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Effects of binder choice in converter and blast furnace sludge briquette preparation: Environmental and practical implications

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ABSTRACT

Blast furnace and converter sludges are fine-grained waste materials characterized as dangerous waste with a negative impact on the environment. One way of recycling of such materials is briquetting followed by reuse of the material in the blast furnace. In the briquetting process, an important step is the choice of the binder suitable for manufacturing the briquettes with suitable mechanical properties. In this work, the effect of the binder choice (laundry starch UNIPRET, Portland cement) on the reduction of iron oxides in the assessed waste materials during thermal treatment (900, 1000, 1100 °C) is evaluated. Simultaneously, the effect of the binder choice on the amount and composition of the resulting waste gas was evaluated as well as its possible impact on the environment. The performed experiments proved the mutual relationship between the level of iron oxides to metal iron conversion, the binder content and retention temperature. Type of binder also affected the volume of the resulting waste gas. Factor analysis for mixed data (FAMD) proved that the resulting concentrations of the assessed hydrocarbons were correlated (apart from ethyne) and that they are closely associated with the binder applied. Conversely, the concentrations of ethyne, carbon monoxide and carbon dioxide were not associated with the binder but with the retention temperature. FAMD did not show any direct effect of final retention temperature on the amount of the rest of the resulting hydrocarbons. In comparison with the starch-containing briquettes, the cement-containing briquettes were also proved to lead to lower resulting concentrations of PAHs in the waste gas.

1. Introduction

Blast furnaces and oxygen converters are the most common technologies in the process of iron and steel production. Despite the recent efforts to minimize the production of waste, integrated production of steel and pig iron is a substantial source of liquid, solid and gas pollutants. Apart from the large quantities of slags (Yasipourtehrani et al., 2017) – nowadays commonly utilized in civil engineering – solid, very fine waste material is also caught during the multi-step flue gas cleaning in the production of agglomerates, iron and steel. Considerable portion of these waste-products cannot be utilized to their full potential and end up deposited in landfills where they affect the environment negatively.

Complete recovery of the fine-grained metallurgical wastes (in the metallurgical aggregate) is complicated by the presence of Zn (9.0–14.0 wt.%) in the form of zincite (ZnO) and zinc ferrite ($ZnFe_2O_4$) due to the origin of both the compounds in the processed scrap (Havlik et al., 2005; Langová and Matýsek, 2010). Other elements preventing the direct recycling of the fine-grained waste in metallurgy are Pb, Cd, Cu, S, Cl, F, Na and K (Trung et al., 2011; Vereš et al., 2012). Apart from the content of the unwanted accompanying substances negatively influencing the final product (pig iron or steel), the second negative factor is the actual fine-grained character of the material preventing it to serve as a feed material for blast furnaces. Blast furnace sludges (Fe content up to 50 wt.%) contain approximately 60% particles smaller than 45 μm. Steel work sludges (Fe content up to 60 wt.%) are finer and contain 70–90% particles smaller than 20 μm (Řepka et al., 2006).

Recycling of the fine-grained metallurgical wastes is, therefore, associated with solving of two crucial problems: (a) removal of the

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unwanted admixtures e.g. by hydrometallurgical (Cantarino et al., 2012; Drobíková and Gabor, 2013; Trung et al., 2011; Vereš et al., 2012) or pyrometallurgical processes (Huaiwei and Xin, 2011; Takano et al., 2005) and (b) with the manufacturing of a product suitable for the blast furnace batch or the steel work aggregate by briquetting or pelletizing.

Briquetting or pelletizing by the means of stabilization/solidification also needs to meet several requirements (Spence and Shi, 2005; Valls and Vàzquez, 2000). The imperative addition of a binder for the briquette or pellet formation should not introduce to the production process any constituents negatively influencing the quality of the final product – either pig iron or steel – as well as it should not increase the production of gas pollutants, predominantly organic compounds such as polychlorinated biphenyls-PCBs (Buekens et al., 2001) and dioxins-PCDD/PCDF (Buekens et al., 2000) or polycyclic aromatic hydrocarbons-PAHs (Han et al., 2012; Zhao et al., 2015). After the solidification, the product has to stay firm so the manufactured briquettes would satisfy the mechanical properties requirements. Finally, the binder should be affordable. The binders can be either solid or liquid materials, either inorganic (lime, cement, clays, waterglass) or organic (petroleum bitumen, tar, bitumen, plastics, resin, starch or molasses) (Batchelor, 2006; El-Hussiny and Shalabi, 2011). Molasses and other common binders are not suitable for the briquetting of the fine-grained metallurgical wastes due to the content of phosphorus and sulphur. Contrarily, resins are suitable – e.g. acrylic resins (Singh and Tathavadker, 2011), formaldehyde resins (Benk and Coban, 2011), phenolic resins (Singh and Tathavadker, 2011), plastic waste (Lee and Song, 2007; Murakami and Kasai, 2011), biomass or biochar (Abd Rashid et al., 2014; Guo et al., 2015). The choice of the binder should be guided also by its effect on the chemical reactions in the aggregate, mainly on the iron oxide reduction (Drobíková and Gabor, 2013; Drobíková et al., 2016). Moreover, during the thermal treatment, the formation of unwanted gaseous by-products with possible negative impact on the environment should be limited (Wang et al., 2018).

2. Experimental

2.1. Materials and methods

The waste materials used in this work are blast furnace sludge (BFS) and converter sludge (CS) generated during multistep waste gas cleaning originating in the metallurgical complex located in Ostrava. The solid particulates of blast furnace sludge and converter sludge were briquetted both with organic and inorganic binder. The binder used for the briquette produced was be chosen with regard to its composition and affordability. Thus, laundry starch with the brand name UNIPRET (SU) made by the company Natura a. s. was applied. As an inorganic binder, commonly available Portland cement (PC) was used. Particular forms of iron (total and metallic Fe) were determined according to the standard ČSN 72 2041 parts 9 and 10 (Czech Office for Standards, 1992a, b).

2.1.1. X-ray fluorescence spectroscopy

Chemical compositions of solid samples were determined using an energy dispersive fluorescence spectrometer (XRFS) SPECTRO XLAB (SPECTRO Analytical Instruments GmbH). For this measurement, samples in powder form were pressed into tablets using wax as a binder.

2.1.2. X-ray powder diffraction

X-ray powder diffraction (XRPD) patterns were recorded under Co Kα irradiation (λ = 1.789 Å) using the Bruker D8 Advance diffractometer (Bruker AXS) equipped with a fast position sensitive detector VÅNTEC 1. Samples in powder form were pressed in a rotational holder. Reflection mode was used for all measurements. Phase composition was evaluated using database PDF 2 Release 2004 (International Centre for Diffraction Data).

2.1.3. Thermal analysis

Thermal analysis was carried out using simultaneous TG-DSC apparatus Netzsch STA 409 EP. All experiments were conducted under identical conditions: the samples (101 mg in weight) were heated up to 1200 °C in crucibles (aluminium oxide) in a dynamic atmosphere of dry argon (with a flow rate of 100 $cm^3\ min^{-1}$) at a heating rate of 10 °C min^{-1}.

2.1.4. Kinetic parameters determination

From the thermogravimetric data, rate constants (k), activation energy (E), order of reaction (n) and frequency factor (A) are determined using the basic kinetic Eq. (1):

$$d\alpha/dt = k(T)\cdot g(\alpha), \tag{1}$$

where α is the extent of conversion, t is time and T absolute temperature. The degree to which the rate constant is dependent on the absolute temperature is described by the Arrhenius Eq. (2):

$$k(T) = A\exp\cdot(-E/RT), \tag{2}$$

where A is frequency factor, E is activation energy and R is gas constant. Function of weight $g(a)$ is dependent on the particular reaction mechanism. Several expressions of this function exist, however, in applied science, the expression analogous to the kinetics of homogeneous reactions is used the most (3):

$$g(\alpha) = (1-\alpha)^n \tag{3}$$

By substitution of (2) and (3) to (1) we get a kinetic equation expressed as:

$$d\alpha/dt = A\exp\cdot(-E/RT)(1-\alpha)^n \tag{4}$$

For the linear increase of the temperature with the heating rate $\beta = dT/dt$, it is possible to substitute the extent of conversion dependent on time with it being dependent on the growing temperature. Then, the relationship can be expressed as:

$$d\alpha/dT = 1/\beta A\exp\cdot(-E/RT)(1-\alpha)^n, \tag{5}$$

provided that the parameters E, A and n are not dependent neither on the temperature nor the mass of the reacting heated compound. The Eq. (4) is valid in every point of the simple TG curve, hence, the curve can be, theoretically, calculated from the same equation. For the determination and evaluation of the kinetic parameters of the ongoing thermal processes in the samples of both the blast furnace and the converter sludge, direct nonlinear regression was used.

2.2. Samples treatment

2.2.1. Briquetting process

Mixtures of waste material with binders were prepared: the original BFS (16.3 wt.% of water) with grain size < 1 mm was mixed with the addition of either 15% of organic binder (FU15 briquette) (Drobíková et al., 2016) and 10% of inorganic binder (FC10 briquette). The CS (11.1 wt.% of water) with grain size < 1 mm was mixed with the addition of 15% of organic binder (CU15 briquette) and 15% of inorganic binder (CC15 briquette).

Homogenization of the waste material/binder mixture was performed by mixing using a three dimensional shaker Turbula T2F for 20 min (35 revolutions per minute). Subsequently, necessary amount of water (max 50 mL) was added and the mixture was mixed again thoroughly. The prepared mixture was then subjected