



BRIQUETTING OF EAF DUST FOR ITS UTILISATION IN METALLURGICAL PROCESSES

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Dust generated at an electric arc furnace during steel production industry is still not a solved problem. Electric arc furnace dust (EAF) is a hazardous solid waste. Sintering of well-prepared briquetted mixtures in a shaft furnace is one of possible methods of EAFD utilisation. Simultaneously some metal oxides from exhaust gases can be separated. In this way, various metals are obtained, particularly zinc is recovered. As a result, zinc-free briquettes are received with high iron content which can be used in the steelmaking process. The purpose of the research was selecting the appropriate chemical composition of briquettes of the required strength and coke content necessary for the reduction of zinc oxide in a shaft furnace. Based on the results of the research the composition of the briquettes was selected. The best binder hydrated lime and sugar molasses and the range of proper moisture of mixture to receive briquettes of high mechanical strength were also chosen and tested. Additionally, in order to determine the thermal stability for the selected mixtures for briquetting thermal analysis was performed. A technological line of briquetting was developed to apply in a steelworks.

Keywords: electric arc furnace dust; recycling; briquetting; zinc oxide

1. INTRODUCTION

Electric arc furnace dust (EAFD) is one of by-products of steelmaking industry (Dukelow et al., 1995). This kind of waste has been classified as hazardous due to containing some heavy metals such as zinc, cadmium, copper or lead (Jursová, 2010). Dust from electric arc furnaces includes approximately 30-40% of zinc and 20% of iron. Steel mills receive steel scrap largely coated with zinc. About 50% of the world production of zinc is used for galvanising steel components, which prolongs their life by three- to fivefold. An increasing amount of zinc is being consumed when galvanising sheets for car production. It is estimated that zinc content of the dust steelmaking will constantly grow. Due to the high content of zinc in the steelmaking dusts new methods of dust removal are needed. When galvanised scrap is used in the electric arc furnaces, most of the zinc from the steel scrap ends up in the dust and fume. About 98% of the zinc is volatilised and carried out the furnace with other gaseous or particulate compounds generated during steelmaking reactions. Slag and steel contain approximately 0.1 - 2% of zink residues (Joulazadeh and Joulazadeh, 2010; Menad et al., 2010). 15-25 kg of EAF dust is generated during the production of 1 ton of steel in an electric arc furnace (Guezennec et al., 2005). More than 60 thousand

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tons of EAFD are generated each year in Poland. Machado et al. (2006) reported that the world generation of EAFD is estimated to be c.a. 3.7 million tons per year.

The recovered zinc could provide a valuable feed material in the metallurgy of non-ferrous metals. The two basic methods of recovery of zinc include: hydrometallurgical and pyrometallurgical method (Havlik et al., 2006; Jha et al., 2001; Leclerc et al., 2002; Leclerc et al., 2003; Shawabkeh et al., 2010; Youcai et al., 2000). Hydrometallurgical methods are based on leaching solutions of zinc waste using sulphuric acid or hydrochloric acid. The resulting solution from the zinc recovery can be processed using a variety of methods such as: electrolysis, precipitation of insoluble zinc compounds, crystallisation or extraction with ion exchangers. Pyrometallurgical methods rely on high-temperature processing of metalliferous raw materials. The commonly used method of zinc dust processing from melting steel scrap is the process run in the Waelz furnace. This method is constantly modified by reducing the amount of coke or natural gas consumption. The input to the Waelz furnace is a zinciferous material, coke and fluxes. Due to the inclination and rotation of the furnace, the feed material moves along the furnace in the opposite direction of the air flow and natural gas. One of the main components of steel dust is iron oxide (III) Fe₂O₃. It is estimated that approximately 20-50 % of the total amount of zinc is in the form of $ZnO \cdot Fe_2O_3$, while the rest is present as ZnO (II). The biggest problem during EAFD recycling is the possibility of separating pure ZnO from the relatively stable zinc ferrite ZnO·Fe₂O₃. Currently, in order to obtain zinc oxide, steelmaking dust is processed by pyrometallurgy methods. High energy consumption, low yield of zinc and a large amount of pollution generated, make researches still search for alternative methods of processing this waste.

An alternative for the Waelz method is to carry out zinc reduction process in a shaft furnace. However, the method requires briquetting of waste (Hryniewicz and Janewicz, 2008; Magdziarz et al., 2011). The addition of scale increases the content of iron in the prepared agglomerates. This allows to use briquettes, after reduction in a shaft furnace, as a valuable input to a converter or an electric arc furnace (Szumiec et al. 2007). This is possible because iron goes to the steel bath and not to the slag (Ballajee et al., 1995; Harrison et al., 1995; Mihok and Baricova, 2003; Rees, 1999).

The aim of the project, carried out at the AGH University of Science and Technology in Cracow, is to investigate the composition of briquettes and improve their mechanical strength. The analysed briquettes contained EAF dust, oiled mill scale and coke breeze as a high-carbon component. Different types of binders were tested. Prepared briquettes were sintered in a shaft furnace while oxides of some metals were simultaneously separated from exhaust gases. In this way, a standard value feedstock component for steel melting process is obtained and precious metals, particularly zinc, are recovered. The level of reduction must be very high, because zinc is very undesirable in metallurgical processes due to its destructive effect on refractory lining. The obtained briquettes can be used in electric arc furnace processes as an iron-bearing material, preceded by reduction of zinc. The aim of the work was to select the appropriate composition of briquettes of compressive strength and to develop an optimal briquetting technology. The article presents also the results of thermal and chemical analysis of different briquette compositions.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

The study was conducted using a steelmaking EAFD from Rolled Products Division of Steelmaking Industry in Poland. The chemical composition of dust was Zn (35%), Fe (18%), Cl (9%), Pb (3%), Ca (2.5%), Si (2%), Mn (1.5%) and C (1%). Coke breeze of grain size under 2.0 mm was used as a high carbon component. For the tests a mixture was prepared which contained 67% of EAFD, 27% of scale and 6% of coke ensuring adequate reduction of oxides.

The tests were preceded by a selection of binding materials. Coke-oven tar, waste sulphite liquor, cement and a binary binder in the form of sugar molasses and calcium hydroxide can be used as binding materials. Initially, coke-oven tar and cement were discarded for environmental protection reasons or due to a long period of seasoning consolidated material, required for bindings to occur. Moreover, cement is a ballast in metallurgical processes. As a result the mixtures shown in Table 1 for preliminary tests of thermogravimetric analysis were prepared.

Sample	Composition	Volatile matter [%]	Moisture [%]
B1	67% steelmaking dust, 27% mill scale, 6% coke	3.68	1.5
B2	B1 + 3% Ca(OH) ₂ + 6% molasses	4.60	5.9
B3	B1 + 7% Ca(OH) ₂ + 6% molasses	6.90	6.1
B4	B1 + 10% waste sulphite liquor	8.48	4.9
B5	B1 + 2% Ca(OH) ₂ + 4% molasses	7.12	5.1
B6	B1 + 1% Ca(OH) ₂ + 4% molasses	5.60	3.8

Table 1. The chemical composition, volatile matter and moisture of studied samples

A thermogravimetric analysis was conducted using a Mettler Toledo TGA/SDTA 851 apparatus. The TGA instrument was calibrated using indium, zinc and aluminium. Its accuracy was equal to 10–6 g. For the thermal analysis, samples were placed in alumina crucibles. Approximately 15 mg of a sample were heated from ambient temperature to 1000 °C at a constant rate of 10°C/min and a 40 ml/min air flow rate. Each sample had to be measured under exactly the same conditions, including temperature range, atmosphere, and heating rate, to determine the most repeatable and precise results. TG curves for each sample were obtained as the outputs for thermal conversion. The ordinate on the TG curves was the percentage ratio of the instantaneous weight of the sample to its initial weight. TG curves were used to assess the thermal characteristics of the studied samples.

The process of briquetting the prepared mixtures was examined by means of experimental equipment, located in the laboratory of the Department of Manufacturing Systems AGH UST. It includes mixers which are used to prepare material for consolidation and roll presses equipped with rolls of various diameters. The mixers have heated jackets enabling to combine the processes of averaging and drying. A press with the diameter of rolls of 450 mm, marked with the symbol LPW 450 was used in tests. The tests were preceded by the choice of the press compaction unit. Considering the material properties and the briquette shape, the LPW 450 press was equipped with a gravitational feeder and a non-symmetrical compaction system was installed. It enables producing briquettes in the form of a saddle and volume capacity of approx. 6.5 cm³.

The experimental equipment was equipped with workstations designed for determining the physical properties of the feed and the mechanical strength of the consolidated material. According to the decision which had been made before, the measure of quality of the briquettes was their resistance to dropping and compressive strength. The resistance of the briquettes to dropping consisted in simultaneously dropping 10 randomly selected briquettes three times from the height of 2 m onto a steel plate. Then, they were sifted through a sieve with the mesh size equal to 2/3 of the average calculated on the basis of 2 largest dimensions of the briquette. The resistance of the briquettes to dropping is represented by the percent share of the sifting in the total weight of the briquette sample. On the other hand, the measure of the compressive strength was the mean value of the force destroying 10 briquette determined in course of a monoaxial compression test, performed between parallel flat surfaces.

Following the approved assumptions, briquettes containing precious metals, including zinc, can constitute a feedstock which should be sintered in a shaft furnace while precious metals can be

simultaneously recovered. Therefore, they should feature adequate mechanical strength. Based on preliminary experiments it was found that the compressive strength of briquettes obtained in laboratory conditions cannot be lower than 200 N, and their minimum resistance to dropping is 85% (Hryniewicz and Janewicz, 2008). Additionally, briquettes must feature low relative moisture not exceeding 8% and high-temperature resistance up to 1000 °C. Furthermore, it should be required that the briquettes do not have ballast and can be supplied to the shaft furnace immediately after being produced.

3. RESULTS AND DISCUSSION

The characteristics of the TGA analysis are presented in Figs. 1 and 2. The profile of TG curve is similar for all studied briquettes. By comparing the TG curves for all tested materials, the different mass loss was obtained. The B1 briquette characterised the lowest mass loss (17%) at 1000 °C. The biggest mass loss was observed for the samples B3, B4 and B5: 23%, 21% and 20%, respectively. This was due to the high content of volatile matter and moisture in these samples. The mass loss was c.a. 5% for B2, B3, B4 and B5 samples in the range of temperature from ambient to 150°C. It was caused by evaporation of water. For the samples B1 and B6 the mass loss was c.a. 2%, as a result of low moisture content in them. The next stage of mass loss (about 10%) was observed in the temperature range of 400-500°C. This resulted from the oxidation of combustible components present in briquettes. Further loss in mass may be caused by the combustion of coke (above 650 °C).

It can be seen that the addition of different types of binder affects slightly the growth of mass loss. All tested mixtures assessed in TG analysis can be used in further laboratory briquetting studies.

Preliminary briquetting tests showed that briquettes produced with sulphite lye (mixture B4) did not have satisfactory mechanical strength. Definitely, the best binding material was a binary binder in the form of molasses and hydrated lime. It enables to make briquettes of high mechanical strength out of EAFD. Both components mentioned above do not constitute ballast. Therefore, that the binary binder was used in further tests.

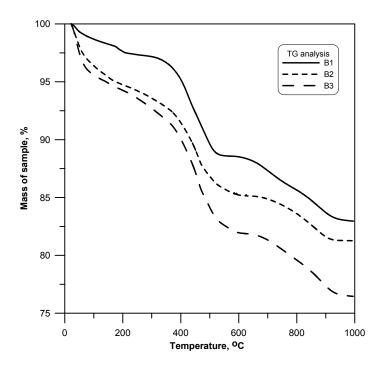


Fig. 1. TG curves for briquettes B1, B2, B3

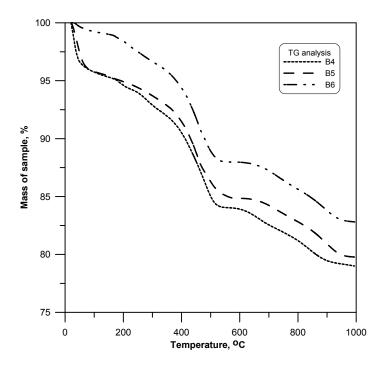


Fig. 2. TG curves for briquettes B4, B5, B6

Following the preliminary thermogravimetric analysis of B2, B3, B5, B6, a plan to achieve the following objectives was developed:

- to select a composition of a binder containing 2 components,
- to determine a range of required moisture content,
- to determine a range of required moisture content,

to check the possibility of producing such briquettes that will be suitable for supplying into a shaft furnace immediately after their production.

Following further research tests, it was found that a preferable composition of the binary binder was 3% by weight of hydrated lime and 5% by weight of sugar molasses. Subsequent research tests were conducted with a binder composed as specified above, but with a varying moisture content. Results are presented in Figs. 3 and 4. While analysing the diagrams showing the dependence of the resistance of the briquettes to dropping (Fig. 3) and their compressive strength (Fig. 4) on the moisture content it was found that the relative moisture of the material prepared for briquetting should be within the range of 3.0–6.3%. If it does not exceed 5.5%, briquettes feature such mechanical strength that allows to supply them into a shaft furnace immediately after their production. For a higher moisture level, reaching 5.5-6.3%, briquettes need to be seasoned for a period of approx. 24 hours. They should not be dried because this would lower their mechanical strength. The best results were achieved for a mixture with a relative moisture of 4.1%. Briquettes had the compressive strength was higher and simultaneously their resistance to dropping decreased when scale which had not been sifted was used in the mixture.

It is expected that industrial briquettes will be larger than those obtained in a laboratory and their volume capacity will be approx. 13 cm³. It was found that the compressive strength of briquettes will increase three times and the resistance to dropping will not change if production changes from the laboratory scale to the industrial one. Therefore, achieving positive results of strength tests will mean that the compressive strength of industrial briquettes will not be lower than 700 N and the resistance to dropping will exceed 85%.

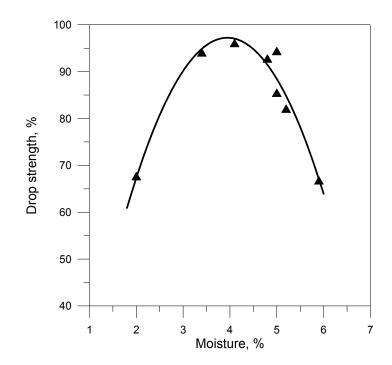


Fig. 3. Drop strength of briquettes (a binder in the form of 3 % Ca(OH)₂ and 5 % sugar molasses) versus moisture content

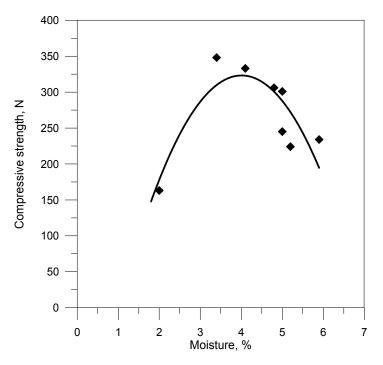


Fig. 4. Compressive strength of briquettes (a binder in the form of 3 % Ca(OH)₂ and 5 % sugar molasses) versus moisture content

4. APPLICATION OF RESEARCH FINDINGS

In this study the concept of consolidating metallurgical waste used for a shaft furnace in a roll press was developed. The concept is schematically presented in Fig. 5. It was assumed that properly adjusted mixtures of dry components were averaged and 3% by weight of dusty calcium hydroxide and water in such amount as to ensure the relative moisture of the mixture within the range of 2.0-4.0% were added.

Then, a 70° Bx molasses was added as a binder in the amount of 5% by weight and the entire compound was thoroughly mixed. The mixture was briquetted in a roll press equipped with a non-symmetrical compaction system which enables to produce briquettes without a parting plane. Then, briquettes were classified and their mechanical strength was periodically evaluated. The subgrain was returned to briquetting. If briquettes had adequate mechanical strength, they could be fed directly into the shaft furnace or deliver to a storage site. Otherwise, they were seasoned under roofing.

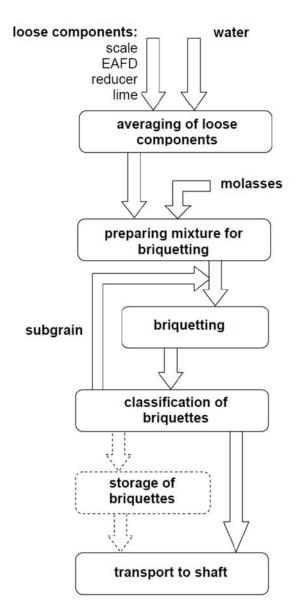


Fig. 5. A concept of briquetting mixtures containing a share of waste iron-bearing dusts containing zinc

Considering problems with unloading the standard 80° Bx molasses and distributing it in the mixture, in the presented solution it is recommended to hydrate it up to 30%. While designing an industrial briquetting line for briquetting mixtures including EAFD containing zinc, special attention should be paid to the need of thoroughly averaging the material provided for briquetting. In case of other mixture compositions than those examined, it will be necessary to experimentally confirm the possibility and conditions of briquetting. The conducted tests proved that properly composed mixtures of metallurgical oxide wastes (EAFD and mill scale) and high-carbon components can be used to produce durable briquettes which meet the requirements of sintering in a shaft furnace while simultaneously recovering precious metals. Adding hydrated lime in the amount of 3 % by weight and sugar molasses in the amount of 5 % by weight to the mixture is an essential requirement. The relative moisture of the

material prepared for briquetting should be within 3.0% - 6.3%, which requires adding water to the mixture. If the relative moisture in the mixture does not exceed 5.5%, the mixture can be used to produce briquettes with such mechanical strength that allows to supply them into a shaft furnace immediately after their production. In case of higher relative moisture content within the range of 5.5-6.3 %, briquettes need to be seasoned for a period of approx. 24 hours. Drying the briquettes immediately after their production will result in degradation of their resistance properties. When considering the quality of briquettes, it is possible to use both fine coke and coal dust as a high-carbon additive. The thermal analysis showed that the kind of binder did not affect the thermal decomposition of briquettes. Implementing the test results into industrial practice should help in solving the problem of utilising metallurgical wastes as well as recovering precious metals.

5. CONCLUSIONS

This article presented a new method of EAF dust utilisation which consists of sintering of wellprepared briquetted mixtures in a shaft furnace and simultaneously separating metal oxides from the exhaust. This method allows to recover DEAF metals, particularly zinc. As a result, zinc-free briquettes are produced with high iron content. These briquettes can be used in steelmaking processes. Based on the results of the research the following conditions were selected: the composition of briquettes, the appropriate amounts of binder (hydrated lime and sugar molasses) and the range of the proper moisture content of the mixture to produce briquettes of high mechanical strength. Additionally, in order to determine the thermal stability for the selected mixtures for briquetting thermal analysis was performed. The presented technological line of briquetting was developed for application in steelworks.

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