ZESZYTY NAUKOWE POLITECHNIKI ŚLĄSKIEJ 1996
Seria: GÓRNICTWO z. 231 Nr kol. 1349

F. MICHALIKOVÁ, L'. FLOREKOVÁ

Department of Mining, Ecology Management and Geotechnology
Technical University of Košice, Slovakia

BASIC PROPERTIES OF POWER INDUSTRY FLY ASHES FROM THE POINT OF VIEW OF POSSIBILITIES OF THEIR UTILIZATION

Summary. The mineralogical composition of products of coal combustion changes upon different burning equipment in power plants. The differences in the properties of fly ashes caused by different burning are presented in the current paper.

PODSTAWOWE WŁASNOŚCI POPIOŁÓW LOTNYCH Z PRZEMYSŁU ENERGETYCZNEGO Z PUNKTU WIDZENIA ICH UTYLIZACJI

Streszczenie. Autorki omawiają różnice we własnościach popiołów lotnych, utworzonych w różnych procesach spalania. Są one widoczne w morfologii ziarn, a skład mineralny i chemiczny popiołów lotnych jest silnie modyfikowany procesami odsiarczania spalin. Po oddzieleniu faz magnetycznych, które mogą być użyte do obciążania płuczek węglowych, oraz frakcji wzbogaconych w resztki węgla, które można wykorzystać jako paliwo wtórne, oczyszczone popioły lotne mogą nabrać nowych właściwości, umożliwiających ich inne zastosowanie w różnych działach przemysłu.

1. Introduction

Unprocessed fly ashes, formed during burning of coal in heating and power plants, are considered to be wastes. It is necessary to know their physical, chemical and mineralogical properties when planning a waste utilization, and on this basis suitable procedures of separation of individual components may be chosen. Besides reclaiming the useful components, the fly ashes are being "purified" and become themselves a suitable raw material for the industrial utilization.

2. Physical properties

In the Slovak power industry three types of burning equipment are currently used: stoker-fired boilers, pulverized-fuel boilers, and fluidized bed boilers (one-stage and circulating ones). Their burning temperatures and basic parameters of coals charged and fly ashes produced are given in Table 1. In selection of technological processes, used for reclaiming individual usable components from fly ashes, the grain size distribution or surface area, density and morphological features are more important properties.

The grain sizes of fly ashes are in the range of 0-0.5 mm (rarely up to 1 mm), and are controlled by the grain size of coal being burnt, type of burning equipment, and temperature of burning.

Table 1

Basic technological parametrs

Type of boiler	Temperature of burning	Type of coal burnt	Input coal grain size [mm]	Output fly ash grain size	Fly ash surface area [$m^2 \cdot g^{-1}$]
Stoker	1300 - 1600	black	0 - 0,2	0 - 0,2	2 - 4
Pulverized-fuel	950 - 1100 (1000 - 1250)	brown	0 - 2 (0 - 5)	0 - 0,2	3 - 5
Fluidized bed (one-stage)	800 - 850	black and brown	1 - 6.5	40 % < 0,045	7 - 17
Fluidized bed (circulating)	800 - 850	black and brown	1 - 6,5	50 90 % < 0,045	7 - 17

The density of fly ashes changes from 1.9 $g \cdot cm^{-3}$ (Novàky, Melnik) to 2.6 $g \cdot cm^{-3}$ (Tisovà, Ostrava).

The morphology of fly ashes depends on the temperature of burning. The fly ashes formed from black coal, burnt in stoker-fired boilers, are characterized by spherical shapes of their particles. When burning brown coal in pulverized-fuel boilers, the particles preserve the contours of original coal grains but are rounded due to fusion. The grains with the spherical shapes are almost absent, except for micron-sized particles. The fly ashes from fluidized bed boilers, fired with both black and brown coals, have the morphology of original coal grains, and particles with rounded shapes are rare. The occurrence of glassy phases is significantly lower in comparison with the stoker-fired and pulverized-fuel boilers, and depends on the presence of low-fusible components in the ash, melting point of which being in the range of temperatures in a fluidized bed boiler, i.e. 800-850° C.

The compactness and freeze rezistance are the properties deciding on the use of fly ashes for road construction.

Melting of fly ashes is another property that must be considered with regard e.g. to their use as components of fired ceramic products.

3. Chemical properties

The chemical composition of fly ashes gives, to a certain measure, an information on the composition of the coal from which they have been formed by burning. Reactions are affected by the presence of water, water vapour, sulphur, deficiency of oxygen, construction of a combustion chamber, process of burning, and content of combustible substances.

Iron

The content of iron in fly ashes is between 3 and 11%. The particles of fly ashes are composed mainly, beside silicates and aluminosilicates, of iron oxides (major magnetite), and these phases are often intergrown. All the particles of fly ashes behave as paramagnetic-ferromagnetic substances, i.e. substances with a certain magnetic susceptibility. For the separation of the major Fe-bearing components, the low-intensity magnetic separation is being used.

Formation of magnetite, a new mineral phase, depends on the method of combustion and the temperature of coal burning:

- in the fly ashes from stoker-fired boilers about 80% of Fe is in the form of magnetite or metal iron. Magnetic concentrates of those ashes comprise 48-56% Fe with the weight yield 2-7% (according to the Fe content in the burnt coal) and the recovery is 30-36%;
- in pulverized-fuel boilers, in which the Sloval brown coal is being burnt, only 15-30% Fe is changed into the form of magnetite;
- in fluidized bed boilers magnetite binds 40-90% of the total amount of Fe, depending on whether coal is burnt in one-stage or circulating varieties of these boilers.

Sulphur

Compounds of sulphur in fly ashes can adversaly affect their utilization in civil engineering, mainly in consolidation and hardening of cement compounds.

Aluminium

Standard production of aluminium oxide Al_2O_3 and quick-binding cement QBC are examples of the utilization of power plant fly ashes. These technologies are economically advantageous in the cases when the fly ashes used comprise at least 30% of Al_2O_3.

Arsenic

Arsenic is an ubiquitous element. From the point of view of utilization of fly ashes as additives to the porous concrete, it is important that up to 99% of arsenic in the concrete be insoluble. It is known that arsenic may be leached out from dumps or settling ponds of fly ashes. Removal of arsenic and other elements (selenium, cadmium, chromium, lead, silver, zinc) was the subject of investigations of Merril and co-workers [3] who described the method of removal of undesirable elements from communal and industrial waste waters. The technology was tested in a continuous flow under field conditions, and arsenic was removed in 90% and more, while selenium in 80%.

Unburnt remnants of coal

Remnants of unburnt coal, equivalent to the content of combustible substances, are measured as the loss on ignition (l.o.i.). They represent an important component that limits utilization of fly ashes in civil engineering, the main consumer of these products. The maximum l.o.i. for specific applications in civil engineering is determined by the Slovak norm STN 72 2062-69: it is 7% for brown coal-derived ashes, and 10% for black coal-derived ashes.

Also this parameter depends on the method of combustion and the temperature of coal burning:

- in the fly ashes from stoker-fired boilers that are currently in operation, the unburnt coal represents 8-20% (as l.o.i.). If such ashes are to be used in civil engineering, it is necessary to separate out these unburnt remnants, either by sizing or by flotation;
- in pulverized-fuel boilers charged with brown coal, the fly ashes comprise 0.3-0.7% of combustible substances and the separation is unnecessary;

- in fluidized bed boilers, the content of unburnt coal is in the range 0.5-20%, and its amount depends on the type of burning: either in one-stage fluidized bed or in circulating fluidized bed varieties of these boilers. The wet separation is unsuitable there because fly ashes are highly leachable. The authors used a dry process of separation, the electrostatic method, which was successful with the coarser grain size classes of the fly ashes tested. For example, in the grain size fraction 0.3-0.5 mm the l.o.i. of the conductive product was 71%. The separability of combustible substances decreases with the decreasing particle size of fly ashes because of adhesion of their grains.

Other elements

Fly ashes comprise also other chemical elements and reclamation of metals from them has been known for several decades. In most cases iron, aluminium, germanium, uranium, and calcium are reclaimed. Hycnar [5] states that it is possible to acquire the following elements by hydrometallurgical processes: Ag, Al, Cd, Cu, Fe, Mn, Ni, Pb, Sn, Sb, Th, Ti, U, V, Zn, while Al, As, Ca, Cu, Fe, Ga, Ge, Mg, Mn, Ni, Sb, Si, Sn, Th, Ti, U, V may be acquired by pyrometallurgical methods.

Radioactivity

The upper value of the specific radioactivity for fly ashes from power and heat stations used as supplementary materials in civic engineering is 120 $Bq.kg^{-1}$

4. Mineralogical properties

The temperature of burning and the atmosphere in a combustion chamber - oxidizing or reducing - have a dominating influence on the mineralogical composition of fly ashes, besides of course the chemical composition of the coal being burnt. Melting of individual inorganic components takes part at various temperatures, and temperature changes control the formation of eutectic mixtures.

Fly ashes comprise the following groups of minerals [1]:

- silicates and aluminosilicates;
- minerals of iron (magnetite, maghemite, haematite) that are newly-formed phases in the range of FeO-Fe_2O_3 -Fe_3O_4-Fe (in the Chalmová settling pond, pyrite, magnetite and limonite were identified);
- carbonate minerals, e.g. calcite $CaCO_3$ and siderite $FeCO_3$;
- accessory minerals, e.g. quartz and cristobalite SiO_2 , apatite $Ca_5[PO_4]_3F$, then rutile TiO_2 , pyroxenes, feldspars;
- glassy phases, the content of which depends on the conditions of burning;
- remnants of unburnt coal that are represented by a whole range of transitional stages, from the original coal to coke. There are such components like vitrain and clarain in black coal-derived fly ashes. The brown coal-derived fly ashes from Opatovice consist of unaltered or slightly thermally changed coal, the coal of a higher degree of thermal alterations, brown coal coke, and graphite [7].

The fly ashes from fluidized bed boilers are characterized by the content of calcium (Ca). This element is introduced, in most cases in the form of limestones ($CaCO_3$) during desulphurization of fly gases. The crystalline phases of fly ashes after desulphurization are represented by: anhydrite $CaSO_4$, hannebachite $CaSO_4 \cdot 1/2H_2O$, gypsum $CaSO_4 \cdot 2H_20$, portlandite $Ca(OH)_2$, calcite $CaCO_3$, quartz SiO_2, haematite Fe_2O_3 , magnetite Fe_3O_4, ettringite $Ca_6Al_2(SO_3)_4 \cdot (OH)_{12} \cdot 6H_2O$, thaumasite $Ca_6Si_2(SO_3)_4(OH)_{12} \cdot 24H_2O$.

Among "mixed" mineral phases the following should be mentioned: wollastonite $CaSiO_2$, kirschsteinite $CaFe[SiO_4]$, andradite $Ca_3Fe_2[SiO_4]_3$, also particles with their chemical composition close to such zeolites as phillipsite and clinoptilolite [7, 8].

The knowledge of mineral composition or the fact that the newly formed mineral phases are the analogues of naturally occurring minerals make easier the choice of mineral processing procedures for separation of fly ashes. If methods of utilization of those newly formed mineral phases in different branches of industry are found, then the fly ashes may be treated not as wastes to be disposed of and stored but as valuable raw materials. The complex knowledge of physical, chemical, and mainly mineralogical properties of fly ashes enables the selection of suitable technologies for separation processes.

5. Reclamation of useful components and their utilization

Mineral processing technologies make possible to acquire from fly ashes, which at present are treated as wastes, some products usable in the industry. These products comprise:

- flotation concentrates of combustible substances. The remnants of coal in fly ashes may be recycled and serve as a fuel with the total heat value of 26-27 $MJ \cdot kg^{-1}$;
- magnetite concentrates. They may be utilized as a heavy medium in coal cleaning or as an additional raw material in metallurgical processes;
- tailings after flotation of the combustible residuals and after magnetic separation, thus devoid of coal and Fe-bearing phases, called the refined fly ashes. Their new properties may determine their perspective, more sophisticated applications in industrial processes.

Fly ashes may be utilized in numerous branches of industry, and the following ones are worth mentioning:

- civil engineering and production of construction materials. Fly ashes are frequently used in production of such ceramic materials as glazed paving and floor tiles, in manufacturing of porous concrete, agloporite, cement, and concrete, as fine concrete aggregates, as fly ash coils that solidify when cooled, as aggregates to autoclave concretes, in manufacturing of light, non-autoclaved concretes, in production of autoclaved silicate cements for metallurgical mortars, and in road construction;
- metallurgy. They may be used as filling substances in steel casting, as filling mixtures and insulation inserts, thermoinsulation boards, forming materials for casting of steel and alloys;
- mining. The major use of fly ashes include their application as an underground back-fill, cementless binder and thermoinsulation material. It has already been mentioned that the reclaimed magnetic fraction, containing magnetite, may be used in the form of heavy suspensions for coal separation;
- automobile industry. Production of noise-absorbing mixtures consumes some amounts of fly ashes.

6. Conclusions

Utilization of fly ashes saves primary raw materials and energy. In their numerous applications, costs of such operations as mining, crushing, coarse grinding have already been incurred by other industries. These new applications require only investments for the equipment directly associated with separation processes, i.e. with sizing, flotation, and magnetic separation.

Any feasibility study on the methods of utilization of fly ashes from a specific power or heating plant must include the following: detailed investigations of their properties, verification of processing technologies that may be used in reclamation of usable components of the fly ashes, and economical evaluation and marketing research of predicted products (costs incurred versus costs of processing). In this evaluation, also costs that would have been born if the fly ashes had not been utilized should be included. These are costs of storage of the fly ashes in a dump, environmental fees calculated from the predicted environmental impact of the fly ashes treated as wastes, and payments connected with meeting legislative requirements when handling of such wastes.

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Recenzent: Dr inż. Iwona Kuczyńska

Wpłynęło do Redakcji 27.09.1996 r.

Streszczenie

Skład mineralny produktów spalania węgla zmienia się zależnie od wyposażenia kotłowni w siłowniach i elektrociepłowniach. Na te zmiany szczególnie oddziałuje temperatura spalania. W kotłach rusztowych, gdzie temperatura ta jest rzędu 1350-1600° C, nowo tworzące się fazy mineralne są różne od tych, które tworzą się w kotłach pyłowych czy fluidalnych w niższych temperaturach. Autorki omawiają różnice we własnościach popiołów lotnych, utworzonych w różnych procesach spalania. Są one widoczne w morfologii ziarn, a skład mineralny i chemiczny popiołów lotnych jest silnie modyfikowany procesami odsiarczania spalin. Typowe zastosowania popiołów lotnych obejmują: budownictwo drogowe, ceramikę (wytwarzanie cementów, dodatków do betonów, płytek ceramicznych, materiałów ciepło- i dźwiękochłonnych), odlewnictwo (dodatki do mas formierskich), górnictwo (materiały

podsadzkowe). Autorki podkreślają zalety kompleksowego wykorzystania popiołów lotnych. Po oddzieleniu faz magnetycznych, które mogą być użyte do obciążania płuczek węglowych, oraz frakcji wzbogaconych w resztki węgla, które można wykorzystać jako paliwo wtórne, oczyszczone popioły lotne mogą nabrać nowych właściwości, umożliwiających ich inne zastosowanie w różnych działach przemysłu.