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Recycling of blast furnace sludge by briquetting with starch binder: Waste gas from thermal treatment utilizable as a fuel

Klára Drobíková [a,b,*], Daniela Plachá [b], Oldřich Motyka [a,b], Roman Gabor [c], Kateřina Mamulová Kutláková [b], Silvie Vallová [d], Jana Seidlerová [b]

[a] IT4Innovations Centre of Excellence, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, 708 33 Ostrava-Poruba, Czech Republic
[b] VŠB-Technical University of Ostrava, Nanotechnology Centre, 17. listopadu 15/2172, 708 33 Ostrava-Poruba, Czech Republic
[c] VÚHŽ a.s, Dobrá 240, Czech Republic
[d] VŠB-Technical University of Ostrava, Faculty of Metallurgy and Material Engineering, 17. listopadu 15/2172, 708 33 Ostrava-Poruba, Czech Republic

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ABSTRACT

Steel plants generate significant amounts of wastes such as sludge, slag, and dust. Blast furnace sludge is a fine-grained waste characterized as hazardous and affecting the environment negatively. Briquetting is one of the possible ways of recycling of this waste while the formed briquettes serve as a feed material to the blast furnace. Several binders, both organic and inorganic, had been assessed, however, only the solid product had been analysed. The aim of this study was to assess the possibilities of briquetting using commonly available laundry starch as a binder while evaluating the possible utilization of the waste gas originating from the thermal treatment of the briquettes. Briquettes (100 g) were formed with the admixture of starch (UNIPRET) and their mechanical properties were analysed. Consequently, they were subjected to thermal treatment of 900, 1000 and 1100 °C with retention period of 40 min during which was the waste gas collected and its content analysed using gas chromatography. Dependency of the concentration of the compounds forming the waste gas on the temperature used was determined using Principal component analysis (PCA) and correlation matrix. Starch was found to be a very good binder and reduction agent, it was confirmed that metallic iron was formed during the thermal treatment. Approximately 20 l of waste gas was obtained from the treatment of one briquette; main compounds were methane and hydrogen rendering the waste gas utilizable as a fuel while the greatest yield was during the lowest temperatures. Preparation of blast furnace sludge briquettes using starch as a binder and their thermal treatment represents a suitable method for recycling of this type of metallurgical waste. Moreover, the composition of the resulting gas is favourable for its use as a fuel.

1. Introduction

During the production of steel, a considerably large amount of industrial waste is generated. Various solid wastes emerging from steel plants are in the form of sludge and slag, mainly blast furnace slag, blast furnace flue dust and slag, mill scale, mill sludge, etc. These types of waste vary in their physical and chemical composition, their potential for environmental contamination and the way they are processed. The blast furnace sludge generated during multistep cleaning of waste gas contains up to 50% of iron. Currently, landfilling was the only – and prevalent – treatment of this sludge other than recycling, however, when recycled, the mentioned iron oxides have a potential of adding significant economic benefits. The self-reducing mixture of such waste materials and binders represents a possible method of utilization of iron oxides as explained by El-Hussiny and Shalabi (2011). A number of techniques have been developed in order to allow better utilization of iron oxides from iron and steel plants waste. These techniques involve hydrometallurgical, physical and thermal methods as illustrated by Das et al. (2007).

Recycling of the blast furnace sludge is, however, complicated by both the content of hazardous elements and the fine-grained character of the material. Briquetting is one of the possible methods applied in recycling and utilization of fine-grained materials and produces a suitable feed material for the metallurgical furnace. The briquetting process has certain benefits; mainly it saves energy and decreases the environmental pollution. The briquettes produced are relocated several times before they reach the furnace,

* Corresponding author at: VŠB-Technical University of Ostrava, Nanotechnology Centre, 17. listopadu 15, 708 33 Ostrava-Poruba, Czech Republic.
E-mail address: klara.drobikova@vsb.cz (K. Drobíková).

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so certain durability is a prerequisite. In order to produce high-quality briquettes, it is necessary to use a binder connecting the particles of the fine material together. The choice of binder is crucial; it is favourable to combine the binding properties of the material with its reducing properties and affordability. Simultaneously, the binder should not contain any undesirable compounds and elements. There are various types of binder, both inorganic (cement, bentonite, clay, etc.) and organic (starch, pitch, plastics, etc.). Briquettes should be of uniform size, shape, weight and composition (Drobíková and Gabor, 2013).

With regard to reducing properties, solid carbon appears to be the most suitable binder (Kashiwaya et al., 2011), however, there is a tendency to find another source of carbon for the reduction with better binding properties and affordability. Waste materials from iron and steel plants, such as mill scale and blast furnace flue dust (containing iron, iron oxides and others components), were briquetted with hydrocarbonaceous binder by Allen (1975). The briquettes were prepared with 2-15 wt.% binder and treated with an oxygen-containing gas to selectively react with the hydrogen in the binder. Briquettes prepared in this way can be fed back into the iron- or steel-making process as a source of iron or carbon (El-Hussiny and Shalabi, 2011).

Recently, waste plastics have been used as a suitable binder. Waste plastics have the potential to play a significant role in the reduction of iron oxides by supplying reduction gases (H_2 and CO). However, they are difficult to use as reducing agents because the thermal degradation temperatures of plastics are lower than the reduction temperatures of iron oxides. Dankwah et al. (2011) investigated the reduction of electric arc furnace slag by blends of metallurgical coke with high-density polyethylene (HDPE) plastics. The results indicated that the rate of iron oxide reduction in slag was – in comparison with pure coke – significantly higher when coke/plastics blends were used. The reduction mechanism of iron oxides and polyethylene (PE) in the composite at lower temperature was studied by Murakami and Kasai (2011). In order to recycle electric arc furnace (EAF) dust by heat treatment, polyvinyl chloride (PVC) was used as an additive (Lee and Song, 2007).

Use of biomass waste from the agro-industry is a good alternative to coal consumption. Wood waste such as pine sawdust or cedar chips were used for iron ore reduction for example Guo et al. (2015). Several mixtures with varying ratios of pine sawdust (10–30 wt.%) and iron ore were subjected to thermal analysis. The iron ore was reduced to a predominantly metallic iron phase when up to 30 wt.% of pine saw dust was introduced into the mixture. Reduction commenced at approximately 670 °C and was almost completed at 1200 °C (Ueki et al., 2013). Empty fruit bunch char (EFB char) briquette was used for the preparation of composite with iron ore by Yunus et al. (2013). EFB char is known as a renewable and carbon neutral source containing fewer unwanted elements such as alumina, silica and toxic metals (compared to coal ash) but more iron, potassium and phosphorous. Biomass waste from the palm oil industry is an attractive alternative fuel to replace coal as the source of energy in the treatment and processing of low grade iron ores (Abd Rashid et al., 2013, 2014). For the preparation of composite pellets, palm kernel shell (PKS) waste and iron ore were used by Abd Rashid et al. (2014). Pellets with varying ratios of iron ore and PKS were formed with the addition of water. The proportion of PKS used in the mixture was 10, 20, 30 and 40 wt.%. The reduction of composite pellets by PKS as a reducing agent showed that iron oxide in iron ore could be fully reduced to magnetite (and partially to wüstite) when up to 30 wt.% of PKS was present in the mixture. The application of biomass char as a substitute for coke in the rotary hearth furnace (RHF) process for producing direct-reduced iron was studied by Fu et al. (2012). In this study, reduction iron was described using rice crust char, bamboo char and coconut crust char. During the experimental method, the amount of required coal, production cost, and carbon emissions were reduced. This study showed that coconut crust carbon and bamboo carbon have good metallurgical properties. The utilization of biomass fly ash and lime was investigated as cement replacement in blast furnace briquetting by Mäkelä et al. (2011). The authors concluded that the content of harmful elements in fly ash from the biomass did not seem to restrict usage in briquetting. However, the utilization of fly ash as cement replacement resulted in a significant decline in compression strength.

Besides biomass waste, various types of resin (e.g. acrylic resins, formaldehyde resins, phenolic resins) are also used for briquette preparation. Acrylic resins are thermoplastic resins produced by polymerization of various monomers such as acrylic acid, methylacrylic acid and esters of these acids. Thermoplastic resin was used for the preparation of carbon materials for iron ore/carbon composite by Kawanari et al. (2011). Phenolic resin was used as a binder for the preparation of briquettes for the agglomeration process (Singh and Tathavadker, 2011). Aysa Benk used phenol based novalec, resol and a blend of both resins as a binder in briquette production from coke breeze. These briquettes can substitute metallurgical coke in the blast furnace (Benk and Coban, 2011).

There are many studies dealing with thermal treatment and self-reduction of briquettes and consequent analysis of the resulting solid matter; nevertheless, the possible utilization of the resulting waste gas has not been assessed so far. The object of this study is the assessment of blast furnace sludge utilization by forming self-reducing briquettes composed with organic binder (starch) which can be again utilized as a feed to the furnace. It also deals with possible utilization and composition of waste gas which is produced during the thermal treatment of the briquettes.

2. Experimental

2.1. Materials and methods

The waste material used in this work is blast furnace sludge obtained from the metallurgical complex of Ostrava. This waste is generated during multistep cleaning of waste gas. The solid particulates of blast furnace sludge were briquetted with organic binder. The binder used for the briquette produced should be chosen with regard to its composition and affordability. Thus, laundry starch with the brand name UNIPRET made by the company Natura a. s. was applied.

2.1.1. X-ray fluorescence spectroscopy

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

2.1.2. Electron microscopy

The morphology and shapes of waste particles were observed on a raster electron microscope (REM) QUANTA 450 FEG in the VÚHŽ a. s. laboratories. Distributions of blast furnace sludge particles were studied by LASER SCATTERING PARTICLE SIZE DISTRIBUTION ANALYZER LA-950 (HORIBA).

2.1.3. X-ray powder diffraction

X-ray powder diffraction (XRPD) patterns were recorded under Co Kα irradiation ($\lambda = 1.789$ 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