32.7	4.1	0.0	0.6	0.0	1.3	0.2	2.1	38.4	0.2	0.4	0.0	1.4	7.7	28.7	0.39
C1	61.5	21.3	23.7	0.4	1.9	3.7	10.5	11.0	0.4	0.7	0.0	8.4	0.2	1.3	27.5	0.0	1.4	0.0	4.5	11.2	10.4	0.56
C2	58.5	27.6	14.1	0.6	1.3	3.6	11.3	15.4	0.0	0.8	0.0	7.6	0.0	7.0	26.1	0.0	1.3	0.2	4.8	9.7	10.1	0.46

V – vitrinite, Cd – collodetrinite, Ct – collotelinitite, Cg – corpopgelinitite, T – telinitite, G – gelinitite, Vd – vitrodetrinitite, L – liptinitite, Al – alginite, Cu – cutinitite, Ex – exudatinitite, Sp – sporinitite, Re – resinite, Ld – liptodetrinitite, I – inertinitite, F – fusinitite, Fu – funginitite, Ma – macrinitite, Mi – micrinitite, Sf – semifusinitite, Id – inertodetrinitite.

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