

ASH AND SLAG HANDLING**3.5. Applications of ash and slag from power coals****3.5.6. Obtaining different substances from coal combustion by-products****3.5.6.1. Manufacture and properties of magnetite dust from coal combustion products***J. J. Hycnar, Ecocoal Consulting Center Katowice, Poland**B. Kochański, Wyższa Szkoła Zarządzania Marketingowego i Języków Obcych, Katowice, Poland**B. Tora AGH - University of Science and Technology, Poland***ABSTRACT**

Hard and brown coal combustion in a pulverized-fuel boiler is accompanied by forming ferromagnetic compounds contained in fly ash and slag. The ferromagnetic compounds can be found as follows: the highest quantity in the ash of silicate kind, lower quantity in the ash of aluminum kind, and the lowest quantity in the calcium kind of ash. On the basis of test results on the content of magnetic compounds and total content of iron compounds and two-valued iron there were prepared technical and economic criteria regarding the separation of magnetite dust from fly ash. For industrial separation of magnetite dust from dry fly ash there were used original separators of the BWP type with a traveling magnetic field, whereas for magnetite dust separation from water-ash mixture, a separator with permanent magnets of the ZUO/SM-500/I type was employed. Magnetite dust separated in power plants (max. 20 000 t/a), could be characterized by a magnetic fraction of over 85% and total content of iron compounds exceeding 45%. The produced magnetite dust, despite many possibilities of use, was mainly applied in mining industry for making heavy media (to reduce imports), and manufacturing casting powder, as well as for building a mining shaft in quicksand.

1. INTRODUCTION

Depending on the nature and origin of fuel and its combustion technologies, as well as the method of desulfurization and extraction of solid pollutant from the exhaust, combustion adventive products have a very large diversity of their quantity and chemical composition. If we take into consideration, that the combustion process is one of the forms of enrichment of mineral contained in combusted fuel, the series of ash may have increased the quantity of component or components.

Interest in the presence and behaviour of certain elements in coal and products of their combustion is due to many reasons. A number of them affects the conditions of work of chambers boiler furnaces (slagging so-called routing and corrosion of tubes, steam superheater and air heater) and the effectiveness of exhaust dedusting in electrofilters and on the quality of obtaining by-products of combustion. The attention was brought to possibility on extracting concentrates of selected metals from fly ashes and bottom ash in many foreign publications [1-14], however the information about industrial production of metal concentrates from carbon combustion is limited [11-14]. In this range the greater success is observed in waste materials managing, among other things to produce weight in

order to obtain heavy liquid for mining and pigments [15-17].

The research carried out in Poland let the implementation of technology production of metal concentrates [18] like:

- Concentrated calcium oxide, as a separate mineral fertilizer (calcium-magnesium) and material to lime acid soils [19, 20] whose source were selected ash from the combustion of brown coal from the region of Konin and Belchatow;

- Alumina (experimental installation IMMB capacity 6000 t/a, industrial investment in cement mill Nowiny interrupted). Technology developed by professor Grzymek J. and his team allowed to use fly ashes from Turow power station and Turow Coal Mine clays to produce alumina and cement using sintering-decomposition method [20-22];

- Concentrated germanium oxide and gallium, through selection of a high-germanium coals combusted in a cyclone furnace and the emission of ultra fine fly ash [23]. According to the implemented technology, power industry transmitted a several thousand tonnes of ash germanium concentrate to non-ferrous metallurgy;

- Concentrated iron oxides. Through coals selection, combustion process and ashes segregations the method of ferromagnetic fraction extraction from the fly ashes was developed [23-25]. The results of the research and implementation on the evolution and application of magnetite dust [26] are the subjects of this paper.

2. ASSESSMENT OF THE RELEVANCE OF ASHES TO THE EXTRACTION OF MAGNETITE DUST

The basic criterion for assessing the suitability of the fly ashes to obtain magnetite dust is the economics of production and sales of magnetite dust. The evaluation of suitability of ashes to the magnetite dust recovery depended on:

- a) Uptake of representative samples of ash samples from each electrofilters zone
- b) The examination of samples of ash content on magnetic fraction content and total content of iron and divalent iron compounds;
- c) Separation of individual samples of fly ash on experimental station with industrial plate type BWP with slit active part 8, 10 and 15 mm at a constant portion volume. In addition there has

been additional separation of ashes on the 10 mm-slit with three levels of portions. As a result two fractions were obtained – magnetite dust and fly ash impoverished in ferromagnetic compounds, which weight was balanced;

- d) The examination of magnetic separation of fly ashes. In magnetic dust the ferromagnetic fraction content, $Fe^{3+} + Fe^{2+}$, Fe^{2+} , contents of silicon and density were determined. In thin ash the content of magnetic fraction and total content of iron compounds was determined;

- e) Determination of application of the released magnetite dust.

According to the described scheme assessment of suitability for production of magnetite dust using dry method, the fly ashes and bottom ash from 20 electric power stations and thermal-electric power stations, two of them are fired with lignite and eighteen with hard coal, were examined. Results of research and characteristic of magnetite dusts from experimental and industrial installation are shown in table 1.

Table 1. Properties of magnetic dust dry-separated from fly ash.

Nr	Powe plant ESP	Fly ash		Magnetics dust				Yield %
		Comsposition, %		Composition, %				
		magnetic fraction	Iron total Fe^c	magnetic fraction	Iron total Fe^c	SiO_2	density g/cm^3	
1.	Investigation in laboratory scale							
	Power plant Se							
1.1.	I sphere	6,87	10,52	92,61	62,33	9,05	4,23	3,53
	II sphere	6,73	10,30	91,43	61,12	9,93	4,12	0,96
	III sphere	3,21	6,69	80,74	57,63	11,43	4,17	0,40
	Elektrownia Rb							
1.2.	I sphere	6,55	7,49	95,06	51,72	11,69	3,82	2,89
	II sphere	1,99	7,28	94,53	53,42	11,66	3,89	0,19
	III sphere	0,76	5,30	91,44	53,42	12,83	3,68	0,19
2.	Investigations in industrial scale with BWP plate							
2.1.	EC Bd	3,55	4,59	85,82	57,33	-	-	0,5
2.2.	El Co	3,90	5,99	55,12	55,12	10,34	-	1,27
2.3.	El HI	3,09	4,37	94,48	59,34	9,79	-	4,47
2.4.	El. Jw. II	8,30	8,62	57,97	47,88	14,55	3,54	6,08
2.5.	El. Łg	5,08	6,02	55,21	55,14	11,68	-	2,00
2.6.	El. Łz	3,33	5,25	94,31	57,16	9,64	-	1,08
2.7.	El. Ot	9,87	7,23	91,96	57,66	8,01	-	4,81
2.8.	El. Rb	6,28	4,17	94,47	51,04	10,26	3,46	1,50
2.9.	El. Se	10,10	8,88	88,22	50,96	9,50	3,97	3,25
2.10.	EC Żr	9,51	11,02	98,16	55,01	9,70	-	2,94
2.11.	EC Wo	2,99	12,00	94,48	57,83	12,31	-	0,71
2.12.	EC Ga	6,07	-	88,10	60,77	7,19	-	1,01

Analysis of the results shows a very large spread of iron compounds and magnetic fraction content in ashes, which is illustrated on the following data:

- Compounds of divalent iron (Fe^{2+}) from 0,15 % to 2,37 %
- Total content of iron compounds (Fe_t) from 1,06 % to 12,00 %
- Magnetic fraction (D_p) from 0,86 % to 10,10 %

Moreover, there is the impact of collection spot of ash from ESP on the content of these components and the size of the recovery of magnetite dust, ashes from the I zone have the highest contents of ferromagnetic fraction and iron compound and the ashes from the III zone the lowest.

Statistic surveys of the entire results data of examined fly ashes let to establish the relationship between a content of magnetic fraction and content of an iron compounds as a following formulas show:

Relationship between the contents of the magnetic fraction and total content of divalent iron compounds:

$$D_p = 0,93 + 3,05 \times Fe^{+2}$$

Relationship between the contents of the magnetic fraction and total content of iron compounds:

$$D_p = 2,82 + 0,25 \times Fe_t$$

Taking into consideration the quantity of emitted magnetite dust on experimental station with plate type BWP, the dependence between the recovery of magnetite dust "U" and content of magnetic fraction in fly ash was elaborated as follows:

$$U = -0,16 + 0,41 \times D_p$$

For contemporary economic conditions, the process of fly ash separation was justified in case of 1 % magnetite dust emission, which was reached when fly ashes contained:

- Magnetic fraction minimum 5,03 %
- Divalent iron compounds minimum 0,88 %
- Total iron compounds minimum 3,60 %

Finding significant differences properties of magnetite dust from each fly ashes and place of their recovery importantly influences on decision about recovery and place of ash separation. Furthermore, about 80 % of ash is emitted in the first zone of ESP, in the second zone it is 15 % and 5 % in the third zone.

Table 2. **Properties of magnetic dust wet-separated from fly-ash.**

Nr	Power plant ESP	Fly ash		Magnetic dust				Yield %
		Compostion, %		Comsposition, %				
		Magnetic fraction	Iron total Fe ^c	Magnetic fraction	Iron total Fe ^c	SiO ₂	Density g/cm ³	
1.	Laboratory tests with FMA-63 separator (ash to water proportion 1 : 10)							
1.1.	Power Plant Se							
	I sphere	6,87	10,52	83,74	49,33	15,41	4,16	0,57
	II sphere	6,73	10,30	80,90	47,54	16,15	4,42	1,06
	III sphere	3,21	6,69	71,88	44,58	20,64	3,78	0,71
1.2.	Power Plant Rb							
	I sphere	6,55	7,49	64,99	34,04	25,92	3,22	0,20
	II sphere	1,99	7,28	69,18	35,00	22,73	3,31	0,02
	III sphere	0,76	5,30	55,93	32,80	24,55	3,05	0,08
2.	Industrial tests of magnetic dust - ZUO/SM-500/I installation (fluing ash in water, density about 50 g/dm³, plants 2x125 MW_e)							
2.1.	El Se	śr. 4,56	-	94,47 – 96,91	54,90 – 57,28	7,69 – 11,78	4,47 – 4,78	-

Comparing the results of recovery of magnetite dust from dry ashes on BWM ashes and wet on separators with stable magnets the following conclusion are reached:

- The magnetite dust extracted from dry ash has better parameters than the one extracted from hydro-ash on experimental stations;
- The magnetite dust extracted in industrial installations seems to have better quality in case of dust obtained in wet method.

3. METHODS OF EXTRACTING MAGNETITE DUST

Selecting the method of extraction of magnetite dust from fly ashes depends on the solution of ash removal boilers. Having regard to the modalities, the technology and equipment to extract the magnetite dust from dry hot ash and from hydro-ash suspension were developed [27].

The potential for recovery of magnetite dust from milled bottom ashes was examined. The most interesting results were obtained by separation in magnetic field (BWP plate) the bottom ash from lignite combustion (Fe_t 54,27-55,68 %; SiO₂ 8,50-13,55 %; density 4,08-4,23 g/cm³; yield 0,31-0,54 %).

Considering that in the number of electric and thermal-electric power stations the combustion products were taken away hydraulically, the examination of recovery of ferromagnetic fraction from hydro-ashes suspension were carried through according to the described scheme of dry ashes research. Summary of the results obtained in tests of ashes and dust are

The secretion of dry magnetite dust. Essential progress in the production of magnetite dust was brought by starting the production of magnetic separators (type BWP) based on principles of linear electric engines. Technical characteristics of the BWP separator is shown in table 3 [25-27].

On the one hand, the magnetic plate BWP captures the magnetic particles in a dust but on the other hand it transports them (magnetite dust) beyond the zone of separation without – fig. 1.

Where there were no conditions to install BWP plates under electrofilter's funnel in power plants and where hydraulic transport of ashes with composition of ashes and bottom ashes was available, **the method of magnetite dust extraction from water suspension of ash – separator ZUO/SM-500/I.**

Drum separator SM-500 was made basing on powder magnets, which in contemporary conditions provided a maximum intensity of the magnetic field. The tech-

nical characteristics of separator SM-500 is shown in table 3 [27].

Table 3. Technical characteristics of separators used for industrial recovery of magnetite dust from fly ash.

L.p.	Magnetic separator		Field	Magnetic induction, Gs	Voltaige, V	Capacity, t/h [m ³]	Size, mm	Mass,kg
	type	ash						
1.	BWP	Dry, 3 mm lay, Temperature max. 100 ⁰ C	electromagnetic	4000	380	10-20	active zone 300 x1000	
2.	SM-500	water	constant magnetic field	3500	-	[500]	Drum Φ = 400 L= 6 x 700 2 rot/min 2875 x 2590 x 1240	1700

The production of magnetite dust reached values close to 20.000 t/a. Only in five power plants equipped with 35 separators, 13.400 tonnes of magnetite dust a year were produced.

5. APPLICATION OF MAGNETITE DUST DERIVED FROM THE FLY ASHES.

The biggest number of magnetite dust were used in the mining for the production of heavy liquid to enrich the output [27]. However it should be noted, that agglutinations of iron oxides with aluminosilicates occurring in magnetite dust reduce the magnetite dust's density and dust is not a competitor to the typical weight of production of Scandinavian (Fosdalen). However, it allowed to reduce consumption of imported sinker. The magnetite dust from Siersza power plant had the best parameters, then were magnetite dusts obtained from ashes in Jaworzno I, II and Skawina power plants [28].

Significant quantities of magnetite dust were applied in cement industry for adjustment of ferric clinker module. Magnetite dust was also used for production of shield concrete for objects exposed to radiation.

Large economic effects were obtained using magnetite dust for the production of lubricating and exothermic casting powder [29, 30]. The presence of agglutinations of iron oxide with aluminosilicates positively influences on the course of Goldschmidt's reaction. Supplies of magnetite dust to production of casting powder were the object of interest of Italian and German companies.

Great success was the development of technology and application of magnetite dust and microspheres to control quicksands in the construction of the mining shaft [31]. A special case is the usage of magnetite dust to deoil water tanks through their earlier hydrofobization [32].

Interesting are also the experiences of Rock Tron company which manufactures spherical magnetites called MagTronTM, which are assigned to not only to heavy liquid preparation but the production of insulation as well.

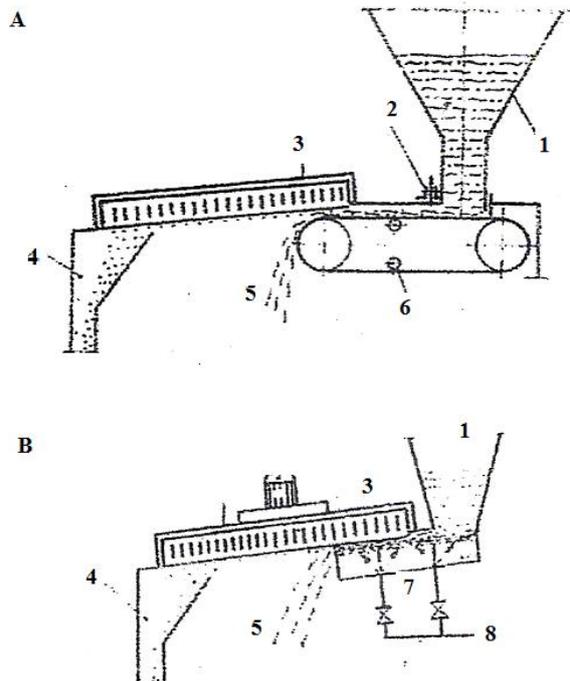


Fig.1 Installation with a BWP separator – a diagram. Fly ash belt feeder (A), aeration feeder (B)

1 — throat of ESP/container of ash; 2 — gap regulator; 3 — BWP separator plate; 4 — magnetic dust chute; 5 — fly ash chute ater magnetic separation; 6 — belt feeder; 7 — aeration feeder; 8 — compressed air; 9 — fan

4. PRODUCTION OF MAGNETITE DUST

In 70-80-ties of the last century there were about 90 separators BWP working and one separator SM-500 (Siersza power plant). Separators BWP worked in power plants and thermal-electric power plants in: Chorzow, Halemba, Siersza, Jaworzno I, Jaworzno II, Rybnik, Lagisza, Laziska, Skawina, Lodz II, Bydgoszcz, Gdansk. The quality of the produced magnetite dust is illustrated by data in table 1 and 2.

6. SUMMARY

The possibility and desirability of extraction of magnetite dust from fly ashes and bottom was positively verified. Now, when we have access to highly efficient magnetite separators (neodymium magnets) and there is strong demand for iron-bearing highly-desintegrated materials, there are conditions to the wide dissemination of the process of ash separation for:

- The Production of magnetite dust for existing and new directions of its application
- The production of ash microfillers of the higher heat-insulating specification
- Rationalizing the management of primary industry

REFERENCES

1. **Morton W.E.:** Direct reduction of fly ash into ferro-silicon. Ash Utilization. Fourth International Ash Utilization Symposium, St. Louis, Mo.. March 24, 25, 1976.
2. **Noone J.M.:** Mineral Extraction from fly ash. AshTech'84 Second International Conference on Ash Technology and Marketing. London September 16th-21st 1984.
3. **Harnby N., Burnet G., Kurtha M.:** Mineral recovery from coal conversion solid wastes. AshTech'84 Second International Conference on Ash Technology and Marketing. London September 16th-21st 1984.
4. **Kruger R.A., Verbaan B., Cornell D.:** Economical utilisation of pulverized fuel ash – recovery of minerals. AshTech'84 Second International Conference on Ash Technology and Marketing. London September 16th-21st 1984.
5. **Szpirt M.Ja., Żujkow B.L., Itkin Ju.W., Żurawlewa Je.T., Wolodariakin I.Ch.:** Koncentrowanie elementów w produktach szlifierki węgla. *Chimija Twiordowo Topliwa* 1985, nr 3.
6. **Abisheva Z.S., Blaida I.A., Ponomareva E.I., Beisembaev B.B.:** Reclaiming of fly ash generated by energy-producing coal combustion resulting in rare metals production. 12th International Coal Preparation Congress. Cracow, Poland, May 23-27, 1994.
7. **Ahn J-W., Um N-I., Han G-C., You K-S, Lee S-J., Cho H-C.:** Characteristic of Magnetic-Substance Classification from Coal Bottom Ash using Wet Magnetic Separator. WOCA 09. The World of Coal Ash. May 4-7, 2009 Lexington, Kentucky, USA.
8. **Moutsatsou A., Itskos G., Koukouzas N., Vounatsos P.:** Synthesis of Aluminum-Based Metal Matrix Composites (MMCs) with Lignite Fly Ash as Reinforcement Material. WOCA 09. The World of Coal Ash. May 4-7, 2009 Lexington, Kentucky, USA.
9. **Groppo J., Honaker R.:** Economical Recovery of Fly Ash-Derived Magnetics and Evaluation for Coal Cleaning. WOCA 09. The World of Coal Ash. May 4-7, 2009 Lexington, Kentucky, USA.
10. **Zhou H., Luo Y., Yu J., Ciao X.:** Feasibility of Recovery Alumina from Coal Fly Ash. WOCA 09. The World of Coal Ash. May 4-7, 2009 Lexington, Kentucky, USA
11. **Arroyo F., Font Q., Fernandez-Pereira C., Querol X., Chimenos J., Zeegers:** Germanium and Gallium Extraction from Gasification Fly Ash: Optimisation for the Up-Scaling of a Recovery Process. WOCA 09. The World of Coal Ash. May 4-7, 2009 Lexington, Kentucky, USA.
12. **Arroyo F., Camacho N.P., Coca P., Fernandez-Pereira C.:** Recovery of Germanium from Coal Fly Ash Leachate by Precipitation. WOCA 09. The World of Coal Ash. May 4-7, 2009 Lexington, Kentucky, USA.
13. **Brennan P.:** Processing of fly ash – New developments. International Conference EuroCoalAsh Copenhagen, Denmark – May 27-28, 2010.
14. **War Eagle Completes Successful First Phase Investigation Into The Recovery Of Germanium And Gallium From Coal Flyash In Spain.** 2007.
15. **Tajchman Z., Tora B.:** Badania nad optymalnym wykorzystaniem odpadów przemysłu hutniczego . X Konferencja „Problemy Zagospodarowania Odpadów”. Wisła 2004.
16. **Tora B., Kurzac M., Tejchman Z.:** Badania możliwości uzyskania pigmentów żelazowych z odpadów metalurgicznych. *Rocznik Ochrona Środowiska* 2009, tom 11, cz. 1.
17. **Łędzki A., Sanak-Rydlewska S., Tora B. i in.:** Możliwości zastosowania żendry powalcowniczej jako obciążnika cieczy ciężkiej. Konferencja „Odpady”. AGH. Kraków 2011.
18. **Hycnar J.:** Metody wydzielenia koncentratów metali z popiołów elektrowniowych. *Fizykochemiczne Problemy Mineralurgii* 1987, str 243-257.
19. **Zięba St.:** Surowce wtórne do nawożenia gleb. PWRiL. Warszawa 1982.
20. **Gibczyńska M., Meller E., Stankowski S., Wereszczaka J.:** Wpływ popiołu z węgla brunatnego na zawartość makroelementów w glebie i pobrane przez pszenżyto jare. Międzynarodowe Seminarium „Przetwarzanie i wykorzystanie popiołów wysokowapniowych”. Bełchatów, 22-24 lutego, 2006.
21. **Grzymek J.:** Metoda spiekowo-rozpadowa wytwarzania tlenku glinu i cementu portlandzkiego z łupków z Nowej Rudy i z pyłów dymnicowych względnie ilów turosszowskich. Ogólnokrajowa konferencja. Turosszów 1971.
22. **Kosacka E., Rajezyk K.:** Metoda spiekowo-rozpadowa J. Grzymka wytwarzania tlenku glinu i cementu z surowców krajowych. *Przegląd Geologiczny* 1974, nr 5.
23. **Hycnar J., Musialik H.:** Badania możliwości otrzymania z odpadów paleniskowych koncentratów bogatych w pierwiastki rzadki. *Prace FPTE nr 2.7.9.Cz. I i II. ZEOPd.* Katowice 1968-1969.
24. **Bartoszek B., Ptański Z., Wróblewski J., Brühl L.:** Urządzenia do separacji magnetycznej materiałów sypkich. Patent nr 48609.
25. **Ptański Z.:** Zasady działania oraz charakterystyka separatora płytowego. *Biuletyn Postępu Techniczno-Ekonomicznego Zjednoczenia Energetyki. Seria Ciepła* 1965, nr ¾.
26. **Garczyński H.:** Separator tlenków żelaza z podajnikiem pneumatycznym. *Energetyka* 1970, nr 12.
27. **Kochański B., Saratowicz A. i inni:** Badania i prace nad doskonaleniem metod i technologii separacji pyłu magnetytowego i innych surowców wtórnych z popiołów lotnych. *Problem Resortowy Temat 154-01. ZDUOEL.* Katowice 1971-1975.
28. **Ambroży J. i inni:** Ocena przydatności pyłu magnetytowego z popiołów lotnych do przygotowania cieczy ciężkiej zawiesinowej dla wzbogacania węgla. *Temat DNU – 283/75. GIG.* Katowice 1975.
29. **Zasyпка** smarująca wlewnice do syfonowego odlewania stali. Patent 132988, 1980.
30. **Hycnar J.:** Zastosowanie popiołów elektrowniowych do wytwarzania materiałów pomocniczych dla hutnictwa stali i odlewnictwa żeliwa i staliwa. *Hutnik* 1988, nr 5.

31. **Sposób** odcinkowego izolowania termicznego i odcinkowego zwiększania przewodności cieplnej otworów wiertniczych. Patent 235294. 1988.
32. **Sposób** usuwania zanieczyszczeń olejowych, tłuszczów, ropy naftowej oraz jej produktów z wód i ścieków. Patent 149243. 1982.
- J. Hycnar, B. Kochański, B. Tora.** Manufacture and properties of magnetite dust from coal combustion products // Proceedings of the IV scientific and practical workshop "Ashes from TPPs: removal, transport, processing, landfilling", Moscow, April 19–20, 2012 — M.: MPEI-Publishers, 2012. P. 192 – 196.