Physical Properties of Pozzolana Fly Ash from Thermal Power Plant of Iasi, Romania – A Cement-like Material for Substructure Works

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Abstract: - The use of fly ash represents a topic, much addressed to in the past years, solving the problems of advanced treatment and intelligent use of fly ash. In this study the physical properties of pozzolanic coal fly ash, a massive waste of a thermal power station in Iasi, Romania, are investigated. The physical properties of bituminous coal fly ash have been studied by laboratory tests of specimens taken from a thermal power plant of Iasi, Romania. The results of these tests are used in this paper to analyze the composition of fly ashes. The recycling of fly ash has become an increasing concern in recent years due to increasing landfill costs and current interest in sustainable development. Soil stabilization involves the addition of fly ash to improve the engineering performance of a soil.

Key-Words: pozzolanic ash, fly ash from thermal power plant, cement-like material, physical methods, compaction characteristics of fly ash

1 Introduction

Pozzolana was used since Antiquity its name coming from the volcanic ash from Pozzuoli, a harbour of Southern Italy, 11 Km west of Naples, where it was discovered for the first time. The town is on the Bay of Pozzuoli, a section of the Bay of Naples, 27 Km from Vesuvius. In 79 A.D. this volcanic ash completely buried the city of Pompeii, near modern Naples, thus preserving it for today.

Romans, replacing the limestone with shale and shale-limestone in lime ovens and increasing combustion temperature, have obtained a fine milled material, which mixed with volcanic ash is considered the first cement in history. This mixture was called "pozzolanic cement".

Vitruvius, in his ten-volume *De Architectura*, devotes a chapter (Book II, ch. VI) to this "powder which, by nature, produces wonderful results". He speaks there of four types of pozzolana: black, white, grey and red. Vitruvius specified a ratio of 1 part lime to 3 parts of pozzolana for cement used in buildings and 1 part lime to 2 parts pozzolana for underwater structures. The ratio for modern structures using pozzolana cement is more or less the same [12].

The use of fly ash as a pozzolanic ingredient was recognized as early as 1914, although the earliest noteworthy study of its use was in 1937. Before its use was lost to the Dark Ages, Roman structures such as the Coliseum (fig.1), the Baths of Caracalla, the Pantheon (fig.2) in Rome, the Pont du Gard aqueduct in South France or the Appian Way used volcanic ash (which possesses similar properties to fly ash) as pozzolana in their kind of waterproof and very strong concrete. This kind of concrete hardens under water and was extensively used in the Roman world when making large outdoor structures such as jetties, harbour works, and water channels. The Roman port at Cosa was built of pozzolana that was poured underwater, apparently using a long tube to carefully lay it up without allowing sea water to mix with it. The three piers are still visible today, with the underwater portions in generally excellent condition after 2100 years [15].

The fine-grained volcanic tuffs erupting during the seventeenth century B.C. on the island of Thera (Santorini) in Greece, called "Santorini earth", were quarried as pozzolana during the mid nineteenth century A.D. and shipped to Egypt for cement lining the Suez Canal. Pozzolanic natural cement was for millennia the only available material for lining cisterns and aqueducts and binding the brick and stone of water-front structures and monumental buildings. The lining of a cistern in Kamiros, Rhodes (230 km east of Santorini), dating from the 6th or 7th century B.C. is still in existence [3]. It was only in the latter part of the 19th century that pozzolanic cement was gradually replaced by Portland cement.

Fig.1 Details of Coliseum in Rome

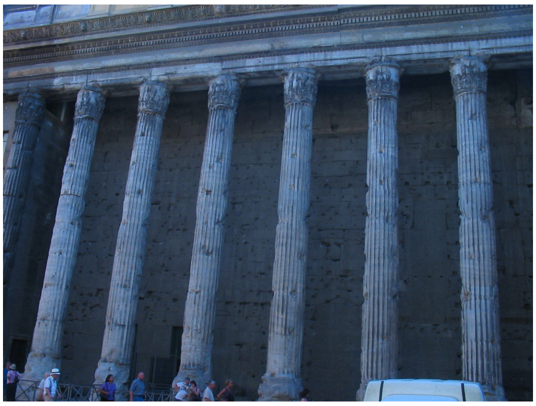

Fig.2 Entrance to the Pantheon in Rome

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2 Fly ash general features

Natural pozzolanic ash is still being used in various countries like Greece, Italy, Germany, Mexico and China [13], because it reduces cost and improves quality and durability of concrete.

The substitution of Portland cement with fly ash reduces the greenhouse effect of concrete significantly reducing carbon emissions associated with construction activity. Zero CO_2 is produced using fly ash wastes in comparison with one ton of CO_2 produced for one ton of Portland cement.

An industrial source of materials with pozzolanic properties is the siliceous fly ash from coal-fired power plants.

Fly ash is a mineral waste, one of the residues generated from the combustion of solid fuels (coals). Fly ash is generally captured from the chimneys of coal-fired power plants. There are millions of tons of fly ash produced and stored in each thermal power plant.

Depending upon the source and makeup of the coal being burned, the components of fly ash vary considerably, but all fly ashes include substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline) and calcium oxide (CaO).

These wastes are polluting materials. New fly ash production by burning the coal produces approximately twenty to thirty tons of CO_2 per ton of fly ash. Fly ash contains trace concentrations of heavy metals and other substances that are known to be detrimental to health in sufficient quantities. Toxic constituents include: barium (806 ppm), strontium (775 ppm), boron (311 ppm), vanadium (252 ppm), manganese (250 ppm), zinc (178 ppm), chromium (136 ppm), copper (112 ppm), chromium VI (90 ppm), nickel (77.6 ppm), lead (56 ppm), arsenic (43.4 ppm), cobalt (35.9 ppm), fluorine (29 ppm), thallium (9 ppm), selenium (7.7 ppm), beryllium (5 ppm), cadmium (3.4 ppm), mercury, molybdenum, radium, thorium, vanadium, along with dioxins and polycyclic aromatic hydrocarbons (PAH) compounds [6]. Fly ash typically contained 10 to 30 ppm of uranium, comparable to the levels found in some granites rocks, phosphate rock, and black shale. However, coal fly ash did not need to be regulated as a hazardous waste because its radioactivity can be compared with that of common soils or rocks.

In the past, fly ash produced from coal combustion was simply entrained in flue gases and was generally released into the atmosphere, but pollution control equipment mandated in recent decades requires to be captured prior to release. Fly ash material solidifies while suspended in the exhaust gases and is collected by electrostatic precipitators or filter bags.

The issue of the radioactivity of the fly ash resulted from thermal power plants generated numerous disputes between various beneficiaries and decision factors on environment and public health.

In the context of a carried on research were emphasized the values resulted from measuring the radioactivity of ashes from thermal power plants; it was founded that the fly ashes are proper for achievement of specific elements and structures of architectural open spaces, such as road construction, river channel adjustments, retaining walls and shore defense and in no way construction intended for housing or social activities. It is increasingly finding use in the synthesis of geopolymers and zeolites as well.

3 Chemical analysis of fly ash from Iasi thermal power plant

In thermal power plants of Romania, large amounts of fly ash as fine gray powder result from the combustion of fine grounded lignite coal from Oltenia Basin.

In comparison with fly ashes resulted from burning hard coal, those resulting from the combustion of lignite have relative small differences in oxides content excepting CaO present in large quantities in the fly ashes resulted from lignite combustion [20].

The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned (anthracite, bituminous, subbituminous, and lignite) [6].

The burning of harder anthracite and bituminous coal produces a fly ash pozzolanic in nature, which contains less than 10% lime (CaO).

Fly ash produced from the burning of lignite, in addition to having pozzolanic properties, also has some self-cementing properties. In the presence of water, this fly ash will harden and gain strength over time. This fly ash generally contains more than 20% lime (CaO).

Table 1 Chemical composition of fly ash from different types of coal

Component	Anthracite or bituminous	Sub-bituminous coal	Lignite
	%	%	%
SiO_2	20-60	40-60	15-45
Al_2O_3	5-35	20-30	20-25
Fe_2O_3	10-40	4-10	4-15
CaO	1-12	5-30	15-40
Loss of ignition	0-15	0-3	0-5

The determination of pH of fly ash from Iasi thermal power plant was performed using the following method: 50 g fly ash was mixed with 250 cm^3 distilled water. The mixture was shaken for 30 minutes, left 1 hour and then the pH was read. The obtained value of 5.8 situates the Iasi fly ash at the limit between acid and alkaline solution.

In general, fly ash is composed of three groups of solid components (table 1) [5].

The first group exhibits low water reactivity but possesses surface electric charge (may adsorb metal cations, for example Cd, Ni, Pb, or oxyanions). These solids are made of SiO_2, Al_2O_3, and Fe_2O_3.

The second group of components present in coal fly ash represents metals or metalloids adsorbed onto the oxide surfaces. The chemical behavior and release of heavy metals and oxyanions to water is highly interrelated to the surface electric properties of oxides.

The third group includes highly water reactive components. Generally, this group include oxides of Ca (215,000 ppm), Mg (16,000 ppm), K (23,000 ppm), Na (2,000 ppm) as well as gypsum ($CaS0_4$,$2H_2O$), and sulfite (SO_3). Some fly ashes from bituminous coal are acidic and have no liming value. Most fly ashes from lignite, however, have a considerable liming value because of their content of alkali oxides and significant quantities of anhydrous Ca- or Mg-sulfates. Fly ashes from bituminous coal are low in Ca- and Mg- [11].

Table 2 presents the chemical composition of fly ash from thermal power plant of Iasi and the admissibility conditions effectual in Romania for the three main oxides compounds that make up the fly ashes: silica (SiO_2), burnt lime (CaO), and alumina (Al_2O_3).

An interrelation exists between the content of oxides components and hydraulic activity of fly ashes from thermal power plant. The assessment of hydraulic activity according to oxides composition is based on the following indices [1]:

- The basicity index:

$$I_b = \frac{(\%)CaO}{(\%)SiO_2}$$

- The basicity module:

$$M_b = \frac{(\%)CaO + (\%)MgO}{(\%)SiO_2 + (\%)Al_2O_3}$$

- The activity index:

$$i_a = \frac{(\%)SiO_3}{(\%)Al_2O_2}$$

- The quality index:

$$I_c = \frac{(\%)CaO + (\%)CaS + (\%)0.5MgO + (\%)Al_2O_3}{(\%)SiO_2 + (\%)MnO}$$

Table 2 Chemical composition of fly ash from thermal power plant of Iasi

Thermal power plant	Chemical composition (adverage values)					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	Other
Iasi	% 50.05	% 32.42	% 7.58	% 5.60	% 3.76	% 0.59
	Σ = 90.05					
admissibility conditions	$SiO_2 + Al_2O_3 + Fe_2O_3 > 70$			min. 5.0	max. 3.0	max. 5.0

Table 3 Characteristics of fly ash from Iasi thermal power plant

Indices			Basicity module	CaO %	Fly ash type
basicity	activity	quality			
0.112	1.54	0.78	0.095	5.60	alumino-siliceous

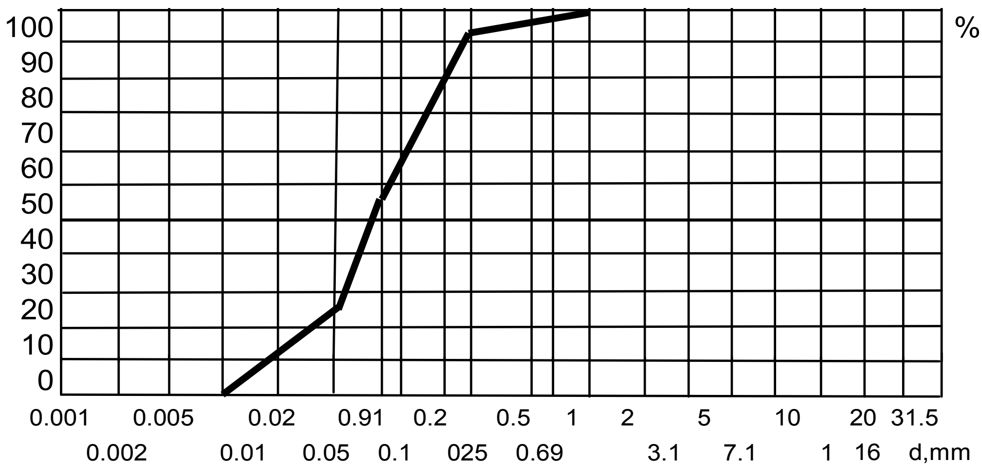

Fig.3 Grain-size distribution curve of Iasi fly ash

4 Physical features of fly ash from Iasi thermal power plant

Fly ash particles are generally spherical in shape and range in size from 0.5 µm to 100 µm (fig.3). 75% of the ash must have a fineness of 45 µm or less, and have a carbon content of less than 4%. The basic spherical shape indicates that particles were formed under uncrowded freefall conditions and a relatively sudden cooling maintained the spherical shape [16]. They consist mostly of silicon dioxide (SiO_2), which is present in two forms: amorphous, which is rounded and smooth, and crystalline, which is sharp, pointed and hazardous; aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3). Fly ashes are generally highly heterogeneous, consisting of a mixture of glassy particles with various identifiable crystalline phases such as quartz, mullite, and various iron oxides [7].

In terms of mineralogy, fly ashes structurally consist of a crystalline phase and a vitreous phase. Experimentally was found that ashes having a large quantity of vitreous phase have superior cementing properties [8].

The particle size distribution of most bituminous coal fly ashes is generally similar to that of silt.

The specific gravity of fly ash usually ranges from 2.1 g/cm^3 to 3.0 g/cm^3, while its specific surface area (measured by the Blaine air permeability method) may range from 1,700 to 10,000 cm^2/g.

The colour of fly ash can vary from tan to gray or black, depending on the amount of unburned carbon in the ash. The lighter is the colour the lower is the carbon content. Lignite or subbituminous fly ashes are usually light tan to buff in colour, indicating relatively low amounts of carbon as well as the presence of some lime or calcium. Bituminous fly ashes are usually some shade of gray, with the lighter shades of gray generally indicating a higher quality of ash.

The features of fly ash are: spherical shape, ball bearing effect that creates a lubricating action, higher strength, decreased permeability, reduced sulfate attack, reduced efflorescence, reduced shrinkage, reduced heat of hydration, reduced alkali silica reactivity, workability, improved finishing, reduced segregation, and reduced slump loss [18].

The permeability of well-compacted fly ash has been found to range from 10^{-4} to 10^{-6} cm/s, which is roughly equivalent to the normal range of permeability of silty sand to silty clay soil [17]. The permeability of a material is affected by its density or degree of compaction, its grain size distribution, and its internal pore structure [9]. Since fly ash consists almost entirely of spherical shaped particles, the particles are able to be densely packed during compaction, resulting in comparatively low permeability values and minimizing seepage of water through a fly ash embankment [10].

In Table 4 physical features of fly ash from Iasi thermal power plant are presented.

Table 4 Physical features of Iasi fly ash

Physical features		Iasi fly ash
Specific surface (Blaine No.) cm^2/g		3490
Density g/cm^3		2.209
Bulk density g/cm^3	loose state	0.735
	densest state	0.947

5 Compaction characteristics of fly ash from thermal power plant of Iasi

Table 5 Compaction characteristics of Iasi fly ashes

Compaction characteristics	Iasi fly ash
ρ_{dmax} (g/cm^3)	1.084
w_{opt} (%)	35

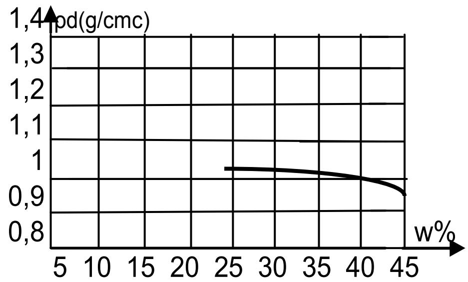

Fig.4 Modified Proctor compaction test curve

Compared to low calcium fly ash, optimum moisture content is low and maximum dry density is high for high calcium fly ash. Optimum moisture content is directly proportional and maximum dry density is inversely proportional to the carbon content [19].

In Table 5 and Figure 4 laboratory compaction characteristics (modified Proctor compaction test) of fly ashes from Iasi thermal power plant are presented.

6 Conclusion

The ash obtained by burning energy pitcoal in thermal power plant from Iasi, Romania has been used in this study. Generally, fly ash is the finer material (65% to 80%) of the coal ash and its properties vary greatly with coal source, type of coal burned and type of ash collector.

The reuse of fly ash as an engineering material primarily stems from its pozzolanic nature, spherical shape, and relative uniformity [4].

Comparing chemical composition with the admissibility conditions of fly ash from Iasi thermal plant the following results were obtained [2]:

- The fly ash obeys the conditions relating to major oxides components (SiO_2, Al_2O_3, and Fe_2O_3);
- CaO content is within permissible limits;
- For fly ash used in stabilized road structures SO_3 content is within a maximum of 4% although is greater than the permitted limit for use it as additive in concrete and mortars.

Advantages for the use of thermal ash are [14]:

- Fly ash captured from percolators of thermal power plants can be veritable cement that can be used in road works in the implementation of the form, foundation or base layers.
- The relatively high values for Ra_{226}, Th_{232} and K_{40}, [Bq / kg] are significantly reduced when fly ashes are included in the composition of some structures that constitute the material used in the implementation of road layers.
- Using of thermal ash, which is a pollutant waste, improves the ecological environment and diminishes landfill areas for storage of such waste.
- Having characteristics and composition of thermal fly ashes, base layer made with the above concrete has a high resistance to compression, and increases the viability of traffic routes, embankments, base layers and dams [22].

Table 11 presents the most important applications of fly ash in construction works [21].

Fly ash recycling also includes usage in: embankments and structural fill [3], waste stabilization and solidification, mine reclamation, stabilization of soft soils, flowable fill, roofing tiles, and roller compacted concrete dams [23].

Because fly ash contains toxic elements, disposal sites should be monitored for excessive buildup of heavy metals, salts and alkalinity. Potential heavy metal problems with power plant wastes are greatly reduced by the pronounced liming effects of the wastes. A problem that some consider an environmental issue is the movement of heavy metals from fly ash in ponds or landfills to drainage waters.

Table 6 Fly ash construction-related applications

Applications	Percent of total used
Cement production and/or concrete products	60
Structural fills or embankments	17
Stabilization of waste materials	14
Road base or subbase materials	5
Flowable fill and grouting mixes	2
Mineral filler in asphalt paving	2
Approximate Total	100

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