Magnetic Separation of Magnetite Iron Novelties from Black Coal Fluid Bed-Ash

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Abstract

This contribution presents possible separation method of valuable component – iron – from bed-ash resulting from combustion of black coal in fluid boilers of EVO Vojany thermal power plant. Valuable component is composed of particles of magnetite mineral novelties. All the particles act as mineral compounds paramagnetic up to ferromagnetic. Used mineral processing methods are based on knowledge of physical (influence of magnetic field), chemical and mineralogical (mineral novelties of Fe component) knowledge. Leachability of fluid ashes is high – pH 9 to 11. It is therefore necessary to use only dry preparation (classification) and mineral processing methods. Separation of Fe component from black coal fluid bed-ash is realized in process of dry low intensity magnetic separation, resulting in production of magnetite iron rich magnetic product – concentrate and non-magnetic product – tailings with low Fe content, containing mainly alum-silicate novelties of Fe, Ca, Al, Mg and other. Both products – concentrate and tailings – are further processed. Magnetic product is cleaned using dry low intensity magnetic separation and if further increase of Fe grade in final concentrate is needed, then also using second stage cleaning wet low intensity magnetic separation process. Non-magnetic product from roughing stage can be further processed by scavenging magnetic separation. Non-magnetic product from scavenging operation can be used as final product used in building industries. Magnetic product from cleaning operation is a final product with properties allowing its usage in industries, iron, or steel production. Morphology of produced Fe concentrates were studied using electron microscope and particles were analyzed using EDX analysis aimed on determination of highest Fe contents in individual products. Product of dry low intensity magnetic separation contained particles with 70 to 86% Fe. Product of wet low intensity magnetic separation the spectrum of EDX analyses ranges from 87 to 91% Fe. Electron microscope studies confirmed that in the process of wet low intensity magnetic separation, dust particles are washed away from surface of magnetic particles, resulting in higher Fe grades in final magnetic product after wet processing.

Keywords: magnetic separation, fluid fly ash, magnetite

Introduction

Knowledge of physical, chemical and mineralogical properties of mineral novelties in fluid bottom black coal ash is a basic information for selection of separation techniques. For experiments we used fluid ash from EVO Vojany thermal power plant, K5 boiler. All ash particles act as mineral matters paramagnetic up to ferromagnetic [4, 9].

Analysis

During combustion of coal in fluid boilers at temperatures 800–850°C processes in inorganic component of coal – ash forming matter – lead to formation of mineral novelties [6, 7]. In atmosphere, which can be oxidizing or reducing, mineral novelties of FeO, Fe_2O_3, Fe_3O_4 close to magnetite and even particles with higher Fe content are formed.

From bottom-ash [3, 6, 9, 10] following products can be separated:

- magnetic product – concentrate of magnetite mineral novelty prepared by dry low intensity magnetic separation (DLIMS) with 55–60% Fe content,
- magnetic product – concentrate of magnetite mineral novelty from cleaning DLIMS with 55–60% Fe content
- non-magnetic product – tailings – cleaned of magnetite Fe component with composition fulfilling the requirements for usage in building industry (EN-STN 206-1), having 0,8–2% LOI (loss on ignition) and 2–3% Fe bonded in alum-silicates [1, 2, 4, 6].

Comment:

Preparation of Fe concentrates from ash formed in fusion and granulation boilers of thermal power plants was already described in awarded patents

Tab. 1. Identified phase composition in sample of magnetic product from fluid bed ash

Tab. 1. Skład fazowy próbek produktu magnetycznego popiołu dennego fluidalnego

CHEMICAL FORMULA	MINERALOGICAL NAME	SPACE GROUP	CONTENT [% wt.]
Fe_2O_3	Hematite	(167) *R*-3c	41.1
Fe_3O_4	Magnetite	(227) *F*d-3m	19.8
SiO_2	Quartz	(152) $P3_121$	4.2
Fe_2MgO_4	Magnesioferrite	(227) *F*d-3m	32.9
$Na(AlSi_3O_8)$	Albite	(002) *P*-1	2.0

Tab. 2. Calculated elemental composition of the samples from the present phases

Tab. 2. Wyliczony skład chemiczny próbek

SAMPLE ANALYSIS	Fe [%]	O [%]	Mg [%]	Si [%]	Al [%]	Na [%]
1 – X-ray	61.5	31.6	4.0	2.6	0.2	0.2

Tab. 3. Yields of individual size fractions in fluid bed ash from K5 boiler

Tab. 3. Skład ziarnowy popiołu dennego z kotła K5

Size fraction [mm]	Yield
	[%]
16 – 4	6,31
4 – 2,8	5,45
2 – 2,8	7,34
0 – 2	**80,90**
0 – 16	100,00

[7, 8, 11]. Combustion of coal in fluid boilers is different and ashes with different properties are formed: bed ash and light fly ash [10]. In order to separate Fe component from fluid bed ashes, different approach must be used.

Properties of tested fluid ashes

Heat value of combusted black semi-anthracitic coal is 25–26 $MJ.kg^{-1}$, it contains more than 1% sulphur and 20% ash forming matters.

Turbulent movement of coal particles in fluid layer intensifies combustion, accelerates burning and improves chemical reactions allowing for temperatures 800–850°C, about half of those used in fusion boilers (1400–1600°C) and granulation boilers (1100–1300°C).

In inorganic component of coal – ash forming matter – new compounds are formed – mineral novelties of FeO, Fe_2O_3, Fe_3O_4 type, close to Magnetite Fe_3O_4 [4, 5], but particles with 80–90% Fe content are also present (see Tab. 2, 3, 4, 5). Lower combustion temperatures significantly lowers NO_x emissions. Thermic nitrogen oxides are formed when coal is combusted at high temperatures [1].

Process of fluid combustion of coal leads to formation of main product – thermal energy and side products – solid wastes – bed ash (40 ± 2–5 % wt.) and light fly ash (60 ± 2–5 % wt.). Burnout of carbon from bed ash – in reducing atmosphere – leads to increase of Fe content to 11–13%. Fe content in light fly ash is significantly lower (1–3% and more). Coal is mixed with limestone – sorbent, that can bond over 90% of sulphur released from coal during combustion. Mineral novelties of gypsum, anhydrite and portlandite are formed [4, 5, 6].

Solid residuals rest after combustion for some time in boiler in form of powdery ash, they can't slag, so the maximum temperature must be lower than their melting temperature.

Mineral novelties in fluid ashes [5] are formed by anhydrite $CaSO_4$, hannebachite – $CaSO_4$.1/2

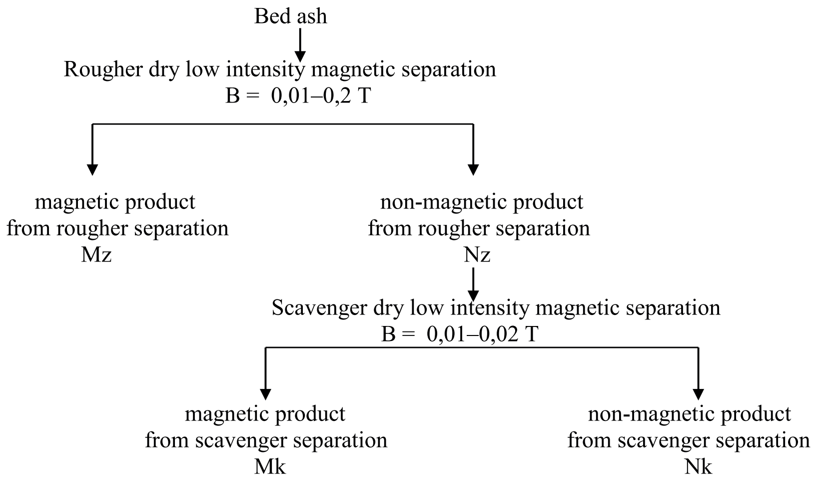

Fig. 1. DLIMS of fluid bed ash

Rys. 1. Popiół denny DLIMS

H_2O, portlandite – $Ca(OH)_2$, gypsum – $CaSO_4.2H_2O$, calcite – $CaCO_3$, quartz – SiO_2, hematite – Fe_2O_3, magnetite – Fe_3O_4, ettringite – $Ca_6Al_2(SO_4)_3(OH)_{12}.6H_2O$, thaumazite – $Ca_6Si_2(SO_4)_2(CO_3)_2(OH)_{12}.24H_2O$. "Blended" mineral novelties include wollastonite $CaSiO_3$, kirschsteinite $CaFeSiO_4$, andradite $Ca_3Fe_2(SiO_4)_3$, magnesioferrite Fe_2MgO_4 and particles with chemical composition similar to zeolites, such as phillipsite and klioptilotite.

Comment:

Fluid ashes does not contain mullite phase and mullite $2SiO_2.3Al_2O_3$, which is formed at temperatures 1050 up to 1200 or 1400°C. Ash forming matters in coal can pass through different thermal changes, partial up to full melting of individual inorganic components, formation of eutectic compounds. Organic component – unburned residuals – are thermally changed to macerals, coke and graphite.

Properties of bed ash and light fly ash differ, although they are formed in one combustion device, but at different conditions. Research of properties was conducted on sample of fluid ash from K5 boiler.

Fluid bed ash [10] from K5 boiler has surface area 2,555 $m^2.g^{-1}$, 0,5–0,8% LOI.

Light fly ash has surface area 30,685 $m^2.g^{-1}$, 12–30% LOI. Surface area of unburned coal residuals is significantly higher.

Pycnometric determination of densities of fluid bed ash and light fly ash from K5 boiler:

- fluid light fly ash: density 2,363–2,410 $g.cm^{-3}$
- fluid bed ash: density 2,825–2,836 $g.cm^{-3}$

Iron concentrates from fluid boilers are mainly composed of magnetite mineral novelty, some maghemite and hematite, infrequently also wűstite.

From environmental point of view it is necessary to conduct separation methods as dry processes, while Fe concentrates from low intensity magnetic separation (DLIMS) can be cleaned by wet process, in order to remove adhered dust particles.

Dry low intensity magnetic separation of bed ash

Use of individual separators is limited by their magnetic induction B (Tesla), necessary for separation of Fe component – concentrate with given Fe content. Using DLIMS it is possible to prepare concentrates with 46-50-55-60 and more % Fe from bed ash.

Yield and Fe content in concentrates can be altered with respect to their usage, i.e. as an additive – raw material for agglomeration process of iron and steel production.

Tab 1. and 2. shows analysis of magnetic product from roughing DLIMS, cleaned by DLIMS.

EDX microanalyses of particles in samples of magnetic product from DLIMS of fluid bed ash showed presence of particles with up to 86% Fe content, in light fly ash particles only 0,6–11% Fe content.

If there is a request for a given value of Fe content in concentrate, it is advised to remove coarser size classes with lower Fe content from material prior to separation in order to conserve energy (Tab. 3.). Cleaning operation using DLIMS can be used to improve concentrate properties.

Separation processes were repeated in 2005–2011. Although samples of bed ash from K5 boiler were different – coal from different localities was used – results of DLIMS and Fe content in concentrates was similar.

Tab. 4. Roughing and scavenging DLIMS of fluid bed ash from K5 boiler

Tab. 4. Wzbogacanie wstępne i główne popiołów DLIMS z kotła K5

(mm)		γ [%]	λ_c [%]	γ_c[%]	λ_{Fe}[%]	ε_{Fe} [%]
0–0,355	**Mz**	20,77	0,12	1,65	**47,92**	82,64
	Nz	79,23	1,87	98,35	2,64	17,36
	Mk	0,35	0,12	0,03	**47,92**	1,38
	Nk	78,88	1,88	98,32	2,44	15,98
	Feed	**100,00**	**1,51**	**100,00**	**12,04**	**100,00**
0,355–1	**Mz**	35,48	0	0	**55,78**	89,85
	Nz	64,52	1,33	100	3,46	10,15
	Mk	0,70	0	0	**55,78**	1,77
	Nk	63,82	1,34	100	2,89	8,37
	Feed	**100,00**	**0,86**	**100,00**	**22,02**	**100,00**
1–2	**Mz**	23,02	0	0	**56,34**	75,18
	Nz	76,98	1,51	100	5,56	24,82
	Mk	3,04	0	0	**56,34**	9,94
	Nk	73,94	1,57	100	3,47	14,88
	Feed	**100,00**	**1,16**	**100**	**17,25**	**100,00**
2–2,8	**Mz**	6,43	0	0	**54,86**	35,56
	Nz	93,57	0,80	100,00	6,84	64,44
	Mk	2,25	0	0	**48,08**	10,89
	Nk	91,32	0,82	100,00	5,82	53,55
	Feed	**100,00**	**0,75**	**100,00**	**9,93**	**100,00**

An example of particle size distribution of individual size fractions of fluid bed ash [10] is presented in Tab. 3.

0–2,8 mm, 0–2 mm and 0–1,6 mm size fraction was separated. Tested sample of bed ash contained 0–0,5% LOI, maximum 0,8% LOI.

Separation was done using flowsheet shown as Fig. 1. using MECHANOBR low intensity magnetic separator.

Bed ash fraction 0–2,8 mm is a feed to DLIMS process with 0,01–0,2 T magnetic induction. Process results in two products: magnetic and non-magnetic product.

Non-magnetic product was feeded to scavenging DLIMS with two output products: magnetic and non-magnetic product, which is a final product and for its pozzolanic properties can be used in building industries.

Magnetic product from scavenging DLIMS when mixed with magnetic product from roughing DLIMS can be further cleaned using DLIMS process.

Magnetic product from cleaning DLIMS process is a final concentrate wit 55–60% Fe content.

Non-magnetic product from cleaning DLIMS process can be grinded to minus 1 mm size in order to liberate the Fe component and then feeded to scavenging DLIMS process. Non-magnetic product is composed of Fe, Al, Ca, Mg and other alum-silicates mineral novelties. It contains 1,2–1,9% Fe in form of alum-silicates [5].

If quality analyses indicate necessity of wet cleaning magnetic separation, then it is also advised to use this process in the final flowsheet [9, 10].

Results of separation of samples presented in Tab 4. and Tab 5. show clear tendency of higher degree of overgrowing of Fe component with alum-silicates in coarser size classes. Highest Fe contents were achieved using 0,355–2 mm fractions, with cleanest product prepared using 0,355–1 mm fraction, having 22,02% Fe.

Tab 5. shows results of EDX analyses on areas of selected particles. EDX spectrum of chemical elements was scanned on Kα orbit. Samples MK01-07 was scanned on samples of magnetic product from DLIMS (without wet cleaning). Product of dry magnetic separation contains also particles with Fe content lower than limiting 55%.

NK1–NK4 are EDX analyses of non-magnetic product from DLIMS with 1–7% Fe.

Conclusion

Knowledge of physical, chemical and mineralogical properties of ashes from combustion of black semi-anthracitic coal in fluid boilers allows preparation of concentrates with 55–60% Fe using roughing and scavenging dry low intensity magnetic separation process of bed ash.

Properties of bed ash and light fly ash differ, although they are formed in one combustion device, but at different conditions. Presence of reducing atmosphere in parts of the chamber leads to secondary concentration of Fe component characterized by relatively high Fe content 11–13%. Light

Tab. 5. EDX analyses of products from DLIMS

Tab. 5. Analiza EDX produktów

Spectrum	MgK	AlK	SiK	KK	CaK	TiK	MnK	FeK
MK01	3,0	4,7	6,6	<0.2	5,0	<0.1	2,1	**78,3**
MK02	1,5	16,9	29,6	0,2	26,4	1,1	0,5	23,8
MK03	0,5	3,9	5,6	0,2	5,8	0,4	1,3	**82,3**
MK04	0,9	1,8	2,8	<0.2	5,6	<0.1	3,5	**85,2**
MK041	2,0	6,1	8,7	<0.1	9,2	<0.2	3,8	**70,0**
MK05	1,1	11,5	17,5	0,3	19,3	0,7	0,4	49,1
MK051	1,4	15,0	25,0	<0.2	20,0	0,7	0,5	37,3
MK06	1,4	2,5	8,6	0,3	1,6	<0.0	4,1	**81,5**
MK07	0,7	0,6	2,1	<0.0	66,4	0,0	0,6	29,5
MK071	4,5	1,0	3,6	<0.0	1,8	<0.0	2,6	**86,6**
NK1	0,8	19,9	54,9	4,8	11,2	1,2	<0.1	7,1
NK2	0,9	17,2	46,0	1,9	25,7	1,3	<0.2	6,7
NK3	1,1	17,8	36,7	1,1	35,7	1,3	<0.2	6,0
NK31	1,0	17,8	36,1	0,7	37,5	1,2	0,0	5,7
NK4	0,0	29,8	59,3	7,0	2,0	0,7	0,0	1,0

fly ash contains only 1–3% Fe bonded in alum-silicate mineral novelties.

Knowledge of chemical and mineralogical properties were further improved by presenting results of electron microscopy measurements aimed at identification of particles with high Fe content.

Using separation techniques – DLIMS – two industrially utilizable product were prepared from fluid bed ash:

– Concentrates with over 60% Fe content from 0–0,2–0,28 mm size fraction of fluid bed ash fulfilling the limiting requirements of Fe, Si, Al, Mg, O and Na content (Tab 4. and 5.), which can be used as a raw material for agglomeration component in iron and steel production.

– Tailings composed mainly of alum-silicates with low Fe content cleaned of magnetite Fe. This products have pozzolanic properties and content of unburned coal residuals (measured as LOI) comprises the EN-STN 206-1 standard for their usage in building industries.

Results of our experiments show, that separation processes can be used to prepare industrially utilizable products from fluid black coal bed ash.

Industrial patent no. 288160 was granted by Industrial Property Office of the Slovak Republic on the presented technique of separation of Fe component from fluid bed ash [9].

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Separacja magnetyczna magnetytu z popiołów fluidalnych z węgla kamiennego

Praca przedstawia dostępne metody separacji cennego składnika – żelaza – z popiołu fluidalnego powstałego ze spalania węgla kamiennego w kotłach fluidalnych w elektrowni cieplnej EVO Vojany. Cenny związek powstaje z cząsteczek nowych form mineralnych magnetytu. Wszystkie cząsteczki mają właściwości paramagnetyczne aż do ferromagnetycznych. Wykorzystane metody przetwarzania oparte są na właściwościach fizycznych (wpływ pola magnetycznego), chemicznych i mineralogicznych (nowe formy mineralne związku żelaza). Odczyn popiołu jest wysoki – pH od 9 do 11. Istotne jest zatem, aby używać suchych metod przygotowania (klasyfikacja) oraz separacji. Oddzielanie związku żelaza od popiołu fluidalnego ze spalania węgla kamiennego zachodzi w procesie separacji magnetycznej na sucho., dzięki której powstaje produkt magnetyczny bogata w magnetyt – koncentrat i substancja niemagnetyczna – odpad z niską zawartością Fe, zawierający głównie nowe formy glinokrzemianów Fe, Ca, Al, Mg i innych. Oba produkty – koncentrat i odpady – podlegają dalszemu przetwarzaniu. Koncentrat magnetyczna jest oczyszczana przy użyciu separacji magnetycznej separacji na sucho, oraz, jeśli zajdzie potrzeba wyższej zawartości żelaza w końcowym produkcie, przechodzi przez drugą fazę oczyszczania przy użyciu separacji magnetycznej na mokro. Produkt niemagnetyczny z fazy obróbki wstępnej może zostać poddany dalszej obróbce opartej na czyszczącej separacji magnetycznej. Taki niemagnetyczny produkt jest gotowy do wykorzystania w przemyśle budowlanym. Produkt magnetyczny po procesie oczyszczania jest gotowym produktem z właściwościami pozwalającymi na wykorzystanie w przemyśle produkcji żelaza lub stali. Morfologia powstałych koncentratów żelaza została zbadana przy użyciu mikroskopu elektronowego, a cząsteczki zostały przeanalizowane przy użyciu analizy rentgenowskiej z dyspersją energii (ang. skrót EDX), w celu określenia najwyższych wartości Fe w poszczególnych produktach. Produkt powstały na skutek separacji magnetycznej zawierał cząsteczki z zawartością żelaza od 70 do 86%. Produkt powstały wskutek separacji magnetycznej na sucho zawierał cząsteczki mające od 70 do 86% Fe. Analiza spektralna EDX produktu przy magnetycznej separacji na mokro wykazała od 87 do 91% Fe. Badania mikroskopem elektronowym potwierdziły, że w procesie separacji magnetycznej na mokro cząsteczki pyłu są zmywane z powierzchni cząsteczek magnetycznych, co w rezultacie daje wyższą wartość Fe w końcowym produkcie magnetycznym na mokro.

Słowa kluczowe: separacja magnetyczna, popioły fluidalne, magnetyt