A Material Used in Substructure and Road Works: Physical Characteristics of Pozzolana Fly Ash from Thermal Power Plant of Iasi, Romania

ANCUTA ROTARU, VASILE BOBOC
Department of Roads and Foundations
Faculty of Civil Engineering and Building Services
“Gheorghe Asachi” Technical University of Iasi
Iasi, 43 Dimitrie Mangeron Blvd., 700050
ROMANIA
arotaru@ce.tuiasi.ro, arotaru502@yahoo.com

Abstract: - Fly ash, a coal combustion product once treated as waste and disposed in landfills, is used today in substructure and road works. The research of fly ash properties may solve the problems of treatment and intelligent use of this residual material. Using laboratory tests specimens, in this study the physical properties of pozzolanic coal fly ash, a bituminous coal waste of Iasi thermal power station, Romania, are investigated to analyze the composition of fly ashes, sometimes in comparison with the composition of those of Suceava thermal power station, Romania. The use of fly ash as a partial replacement for Portland cement is generally limited to the bituminous coal fly ash. Fly ash improves cement performance making it stronger, more durable, and more resistant to chemical attack. The recycling of fly ash has become an increasing concern in recent years and soil stabilization involves also the addition of fly ash to improve the engineering performance of a certain soil. The paper describes some benefits of fly ash use for our environment. The use of fly ash is accepted in recent years primarily due to saving cement, consuming industrial waste and making durable materials, especially due to the improvement in the quality stabilization of fly ash.

Key-Words: pozzolanic ash, fly ash from thermal power plant, cement-like material, physical methods, fly ash environmental issues

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 [20].

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 [26].

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 [7]. It was only in the latter part of the 19th century that pozzolanic cement was gradually replaced by Portland cement.

Pozzolana is a siliceous and aluminous material that in its natural state has a reduced or no capacity to cement. In the presence of water it reacts to calcium hydroxide at an ordinary temperature forming compounds with cementing properties. From the chemical point of view the pozzolans were defined as composite systems formed of calcium (CaO), silica (SiO$_2$) and alumina (Al$_2$O$_3$) in phases that may constitute solid-liquid disperse systems interacting and forming masses that harden in certain conditions and transform themselves into solid and strong materials. [31].

Modern pozzolanic cements are a mix of natural or industrial pozzolana and Portland cement. In addition to underwater use, the pozzolana's high alkalinity makes it especially resistant to common forms of corrosion from sulphates. Once fully hardened, the Portland cement-Pozzolana blend may be stronger than Portland cement due to its lower porosity, which also makes it more resistant to water absorption.

The Portland Pozzolana Cement is normal Portland cement blended with pozzolanic materials (power-station fly ash, burnt clays, ash from burnt plant material or silicious earths), either together or separately. This cement forms extra strong cementing material which resists wet cracking, thermal cracking and has a high degree of cohesion and workability in concrete and mortar.

2 Fly ash general features

Natural pozzolanic ash is still being used in various countries like Greece, Italy, Germany, Mexico and China [24], 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 (178 ppm), chromium (136 ppm), copper (112 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), mercury, molybdenum, radium, thorium, vanadium, along with dioxins and polycyclic aromatic hydrocarbons (PAH) compounds [13]. 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.

Fly ash, even when coming from a single power plant, is not homogeneous with respect to radioactivity content. If the fly ash comes from lignite, as it is the case of thermal power plant in Iasi, it will have a particular radioactive behaviour. Lignite contains natural radionuclides from the Uranium and Thorium series and also 40K, which will be transferred in fly ash, influencing with their activity and concentration the fly ash applications. Determination of the radioactivity content of fly ash can be realized gamma spectrometry and sometimes using an intensive and costly scientific method: alpha spectrometry although the use of such analysis isn't justified in many cases, as the activity levels found in fly ash are generally correct determined by gamma spectroscopy. The most determined radionuclides using gamma spectrometry are 238U, 226Ra and 210Pb [35].

Besides natural radioactivity content, radon exhalation from fly ash is another issue generally determined in its analysis. In road construction field, fly ash laboratory analyses are supplemented with in situ gamma spectrometry [32].

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 [23], river channel adjustments, retaining walls and shore defense and in no way construction intended for housing or social activities (fig.3). 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

Fly ash is one of the burnt coal byproducts (fig.4). Fly ash contents vary by the type of coal that is burnt. 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 [34].

The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned (anthracite, bituminous, subbituminous, and lignite) [13]. 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

<table>
<thead>
<tr>
<th>Component</th>
<th>Anthracite or bituminous</th>
<th>Sub-bituminous coal</th>
<th>Lignite</th>
</tr>
</thead>
<tbody>
<tr>
<td>% SiO₂</td>
<td>20-60%</td>
<td>40-60%</td>
<td>15-45%</td>
</tr>
<tr>
<td>% Al₂O₃</td>
<td>5-35%</td>
<td>20-30%</td>
<td>20-25%</td>
</tr>
<tr>
<td>% Fe₂O₃</td>
<td>10-40%</td>
<td>4-10%</td>
<td>4-15%</td>
</tr>
<tr>
<td>% CaO</td>
<td>1-12%</td>
<td>5-30%</td>
<td>15-40%</td>
</tr>
<tr>
<td>% Loss of ignition</td>
<td>0-15%</td>
<td>0-3%</td>
<td>0-5%</td>
</tr>
</tbody>
</table>

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 cm³ 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 as Table 1 presented [12].

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 SiO₂, Al₂O₃, and Fe₂O₃.

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 (CaSO₄·2H₂O), and sulfate (SO₃). 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- [18].

Tables 2 and 4 presents the chemical composition of fly ash from Iasi thermal power plant and the admissibility conditions effectual in Romania for the main oxides compounds that make up the fly ashes: silica (SiO₂), burnt lime (CaO), and alumina (Al₂O₃). In comparison, Tables 3 and 5 shows the chemical composition of fly ash from Suceava thermal power plant, another town from Moldavia region, Romania.

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 [4]:

![Fig.4 Fly ash made in a dry boiler](image-url)
- The basicity index:
\[ I_b = \frac{(\%)/CaO}{(\%)/SiO_2} \]

- The activity index:
\[ i_a = \frac{(\%)/SiO_2}{(\%)/Al_2O_3} \]

- The basicity module:
\[ M_b = \frac{(\%)/CaO + (\%)/MgO}{(\%)/SiO_2 + (\%)/Al_2O_3} \]

- 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

<table>
<thead>
<tr>
<th>Thermal power plant</th>
<th>Chemical composition (average values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iasi</td>
<td>SiO_2</td>
</tr>
<tr>
<td></td>
<td>%</td>
</tr>
<tr>
<td>Iasi</td>
<td>50.05</td>
</tr>
<tr>
<td>Σ = 90.05</td>
<td></td>
</tr>
</tbody>
</table>

Admissibility conditions:
- SiO_2 + Al_2O_3 + Fe_2O_3 > 70%
- min. 5.0%
- max. 5.0%

### Table 3 Chemical composition of fly ash from thermal power plant of Suceava

<table>
<thead>
<tr>
<th>Thermal power plant</th>
<th>Chemical composition (average values) determined from X-ray Fluorescent analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suceava</td>
<td>SiO_2</td>
</tr>
<tr>
<td></td>
<td>%</td>
</tr>
<tr>
<td>Suceava</td>
<td>57.50</td>
</tr>
<tr>
<td>(determination according to DIN EN 196-2)</td>
<td></td>
</tr>
<tr>
<td>Σ = 84.51</td>
<td></td>
</tr>
</tbody>
</table>

Admissibility conditions:
- SiO_2 + Al_2O_3 + Fe_2O_3 > 70%
- min. 5.0%
- max. 3.0%

### Table 4 Characteristics of fly ash from Iasi thermal power plant

<table>
<thead>
<tr>
<th>Indices</th>
<th>Basicity</th>
<th>activity</th>
<th>quality</th>
<th>CaO</th>
<th>Fly ash type</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.112</td>
<td>1.54</td>
<td>0.78</td>
<td>0.095</td>
<td>5.60</td>
<td>aluminosiliceous</td>
</tr>
</tbody>
</table>

### Table 5 Chemical investigation of Suceava fly ash

<table>
<thead>
<tr>
<th>Components</th>
<th>Determined values</th>
<th>Admissibility conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss of ignition</td>
<td>4.80</td>
<td>&lt; 5.00</td>
</tr>
<tr>
<td>SO_3</td>
<td>0.40</td>
<td>&lt; 3.00</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.01</td>
<td>&lt; 0.10</td>
</tr>
<tr>
<td>CaO_free</td>
<td>0.34</td>
<td>&lt; 1.00</td>
</tr>
</tbody>
</table>
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.5). 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 [27]. 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$_2$O$_3$) and iron oxide (Fe$_2$O$_3$). The carbonaceous material in fly ash is composed of angular particles. The particle size distribution of most bituminous coal fly ashes is similar to that of silt (less than 0.075 mm). Although subbituminous coal fly ashes are also silt-sized, they are slightly coarser than bituminous coal fly ashes [10].

Fly ashes are generally highly heterogeneous (fig.6), consisting of a mixture of glassy particles with various identifiable crystalline phase such as quartz, mullite, and various iron oxides [14].

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 [16].

The particle size distribution of most bituminous coal fly ashes is generally similar to that of silt (fig.5).

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 (fig.7). 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 [29]. The shrinkage determined at 7 days, 14 days and 28 days demonstrated that after 10 days it has been stopped and the material stabilized. The shrinkage varied from 0.70 mm/m at 7 days to 0.90 mm/m at 10 days. These values pose the shrinkage of the fly ash over an ordinary concrete class (ε < 0.42) but under ordinary mortar shrinkage (ε < 2 mm/m). The thermal conductivity coefficient is the same like brick coefficient and less than concrete coefficient. Fly ash has also good hydraulic properties. For a fly ash mixture with 20% water, 32% sand and 48% blended binders the average apparent density ρ is about 1840 kg/m^3 at 7 days and about 1770 kg/m^3 at 28 days. For a fly ash mixtures with 20% water, 32% sand and 48% blended binders the average apparent density ρ is about 1970 kg/m^3 at 7 days and about 1915 kg/m^3 at 28 days. 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 [28]. The permeability of a material is affected by its density or degree of compaction, its grain size distribution, and its internal pore structure [17]. 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 [22].

In Table 6 physical features of fly ash from Iasi thermal power plant are presented and in Table 7 some physical features of fly ash from Suceava thermal power plant are determined for comparing.

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

The compaction was realized on jolting table in two sequences: 30 jolts in 30 seconds for the first half fresh material and 30 jolts in 30 seconds for the steel mould filled with all fresh material quantity [1].

Table 8 Compaction characteristics of Iasi fly ash

<table>
<thead>
<tr>
<th>Compaction characteristics</th>
<th>Iasi fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρdmax (g/cm^3)</td>
<td>1.084</td>
</tr>
<tr>
<td>wopt (%)</td>
<td>35</td>
</tr>
</tbody>
</table>

Fig. 8 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 (fig.8). Optimum moisture content is directly proportional and maximum dry density is inversely proportional to the carbon content [30]. In Table 8 and Figure 8 laboratory compaction characteristics (modified Proctor compaction test) of fly ashes from Iasi thermal power plant are presented.

6 Environmental issues concerning fly ash from thermal power plants

Much of the fly ash generated in power plants is disposed in landfills. This ash, however, is capable of being recovered and used. Fly ash has been successfully used as a mineral admixture in Portland cement concrete being important in strengthening the concrete composition.
Physical properties of the fly ash influencing the Portland cement concrete are: texture, loss on ignition, pozzolanic reactivity, and chemical content. Another utilization of fly ash is substitute mineral filler in asphalt paving mixtures. This material consists of particles less than 0.075 mm grain size that fill the voids in a paving mix and serves to improve the cohesion of the asphalt cement and the stability of the mixture.

Fly ash is used as an embankment or structural fill material, particularly in Europe, performing as a well-compacted soil. As an embankment or fill material, fly ash is a substitute for natural soils weather it works at its optimum moisture content to ensure that the material is not too dry and dusty or too wet and unmanageable.

Fly ash disposal can be done in a wet mode or in a dry mode. Dry storage has some risks regarding material loose due to its dispersion by the wind and, consequently, air pollution, especially into populated areas. If the fly ash is mixed with water, the mixture prevents fly ash dispersion by wind.

The quantity of fly ash resulted in technological process of thermal power plants sensibly diminished due to retechnologization. Suceava thermal power plant, the comparative example of this study, generated only 30 thousand tons of fly ash in 2006 in comparison with 230 thousand tons resulted in the previous years. Nevertheless, Moldavian thermal power plants have an insufficient storage capacity and the fly ash is transported and stored as hydromixture.

Advantages for the use of thermal ash are:
- 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.

Table 9 presents the most important applications of fly ash in construction works. Fly ash recycling also includes usage in: embankments and structural fill, waste stabilization and solidification, mine reclamation, stabilization of soft soils, flowable fill, roofing tiles, and roller compacted concrete dams.
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 [19]. 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 9 Fly ash construction-related applications

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

### References


[27] Ono T. and Yamasaki Y., Particle Shape Control by Rounding Irregular Shaped Particles. Effects of Particle Shapes on Fluidity of Pulverized Coal in CWM and Fly-ash Particles, Funtai Kogaku Kaishi, 1998, 35(9).


