Substitution of magnetite in dense medium separation by Zinc-Lead waste

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Abstract. Dense Medium (or Heavy Medium) Separation (DMS) is one of the most efficient and commonly used method of separation in different mining branches. Dense Medium for coal processing is based on the suspension of fine and dense material, usually magnetite or ferrosilicon, in water. Magnetite for that purpose is the most commonly used mineral in Polish mines, but has to be entirely imported from abroad. Ferrosilicon, recovered from Zinc-Lead waste could be an alternate to magnetite for use in DMS coal processing. In this study an attempt of recovering that material from “Miasteczko Śląskie” Zinc Plant wastes was made. By simple separation and comminution processes, large amount of magnetic fraction, which could be successfully used in dense medium as the substitution for the magnetite was obtained. Almost 70% of collected waste from lead refining process is proper for the use in the DMS process. Obtained fraction is relatively brittle and easy to grind, which should generate minor costs of production. Almost entire fraction is also highly reactive for magnetic field, which will be helpful in the recovery from dense medium solution, using existing magnetic separators in coal processing plants. Chemical analysis show that concentration of a few metals is significant, which may cause environmental obstacles. But that can also be solved, using simple method of recovery of metal ions from process water.

1. Introduction
Reuse and recovery of waste is the most desired way of waste management, following the prevention of waste formation. At the same time, storage and disposal are the less desired and most harmful for the environment [1]. That principle is essential not only in the industry but in general consideration of waste management. Searching for the ways of reusing wastes, instead of disposal, can improve the waste management in the companies and help saving natural resources.

There are a lot of known, common and also unconventional technologies of recovering different metals from industrial solid [2,3] and liquid wastes [4,5]. Metallurgical waste can also be reused as an aggregate or concrete component, which can even upgrade the concrete properties [6]. Some research was also performed in the field of recovering magnetite dust from carbon combustion by-products [7].
Outstanding way of utilize certain sort of zinc industry waste is recovering the ferromagnetic fraction, which can then be used as the substitute for magnetite in Dense (or Heavy) Medium Separation (DMS/ HMS). Average use of magnetite in single processing plant at the Polish coal mine is approx 700-800 grams per Mg of processed coal. What’s more magnetite used in DMS in Polish coal industry, has to be entirely imported from abroad.

In this study an attempt was made to verify if properties of Zinc-Lead slags disposed in Miasteczko Śląskie site in Poland could be of use as an alternative material to magnetite in DMS process.

2. Production of Zinc-Lead in Miasteczko Śląskie Plant

Production of Zinc-Lead in the “Miasteczko Śląskie” Plant is based on the Imperial Smelting Process (Blast Furnace Process). The Blast Furnace Process technology consists of Sinter Plant, Furnace Plant and Refining Plant. Process in the Furnace Plant is charged with solid sinter from Sinter Plant, and coke. The products are vapour zinc and slag with lead, collected at the bottom of the furnace. Next step of production takes place in the Refining Plant where selected metals like Copper, Silver, Tin, Arsenic, Antimony, Bismuth are recovered. Refining process generates slag, which is deposited in Hazardous Waste Landfill [8].

According to Polish regulations [9] the code of generated waste is 10 05 01. Black to gray slag are block-shaped and contain ceramic and metallic inclusions. Plant generates about 700 Mg of refining slags per year [8].

Hazardous waste landfill occupies the area of approx. 50 000 square meters. It contains about 40 000 Mg of refining slag (estimated value). Significant content of Fe in the landfill at “Miasteczko Śląskie” Zinc Plant was mentioned in the estimation of heavy metals quantity research. Content of Fe in samples oscillated between 7% and 19%, depending on the layer [8]. Other research show the content of Iron (FeO) at the level of 33.95% [10].

3. Sampling and research methods

Samples of refining slag waste were taken in April 2018 from the Hazardous Waste Landfill of “Miasteczko Śląskie” Zinc Plant. Approximately 70 kilograms of sinters and blocks were collected. Slags were collected from recently disposed part of wastes which have not yet been completely buried with the aggregate. Collection of the waste samples is presented in figure 1.

![Collection of waste samples from “Miasteczko Śląskie” Zinc Plant Hazardous Waste Landfill.](image)

Preliminary preparation was done by mechanical crushing of the samples, with additional use of 25 mm sieve, to separate the friable fraction from sinters. Then, a friable fraction was averaged by quartering method (4 times) to obtain the representative sample from the whole amount of collected waste. At the end of the quartering process, 2 samples of 2700 grams each were obtained. One of the
mentioned samples was then ground, using vibration mill. Duration of grinding was 15 minutes, and single cell contained about 200-240 grams of feed. Milling was used for the magnetic separation and chemical composition tests. Consequently, the material was dried at 100 Celsius degrees.

Magnetic separation of ground friable fraction was done, using Magnetic Disc Separator, type LOG1-4, manufactured by Boxmag – Rapid Limited, Birmingham. Separator was equipped with vibration feeder from The Sinex Engineering Co. Ltd. Chemical composition tests were performed at the JY 2000 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Both of these tests were done at the Faculty of Mining and Geology of Silesian University of Technology. Additionally, the bulk density of samples was measured using the pycnometer method.

4. Results and discussion

4.1. Separation tests
On the basis of preliminary separation process of the waste, we could divide two characteristic fractions. First fraction is the friable and easy-crushing black material, with numerous bright, shiny grains. Second, named “sinters”, consists mostly of hard, crushing-resistant sinters and malleable, metallic plates. Both fractions are presented in the figure 2 and figure 3. Preliminary separation results are presented in the table 1.

| Fraction | Mass [g] | Percentage [%] |
|----------|----------|----------------|
| Feed     | 67 857   | 100.00         |
| Friable  | 46 160   | 68.03          |
| Sinters  | 21 697   | 31.97          |

Figure 2. Friable fraction (left) and sinters (right) obtained from pre-separation.
Friable fraction was then quartered, milled and dried, as described before. Sample was directed to the magnetic separator. Results of separation are presented in the table 2.

**Table 2. Magnetic separation results.**

| Fraction          | Mass [g] | Percentage [%] |
|-------------------|----------|----------------|
| Ferromagnetic     | 256.9    | 91.30          |
| Semi-ferromagnetic| 24.1     | 8.56           |
| Non-magnetic      | 0.4      | 0.14           |
| Total             | 281.4    | 100.00         |

According to [8], amount of refining slag, deposited in “Miasteczko Śląskie” waste landfill in 2008 was approx. 32 500 Mg. Estimated amount of iron in the landfill was 22 400 Mg, which gives 69% of Iron in refining slag. Obtained amount of magnetic fraction shown in table 3 is similar to the amount of Iron presented in the mentioned article [8].

**Table 3. Overall separation results.**

| Fraction         | Percentage [%] |
|------------------|----------------|
| Sinter           | 31.97          |
| Magnetic         |                |
| Ferromagnetic    | 62.11          |
| Semi-ferromagnetic| 5.82          |
| Non-magnetic     | 0.10           |
| Total            | 100.00         |
Table 4 shows, that concentration of iron in friable fraction is approx. 35-40%. That value refers to the amount of Iron, presented in other mentioned research [10]. Despite that, almost entire friable fraction is separated in magnetic field and can be easily recovered. Only negligible amount of sample was non-magnetic (less than 0.2%). That suggests, the considered material can consists of ferrosilicon (FeSi). It lowers the concentration of Iron, but the whole compound is still highly reactive for magnetic field. Gray colour of the magnetic fraction also indicates that compound. Ferrosilicon is the sort of ferroalloy, used as the supplement for metallurgical processes.

Sinters may also contain iron, but due to their high crushing resistance, that fraction is not considered as the potential material for recovery, because of high costs of crushing and grinding.

Amount of Alumina, Titanium, Chrome and Manganese was at the comparable level with magnetite composition. Content of Iron is slightly lower in the magnetic fraction of the waste. Concentration of other investigated elements, which are Nickel, Copper, Zinc and Lead, is significantly higher, comparing to the magnetite. Higher concentration of these metals are obvious in Zinc-Lead ores, from which the investigated waste comes from.

| Selected elements | Friable fraction (feed) | Ferromagnetic | Swedish magnetite |
|-------------------|-------------------------|---------------|------------------|
| Al                | 1.51                    | 1.50          | 1.44             |
| Ti                | 0.05                    | 0.14          | 0.10             |
| Cr                | 0.07                    | 0.08          | 0.01             |
| Mn                | 0.14                    | 0.18          | 0.11             |
| Fe                | 35.2                    | 39.6          | 59.1             |
| Ni                | 0.23                    | 0.18          | 0.01             |
| Cu                | 4.18                    | 3.65          | 0.02             |
| Zn                | 2.11                    | 2.14          | 0.01             |
| Pb                | 5.97                    | 4.5           | 0.02             |
| As                | 0.02                    | 0.02          | 5.41 ppm         |
| Sb                | 0.03                    | 0.02          | 1.23 ppm         |

High concentration of Nickel, Copper, Zinc and Lead is undesirable, because it might cause the environmental contamination. It refers to the process water, where these metals circulate after removing it from the processing coal. Proper coal processing in the dense medium should eliminate the residual dense medium on the coal. The concentration of metal ions will appear in the process water, where metals from the solid fraction may be leached. Installation of simple device for recovering metal ions from water, should solve this problem. Iron reactor, described in [4,5] is cheap and non-mechanical, which makes it failure-free and simple in maintaining. It also has a high effectiveness for removal of mentioned metals [4,5]. These qualities will not increase the costs of coal production, and can even increase the quality of process water in the processing plant circuits.
Concentration of Copper in the magnetic reactive fraction is approx. 4%. Average concentration of Copper in the feed of Polish Copper Processing Plants is usually below 2%, when concentration in flotation slag is approx. 0.15-0.30% [11]. Recovery of Copper should also be considered.

4.2. Density, grain size and other properties
The density of obtained magnetic fraction is 5.16 g/cm³. Density of magnetite, commonly used in the Dense Medium Separation is approx. 4.9-5.2 g/cm³. Experience in coal processing in DMS shows, that density of magnetite or other material in heavy media should be at least twice of the required medium density. Since majority of dense media in coal processing is 1.5 g/cm³ and 1.8 g/cm³ [12,13], density of obtained magnetic fraction is proper for preparation of dense medium for coal enrichment. Grain size of investigated fraction has not been tested. Despite that, grain size depends on the time of exposition in the mill. That parameter is easy to adjust, if necessary.

Simple visual test of dense medium sedimentation was done. Solution of 100 g of material per 1000 ml of water was prepared and left for sedimentation. Sedimentation stages after preparing of sample, and after 5, 15 and 60 minutes are shown in the figure 4. That simple test has shown, that grain size of investigated sample is uneven. There are grains, which sediment fast and small enough to suspend in the solution even after 60 minutes. For better evaluation of material for use in dense medium, precise grinding and grain size tests should be done.

Figure 4. Sedimentation of ferrosilicon dense medium after preparation (left) and after 5 minutes, 15 minutes and 60 minutes of sedimentation.

Block-shaped ferrosilicon is susceptible to self-decay. That process can be accelerated by high concentration of Alumina (higher than 1%) [14]. Self-decay has also been observed in collected waste. That property is desirable, because the comminution process is essential for recovering investigated material for DMS.

5. Conclusions
Ferrosilicon, recovered from Zinc-Lead waste, seem to be a good substitution for magnetite for the Dense Medium Separation purposes. Physical properties are suitable for adaptation of the waste and ferrosilicon recovery. What’s more, waste is susceptible for comminution. Density of material is also proper for use in the dense media. The whole material is highly reactive for magnetic field, so effective recovery from the process water is also possible, using the existing infrastructure at the coal processing plants. The chemical composition seem to be the biggest problem, because of the water contamination possibility. This problem can be solved, by using additional, simple and efficient Iron Reactor for recovering the metal ions from water.
Recovering of the ferrosilicon for dense media can be conducted directly at the Zinc-Lead Plant. Pre-separation process of the waste could separate the friable fraction, which could be used as the intermediate for the dense media purposes. Sinters could be deposited in the landfill, as it takes place now. That solution would reduce the amount of waste directed to the landfill. Separated material could be sold as the intermediate or even ready-to-use material, after proper adaptations (grinding to proper grain size). That material contains significant amounts of Copper, Zinc and Lead, so it could also be directed to the secondary enrichment processing for recovering these metals, if that process would be economically justified.

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6. References
[1] Act of waste (Polish law) 2012 (Ustawa z dn. 14.12.2012 r. o odpadach (Dz.U.2013 poz. 21))
[2] Ostrowska-Popiełska P and Sorek A 2012 Prace Inst. Met. Żel. 4 pp 39-46
[3] Miller V R and Paulson D L 1982 Resourc. And Conserv. 9 pp 95-104
[4] Suponik T and Gajda D 2014 Geochem. i Geol. Środ. Ter. Uprzemiśl.- Monografia ed. M Pozzi (Gliwice: PA Nova) pp 53-67
[5] Suponik T and Gajda D 2014 Proc. Of the Min. Eng. Conf. MEC2014 ed. M Lutyński and T Suponik (Gliwice: GITG) pp 204-211
[6] Zieliński K and Rzeszowski M 2007 Hutnik – Wiad. Hutn. 74 (11) pp 610-5
[7] Hycnar J, Kochański B and Tora B. 2012 J. of Pol. Min. Eng. Soc. 13 (2) pp 1-10
[8] Pozzi M and Nowińska K 2010 Gór. i Geol.. 5 (4) pp 221-9
[9] Ordinance of waste catalogue (Polish law) 2014 (Rozp. Min. Środ. z dn. 9.12.2014 r. w sprawie katalogu odpadów (Dz.U.2014 poz. 1923))
[10] Adamczyk Z and Nowińska K 2013 Civ. and Environ. Eng. Rep. 11 pp 14-21
[11] Stadnicki K and Duchnowska M 2016 Łupek Miedzionośny II ed. P B Kowalczyk and J Dzrymała pp 216-21
[12] Blaschke W 2009 Przeróbka węgla kamiennego – wzbogacanie grawityczne (Kraków: Wyd. IGSMiE-PAN) pp 117-8
[13] Laskowski T, Błaszczyński S and Ślusarek M 1979 Wzbogacanie kopalni w cieczach ciężkich (Katowice: Wyd. Śląsk) p 85
[14] Bułkowski L, Pogorzalek J, Wyrobek A and Goraźdża J 1995 Solid. of Metals and Alloys 24 (1) pp 11-8