RESEARCH CONCERNING THE RECOVERY OF IRON OXIDES FROM THERMOCENTRAL ASHES

*Camelia BĂDULESCU**

Abstract: *The paper presents the research undertaken in order to recover the iron oxides from the ashes resulting from the burning of the Jiu Valley coal. By knowing the processes that take place during the combustion of coal in the outbreaks and the chemical and mineralogical properties of the ashes, the idea of recovering the iron oxides was advanced, with the aim of obtaining an iron concentrate with a content that would make it usable in the steel industry.*

This approach seeks to restore today one of the most important industrial wastes (ash) which, besides being a polluting agent with adverse repercussions on the environment, can also constitute sources of secondary raw materials, which can be used by technologies adapted to their specific characteristics.

Key words: *Jiu Valley coal, ash, iron oxides, marketable Fe concentrate*

1. Introduction

The ashes from thermoelectric power plants, due to the volume and the multiple possibilities of use, represent the most important industrial waste with special economic and ecological implications, whose use must be a major concern, being imposed by a number of factors such as:

- limiting the natural resources of useful minerals;
- environmental protection;
- finding new sources of secondary raw materials that can be used efficiently after their processing by conventional or unconventional technologies;
- limited duration of operation of ash ponds.

Currently in Romania, ash is only used in a proportion of 1% in the construction and construction materials industry, taking into account their specific physic-chemical and mineralogical properties.

In the process of producing electricity in thermos electric power stations, very large quantities of ash are obtained.

In most cases these residues have been and still are considered as waste without use and their disposal represents through the transport, handling and storage operations - important non-productive expenses, which increase the cost price.

The processing of these wastes and the obtaining of reusable by-products is an important problem - at least from a quantitative point of view - and the present work is trying to bring it up to date.

2. Research concerning the recovery of iron oxides from thermocentral ashes

Case study - Ashes from CET Paroșeni

2.1. The chemical and mineralogical characteristics of the ash from CET Paroseni

Knowing the characteristics of the ashes from C.T.E. it is important to establish the areas of their complex and efficient use in various fields.

Coal burning

The ash, consisting of the mineral substances remaining after the combustion of the fuel mass, varies considerably from one fuel to another and has a chemical composition different from that of the initial mineral materials due to the reactions that accompany the burning process.

This does not correspond either qualitatively or quantitatively to the waste because, through combustion, a series of reactions occur:

⇒ at temperatures above 400 ° C, some minerals begin to lose crystallization water such as iron oxide:

$$4FeO + O_2 \rightarrow 2Fe_2O_3$$

⇒ temperature rise above 570°C causes the transformation of iron sulphides into sulfur dioxide and iron oxides as follows: pyrite in the range of 300-500°C dissociates thermally by passing into pyrotine according to the reaction:

$$2FeS_2 \rightarrow 2FeS + S_2$$

At temperatures above 500 ° C, the iron sulphide resulting from the decomposition of pyrite is oxidized to form iron oxides according to the reaction:

$$2FeS + 7/2\ O_2 = Fe_2O_3 + 2SO_2$$

Siderite during heating, undergoes two main thermal transformations, namely: decomposition of carbonate at 450÷600 ºC which takes place with heat absorption and obtaining ferrous oxide and carbon dioxide, and then, with increasing

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temperature, an exothermic effect occurs, related to FeO oxidation to Fe_3O_4, the final product of oxidation being Fe_2O_3. The following transformation reactions take place:

$$3FeCO_3 \rightarrow 3FeO + 3CO_2$$
$$3FeO + CO_2 \rightarrow Fe_3O_4 + CO$$
$$3FeCO_3 \rightarrow Fe_3O_4 + 2CO_2 + CO$$
$$2Fe_3O_4 + CO_2 \rightarrow 3Fe_2O_3 + CO$$

All these transformations are accompanied by secondary reactions, which ultimately determine the chemical composition and properties of the ashes.

Due to their content in the various mineral substances presented above, in the thermodynamic conditions of combustion and cooling, the ashes are presented structurally as consisting of crystalline phases (12-24%) and glass phase (66-88%).

By correlating the thermal analysis, the röntgenostructural and the microscopic observations, the transformations undergone by the main mineral components of the coal at the combustion in thermal power stations were highlighted.

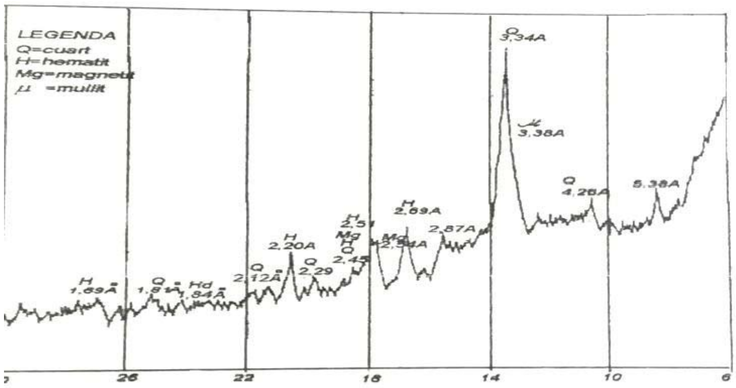


Fig. 1. Röntgendifractometric analysis

The physical and mechanical analyzes showed that the ashes from CTE Paroseni are presented as compact powders, as micro-porous spheres or as compact or cavernous glass spheres, high magnetic susceptibility.

Chemical composition

Inorganic coal substances, through burning turn to ash. It contains a number of elements present in large quantities known as major elements or macro-elements.

They are found in quantities of more than 1% by weight of ash having a weight that decreases in the order: Si, Al, Fe, Ca, Mg, S, Na, K, Ti, P.

Apart from macro-elements whose distribution determines the oxide composition of the ash in coal, there are in small quantities (between 1 ppm and 1%) a number of other elements, known as trace elements, rare elements, minor elements or microelements. Table 1 presents the macro-element contents of the ash from CET Paroșeni.

Table 1. *The macro-elements contents of the ash deposit from CET Paroșeni*

Sample	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	TiO_2 (%)	CaO (%)	MgO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)
Paroseni pound	47,12	8,68	20,08	0,055	6,30	2,50	0,22	0,98	1,87

It is found that the major components are: SiO_2, Al_2O_3 and Fe_2O_3, their sum exceeding 70% which attests the possibility of formation of glass phases as well as of silicates, calcium alumina, etc. with favorable implications on the hydraulic capacity of these ashes.

In the absence of an internationally accepted ash classification criterion, it was proposed by Academic Press (USA) to introduce a classification according to the ratio% SiO2 and% Al_2O_3 as well as the quantities of% CaO and% SO_3. According to this criterion the ashes can be classified into 4 classes:

- alumino-silico ash characterized by the ratio

$$\frac{\%SiO_2}{\%Al_2O_3} \leq 2$$

%CaO < 15

- alumino-silico ash characterized by the ratio

$$\frac{\%SiO_2}{\%Al_2O_3} \geq 2$$

% CaO <15

- sulfocalcic ash, for which:

% CaO >15 şi %SO_3>3

- calcium ash, at which:

%CaO>15 şi SO_3<3.

The ashes from Paroșeni belong to the silico-aluminous type.

The mineralogical analysis of the ashes from CET Paroseni highlighted the following minerals:

Table 2. *The mineralogical analysis of the ashes deposit from Paroșeni*

Mineral	Chemical formula	Content [%]
magnetite	Fe_3O_4	10
hematite	Fe_2O_3	
sfen	$CaTi(SiO_4)$	0,1
pyrite	FeS_2	0,35
calcite	$CaCO_3$	3,0
dolomite	$Ca,Mg(CO_3)$	
oxidized sulphate and carbonate compounds of Pb,Zn,Cu	-	0,1-0,15
	$Al_2O_3.2SiO_2$	
metacaolinite	$Al_4(Si_4O_{10})(OH)_8$	30-35
caolinite	$(Mg,Fe)_5(AlSi_3O_{10})(OH)_8$	
chlorite	-	35-40
complex silicates	SiO_2	5-10

2.2. Magnetic concentration tests

Considering that the weight of iron ores represented by magnetite, hematite, including those resulting from burning pyrite in the ash of Paroșeni is about 10%, the concentration tests were oriented towards magnetic separation.

This method of concentration is based on the different magnetic properties of the minerals subjected to separation. The process of separation in the magnetic field is characterized by a complexity of phenomena related both to the physico-chemical characteristics of the minerals in the composition of the ore and to the nature of the environment in which the separation takes place, as well as to the constructive characteristics of the magnetic separators.

The main factor influencing the magnetic preparation is the magnetic susceptibility which, depending on its permeability, in turn is directly related to the nature of the substance and its electronic structure. The main factors that influence the magnetic susceptibility of useful mineral substances are:

- the presence of mechanical impurities, fixed on the mineral granules;
- the presence of impurities contained in the crystalline network and the chemical composition of minerals. The mode of association of crystals that form mineral granules may influence their susceptibility. If the crystals are of different species, the susceptibility depends on the percentage of magnetic substance. An influence was also found for granules formed of microcrystals of different orientations;
- size of granules. This parameter has a relatively small influence on magnetic susceptibility. From a practical point of view, the influence of the size on the susceptibility can be neglected;
- the intensity of the magnetic field inductor. The influence of the magnetic field on the minerals is appreciable only in the case of ferromagnetic substances, when due to the hysteresis phenomenon it is important to know the value of the magnetic field and all the treatments to which the material was subjected;
- temperature. Ferromagnetic substances are not influenced by the temperature below the Curie point (Curie temperature - represents the maximum temperature up to which a ferromagnetic substance can be magnetized). The temperature can indirectly influence the magnetic susceptibility, if by its variation phenomena of allotropism occurs;
- physical treatments.

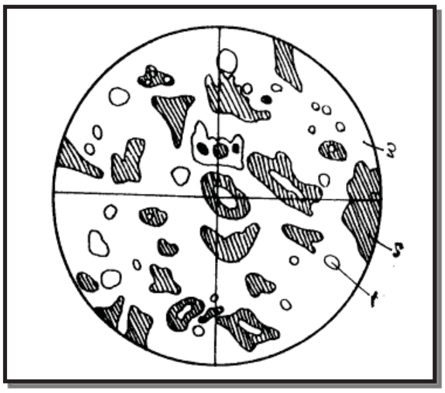
Essentially the process of magnetic concentration consists in the different action of the magnetic forces on the components of a mixture in competition with forces of another nature that act in the opposite direction (mechanical forces, viscosity, etc.).

By the triple action of the magnetic forces, the competing forces and the interaction forces, the concentration mixture is divided inside a magnetic separator into a magnetic component, a non-magnetic one and most often into an intermediate component. Practical experience has shown that non-magnetic impurities appear in separation products in magnetic ones and vice versa, the separation being complete only in ideal cases.

In order to know the intimate structure of the ash and especially the way of presenting the iron compounds in the ash mass, chalcographic sections were executed on ash samples, the image of which is shown in figure 2.

Fig. 2. *Chalcographic section of the ash sample*

1-iron oxides
2-cavities
3-waste basis mass



By microscopically examining the ash sample, one can notice the almost globular shape of the iron compounds and at the same time the free existence of these compounds in the silicon mass of the ash.

This form of presentation can be explained by a prior technical study of the combustion process in the drilling.

Thus, in the case of CTE Paroşeni whose ash were analyzed, taking into account the combustion regime, the type of the outbreak, the quality of the coal, etc., a maximum temperature of about 1800C˚ is recorded in the furnace, so that the melting temperature of the of oxides (1030-1580C˚).

This situation determines the melting of the iron oxides and once the ash is drawn towards the lower part of the furnace, by lowering the temperature, solidification of these compounds takes place under unhindered conditions.

Several magnetic separation tests were performed using the Davis magnetic separator provided by the laboratory, at different magnetic field intensities and different working dilutions.

In the table 3 presents the iron contents obtained at different intensities of the magnetic field, at a working dilution of 5 m^3/t established as optimal.

Table 3. *The variation o iron content, depending of the intensity of the magnetic field*

Sample	The intensity of the magnetic field H ($Ö_e$)	Fe content (%)
1	700	40,91
2	900	45,2
3	1000	48,7
4	1200	51,89

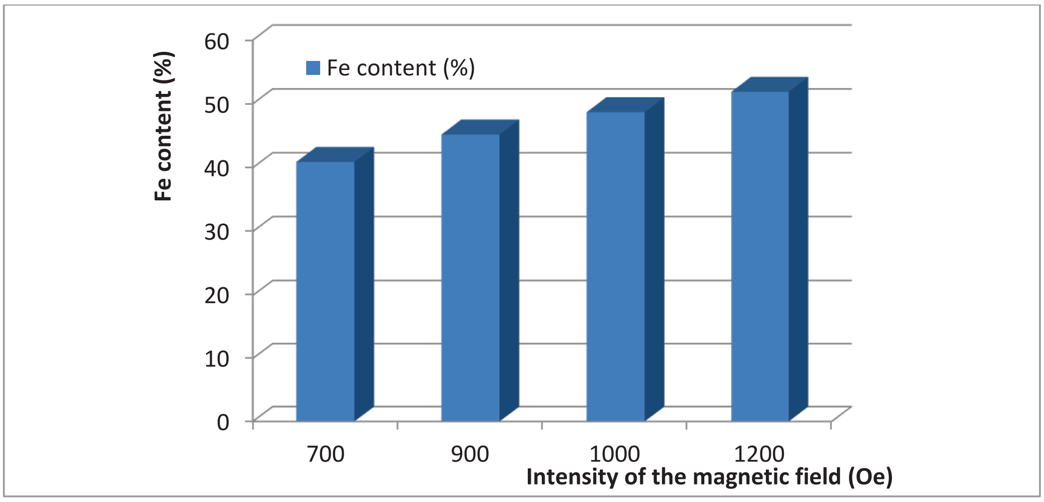


Fig. 3. *The variation of iron content, depending of the intensity of the magnetic field*

The highest iron content was obtained for a magnetic field intensity of 1200 Öe, respectively 51.89%.

The technological scheme of magnetic concentration of the heavy fraction obtained at the pre-concentration on the tables is presented in fig.4.

Table 4 presents the Fe contents, the weight and Fe extractions of the obtained products after following the preparation scheme from fig.4, independent for every operation.

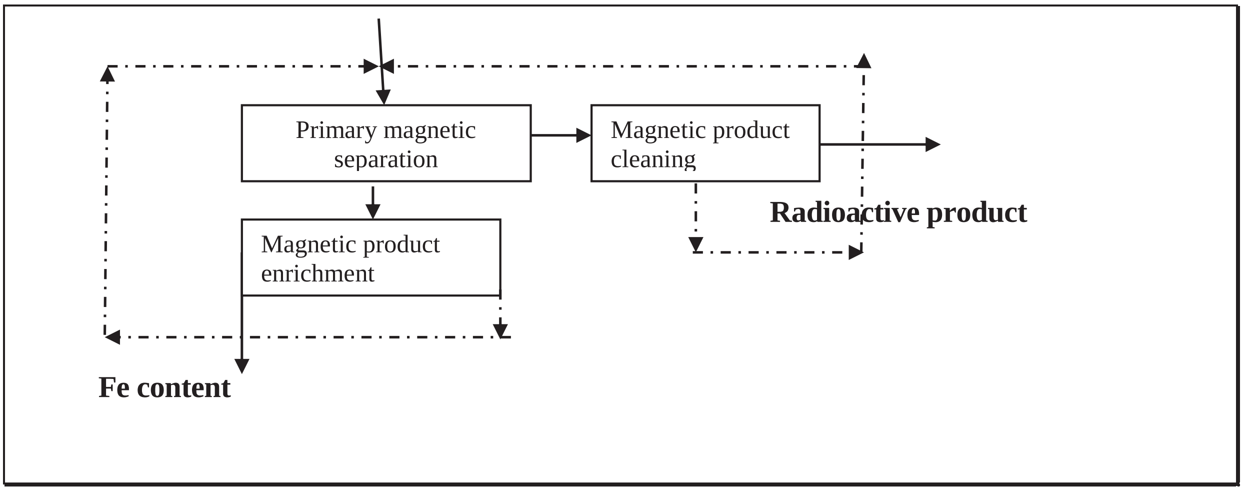


Fig. 4. *Technological scheme for magnetic concentration of ash from CET Paroseni*

Table 4. *The parameters and indices obtained at the magnetic concentration*

Specification	Weight extraction (%)	Fe content (%)	Fe recovery (%)
Primary magnetic separation	89,95 10,05	51,89 27,89	94,027 5,97
Magnetic product enriching	77,24 22,76	55,31 40,23	82,33 17,67
Magnetic product cleaning	30,62 69,38	45,03 20,19	49,44 50,56

Following the reprocessing of the products obtained at the primary magnetic separation, an increase of the iron content was obtained from 51.89% to 55.31% at the enrichment of the magnetic product, respectively a reduction of the iron content from 27.89% to 20.19 % as a result of the non-magnetic product being restated. By applying the wet magnetic concentration method in the weak field, a magnetic product and a non-magnetic radioactive product with 0.016 mRem/h radioactivity were obtained.

3. Conclusions

The research carried out in our country and abroad regarding the obtaining of iron oxide concentrates is a major concern for the complex and integral recovery of the ashes from C.T.E. Paroșeni.

The separation of iron oxides from ash has a double importance and necessity:

- creation of a new source of concentrates of ferrous substances usable in the steel industry;
- deferred ash from C.T.E. for use in obtaining alumina.

In this research field, encouraging results were recorded in different countries such as Poland, Slovakia, Romania.

From the point of view of the chemical composition, respectively of the iron content, the concentrate is similar to the iron concentrates used in the agglomeration or pelletizing process.

The iron is found in these ashes, generally, in the form of magnetite, faialite, hematite, and alkali and alkaline ferrous ferries in a very fine crystalline state, concentrated especially in the spherical granules, accompanied by glass silicates. For the purposes pursued, iron ore minerals of magnetite type are of interest. Magnetite and hematite were identified both in the free granules and especially punctually impregnated in the mass of quartz and silicates. Their weight in the mass of ash is 10-11%.

Conclusive results were obtained by applying the magnetic concentration method, at a magnetic field intensity of 96 KA / m, resulting in a magnetic product whose weight represents 5.92% of the ash mass, at an iron content of 55.31 %.

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