Use of Electric Arc Furnace Dust (EAFD) in Alkali-Activated Fly Ash Binder

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EXECUTIVE SUMMARY

The scenario of increasing fly ash (FA) production in south of Brazil from mineral coal-fired in power plants motivates the study of new alternatives for utilization of this by-product. Furthermore, Electric Arc Furnace Dust (EAFD) production in steel industries is also an environmental problem and alternatives for its disposal are needed. This study proposes the alkali-activation of fly ash as an eco-efficient binder and evaluates the mechanical properties and microstructure effects of EAFD addition to its matrix.

Class F [ASTM, 1998] fly ashes used in this study had low calcium content, were predominantly in the vitreous phase and had some crystalline inclusions of mullite, hematite and quartz. The alkali-activator used was sodium hydroxide 98% pure commercial type (NaOH). Alkali-activation characteristics for the region were studies before, and best compressive strength results were obtained using a molar ratio Na₂O/SiO₂ of 0.4 – main source of Na₂O is the alkali solution of NaOH, while fly ashes are the source of SiO₂. Hygrotermic curing was set at 70°C during a period of 24 hours and is necessary for accelerating strengthening reactions. EAFD used as addition was obtained from a semi-integrated steel mill industry. In mortars, quartz sand was used as fine aggregate, divided in 4 granulometric bands (1.2; 0.6; 0.30; and 0.15 mm), representing each ¼ of total aggregate mass.

Compressive strength test were carried out on mortars and XRD and FTIR analysis were performed on pastes samples. EAFD additions were made with 5%, 15% and 25% of fly ashes mass, and mortars were prepared at a 1:3 ratio (fly ash:sand)

The influences of different addition ratios in compressive strength results indicate the following: 5% EAFD increases strength of samples some 10% to 17% comparing with reference samples of 0% addition; higher compressive strength results were obtained with 15% EAFD addition, which presented a maximum value of 21.15 MPa obtained at 180 days; samples with 25% of EAFD have shown that this ratio exceeds the limit for dust addition, presenting negative influence after the age of 180 days comparing to reference samples.

XRD spectres of alkali-activated samples at the age of 1 day show that crystalline phases were formed after curing at 70 °C temperature. Crystalline peaks of albite were not identified at the age of 1 day in samples containing EAFD, and natron peaks tend to decrease as EAFD addition ratio increases. Characteristic peaks of EAFD (quartz, mullite and hematite) are identified in all samples and also tend to decrease with the addition ratio of EAFD. Same characteristics are identified through different ages of 28 and 180 days.

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FTIR analysis shows that the process of alkali-activation is successful in all samples, regarding the characteristic differences with the fly ash in its original state. Fly ash band at 1084 cm\(^{-1}\) shifts to around 1000 cm\(^{-1}\) in samples with EAFD addition, demonstrating no interference in polymerization and formation of aluminosilicate gel. No wavelength difference was found between reference and EAFD added samples through different ages. Results demonstrate potentiality of binder proposed, especially for precast concrete production. Low carbon emission to atmosphere, sustainable characteristics, reduced energy demand and the use of wastes and by-products are valuable positive aspects. Microstructural XRD analysis suggests the occurrence of reactions with the crystalline EAFD material. FTIR analysis indicates that the additions have no interference in polymerization and aluminossilicate gel formation.

INTRODUCTION

Portland cement, a material of choice for over the last centuries, praised for its mechanical performance, competitive price, and versatility, is also an issue of concern for its environmental impact. Resource and energy consumption and carbon dioxide emission are problems faced by cement industry. Production and study of environmental friendly binders are therefore needed, and alternative materials are listed as choice options for tackling the problem.

Alkali-activated binders have been objective of several studies over the last half century (PACHECO-TORGAL et al., 2008) and are matter of interest in scientific communities for its eco-efficient properties and the possibility of use of different types of industries by-products and wastes as source material, some of them already in use as additions to Portland cement (BUSCHWALD and SCHULZ, 2005). Alkali-activation briefly consists of submitting a source material with aluminates and silicates into an alkali aggressive environment in such way that the former existing bonds change structure into an aluminosilicate gel that provides mechanical strength. These binders are produced by mixing amorphous materials rich in SiO\(_2\) and Al\(_2\)O\(_3\) and submitting them to a strong alkaline medium, using activators such as NaOH, KOH and Na\(_2\)SiO\(_4\). The alkaline medium breaks the covalent bonds Si – O – Si – and Al – O – Al of the precursor material and promotes the polycondensation of the Si – O – Al type into polymeric chains, forming sodium aluminosilicate gel, which is responsible for the durability properties of this material (PALOMO et al., 1999). One such possible alternative is cement obtained from alkali-activated fly ashes (FA), as proposed for the materials in the south of Brazil in this and in previous work (VARGAS, 2006).

The scenario in south of Brazil stimulates researching alternative uses for thermoelectric by-products: the region possesses about 89% of the mineral coal reserves in the country, a total of about 28.8 billion tons. Nevertheless, these resources present a low calorific coefficient of 2600 to 3200 kcal/kg and a high level of fly ashes production – 1 kg of fired coal generates approximately 1 kWh and 400 g of fly ashes. Currently, coal-fired electrical power plants generate about 2 million tons of fly ashes in the region each year. Of this total, 20% to 30% is used by cement and concrete industries in the region, and the rest is disposed into coal strip mining trenches, which may cause extensive environmental damage, such as air, soil and groundwater contamination. Considering the projects of new thermoelectric power plants, coal extraction in the region is predicted to increase from 1.6 to 4.2 million tons per year (ROHDE, 2006; VARGAS, 2006).

Produced in steel mills, electric arc furnace dust (EAFD) is classified as a hazardous waste, not disposable in the environment, according to the Resource Conservation and Recovery Act of the U.S. Environmental Protection Agency (UNITED STATES OF AMERICA, 2008). Its general composition contains heavy metals such as Lead (Pb), Chromium (Cr) and Cadmium (Cd).
Techniques proposed for recycling these metals are still expensive in the region, and further studies of processes for immobilizing the material are still needed.

Several alternative matrices were proposed for immobilizing toxic waste. Palomo and Palacios (2002) evaluated the stabilisation/solidification capacity of alkali-activated fly ash cementing matrix in the presence of toxic elements, and leaching tests carried out indicated that this new binder was able to stabilise and solidify lead in a very efficient way. Deja (2002) studied the properties of alkali-activated slag pastes in the presence of Zinc (Zn), Cd, Cr and Pb ions and found that the degree of immobilization was very high (exceeding 99.9%). Shi and Fernández-Jiménez (2006), reviewing the progresses in use of alkali-activated binders for stabilization/solidification of hazardous and radioactive wastes, concluded that the leachability of contaminants in these binders is lower than that from hardened Portland cement stabilized wastes. Palomo and Fuente (2002) show that boron does not significantly alter the hardening process of alkali-activated fly ashes, that its presence hardly modifies mechanical strength and, taking leaching results into account, that the alternative system was more effective than traditional ones. Vargas (2002) studied the effects of EAFD additions in Portland cement concrete blocks and, although some heavy metals were immobilized, the setting time of the binder was severely altered by the presence of zinc.

The purpose of this study was to evaluate the effects of three EAFD addition ratios to a previous studied binder made of alkali-activated fly ashes (VARGAS, 2006). Mechanical influence of additions was determined in compressive strength tests and microstructure characterization was made using XRD analysis and FTIR wavelength comparisons.

**EXPERIMENTAL**

**Materials**

Class F (ASTM, 1998) fly ash generated by a coal-fired power plant located in southern Brazil was used in this study. Ashes had low calcium content, were predominantly in the vitreous phase and had some crystalline inclusions of mullite, hematite and quartz. XRD spectra containing crystalline peaks are shown in Figure 1 and physical and chemical characterization of fly ash in Table 1.

![XRD spectra of fly ash](image)

**Figure 1:** XRD spectra of fly ash; Q = Quartz; M = Mullite; H = Hematite

The alkali-activator used was sodium hydroxide 98% pure commercial type (NaOH) with 2.13 g/cm³ of density.

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>MgO</th>
<th>K₂O</th>
<th>SO₄</th>
<th>I.R.³ (%)</th>
<th>L.O.I² (%)</th>
<th>Specific density⁵ (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.09</td>
<td>24.02</td>
<td>1.15</td>
<td>6.85</td>
<td>0.21</td>
<td>1.77</td>
<td>0.81</td>
<td>1.75</td>
<td>0.34</td>
<td>97.0</td>
<td>0.02</td>
<td>2.17</td>
</tr>
</tbody>
</table>

³I.R. insoluble residue.
EAFD used as addition was obtained from a semi-integrated steel mill industry, collected by filters outside the electric arch oven. Chemical composition of the material indicates majority of Iron and Zinc, according to Table 2. XRD spectra of EAFD present crystalline peaks of quartz (SiO₂), hematite (Fe₂O₃), franklinite (Fe₂O₃ZnO), zincite (ZnO) and cromite (FeO.Cr₂O₃), as shown in Figure 2.

![Table 2: Chemical composition of EAFD (% of mass)](image)

<table>
<thead>
<tr>
<th>Na</th>
<th>K</th>
<th>Fe</th>
<th>Mg</th>
<th>Ca</th>
<th>Pb</th>
<th>Si</th>
<th>Mn</th>
<th>Cd</th>
<th>Cr</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.35</td>
<td>1.08</td>
<td>27.30</td>
<td>1.87</td>
<td>2.54</td>
<td>0.90</td>
<td>1.70</td>
<td>2.06</td>
<td>0.37</td>
<td>0.13</td>
<td>37.25</td>
</tr>
</tbody>
</table>

![Figure 2: XRD spectra of EAFD](image)

In mortars, quartz river sand was used as fine aggregate, divided in 4 granulometric bands (1.2; 0.6; 0.30; and 0.15 mm), representing each ¼ of total aggregate mass.

Analysis of metal concentration in leaching samples, obtained according to a Brazilian procedure (ABNT, 2004b), is presented in Table 3. Results of Cd and Pb concentrations are above the index limit (ABNT, 2004a), thus classifying EAFD as “Class I” hazardous waste - not disposable in the environment.

![Table 3: EAFD leaching test results (mg/l)](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Zn</th>
<th>Na</th>
<th>Cd</th>
<th>Cr</th>
<th>Pb</th>
<th>Cr+6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mg/l)</td>
<td>913</td>
<td>565</td>
<td>6.9</td>
<td>0.002</td>
<td>61</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Limit (ABNT, 2004a)</td>
<td>nd</td>
<td>nd</td>
<td>0.5</td>
<td>5</td>
<td>1</td>
<td>nd</td>
</tr>
</tbody>
</table>

nd: not defined

**Methods**

Experimental work was made to verify the influence of EAFD additions to alkali-activated fly ash mortar samples, evaluating compressive strength. Paste samples were submitted to XRD analysis and FTIR spectroscopy for wavelength comparisons.

Alkali-activation characteristics for the region were studied before (VARGAS, 2006), and best compressive strength results were obtained using a molar ratio Na₂O/SiO₂ (N/S) of 0.4 – in which the main source of Na₂O is the alkali solution of NaOH, while fly ashes are the source of SiO₂. Hygrotermic curing was set at 70°C during a period of 24 hours necessary for accelerating strengthening reactions.
Pastes and mortar were prepared with N/S = 0.4 with consistency determined according to ABNT (2003). Mortars were prepared at a 1:3 ratio (fly ash:sand; four different granulations), and EAFD additions were made with 5%, 15% and 25% of fly ashes mass. NaOH alkaline solution was prepared 15 hours before mixing with fly ashes to prevent that heat generated in the reaction with water would accelerate alkali-activation. The parameter for water addition was the consistency index of each mortar, established at 160 mm ± 20 mm. This index was adopted because it ensured that the material condensed easily in the 5.0-cm-Ø and 10-cm-high cylindrical molds without exudation. Molar composition to obtain alkali-activated fly ash mortars using NaOH solution is presented in Table 4. Mortars were casted in the cylindrical molds according to ABNT (1996) procedures: 4 layers and 30 pestle strokes applied to each layer.

**Table 4: Molar composition used to obtain alkali-activated fly-ash mortars using NaOH solution.**

<table>
<thead>
<tr>
<th>Pastes and mortars</th>
<th>Pastes*</th>
<th>Mortars+</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/S</td>
<td>S/A</td>
<td>H/N</td>
</tr>
<tr>
<td>0.4</td>
<td>4.45</td>
<td>7.47</td>
</tr>
</tbody>
</table>

N = Na₂O; S = SiO₂; A = Al₂O₃; H = H₂O; w/b - water/binder ratio
* necessary ratios to obtain normal consistency.
+ necessary ratios to ensure that mortar consistency index was within the limits established in the study methods (160 mm ± 20 mm).

## RESULTS

### Compressive strength tests
Mean compressive strength values for N/S 0.40 samples with EAFD additions are shown in table 1.

**Table 4: Mean compressive strength results (MPa)**

<table>
<thead>
<tr>
<th>EAFD/FA</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Age (days)</td>
</tr>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0%</td>
<td>5.96</td>
</tr>
<tr>
<td>5%</td>
<td>7.02</td>
</tr>
<tr>
<td>15%</td>
<td>8.06</td>
</tr>
<tr>
<td>25%</td>
<td>10.47</td>
</tr>
</tbody>
</table>

Figure 1 (a) represents mean compressive results through ages and Figure 1 (b) shows strength gain (%) of EAFD added samples in comparison with the reference 0% EAFD. The influences of different addition ratios in compressive strength results indicate the following: 5% EAFD increases strength of samples some 10% to 17% comparing with reference samples of 0% addition; higher compressive strength results were obtained with 15% EAFD addition, which presented a maximum value of 21.15 MPa obtained at 180 days; samples with 25% of EAFD have shown that this ratio exceeds the limit for EAFD addition, presenting negative influence after the age of 180 days comparing to reference samples.
Microstructural Analysis

XRD

XRD spectres of alkali-activated samples at the age of 1 day (Figure 2) show that crystalline phases were formed after curing at 70 °C temperature. Crystalline peaks of albite were not identified at the age of 1 day in samples containing EAFD, and natron peaks tend to decrease as EAFD addition ratio increases. Characteristic peaks of EAFD (quartz, mullite and hematite) are identified in all samples and also tend to decrease with the addition ratio of EAFD. Same characteristics were observed at the age of 180 days (Figure 3).

Figure 3: (a) Compressive strength (MPa); (b) Strength gain (%)

Figure 4: XRD spectres of: (a) EAFD; (b) FA; and paste samples at age of 1 day with: (c) 0% EAFD; (d) 5% EAFD; (e) 15% EAFD; and 25% EAFD
**Figure 5:** XRD spectres of: (a) EAFD; (b) FA; and paste samples at age of 180 day with: (c) 0% EAFD; (d) 15% EAFD; and (e) 25% EAFD

Observation of XRD peaks of samples with 25% EAFD through time (Figure 6) shows no formation of albite. Natron peaks, present in early age of 1 day, diminishes at the age of 180 days, suggesting that the carbonate may be combining with other elements in the matrix.

**Figure 6:** XRD spectres of: (a) EAFD; (b) FA; and paste samples with N/S 0.4 and 25% EAFD at the ages of: (c) 1day; (d) 28 days; (e) 91 days and (f) 180 days

**FTIR**

Considering FA and alkali-activated samples, independently of age of analysis (Figure 7 and 8), there are characteristic absorption bands common to fly ash before and after activation, namely 3435, 1625, 796, 779, 693, 559 cm\(^{-1}\). As observed in FTIR spectra of original fly ash bands (Figure 7, sample b) 3450 cm\(^{-1}\) and a 1650 cm\(^{-1}\) frequencies indicate the presence of water molecules, results that agree with previous studies (BARBOSA et al., 2000) that identified the presence of water in original metakaolin and in metakaolin alkali-activated samples.

During alkali-activation, bands near 3450 cm\(^{-1}\) and 1650 cm\(^{-1}\) are more intense than original fly ash bands, as observed in figures 7 and 8. Band near 3450 cm\(^{-1}\) is related to vibration and stretching of water molecules H-O-H, and band near 1650 cm\(^{-1}\) is related to angular deformations in H-O-H bonds (PALOMO et al., 1999).
Figure 7: FTIR Spectra of: (a) EAFD; (b) FA; paste samples with 0% EAFD at: (c) 1 day; (d) 28 days; (e) 91 days; (f) 180 days; paste samples with 15% EAFD at: (g) 1 day; (h) 28 days; (i) 91 days; (j) 180 days

![FTIR Spectra](image)

Figure 8: FTIR Spectra of: (a) EAFD; (b) FA; paste samples with 180 days with: (c) 0% EAFD; (d) 5% EAFD; (e) 15% EAFD; and (f) 25% EAFD

Absorption bands near 796 cm\(^{-1}\) e a 693 cm\(^{-1}\) are related to the presence of aluminium and quartz, respectively. Bakharev (2005) proposed that the band near 800 cm\(^{-1}\) is related to vibrations in \(\text{AlO}_4\) and that bands near 688 cm\(^{-1}\) are due to symmetrical stretching vibrations in Si-O-Si bonds in fly ash samples.

560 and 460 cm\(^{-1}\) bands were also identified in fly ash samples before and after alkali-activation. Palomo et al. (1999) obtained similar results and proposed that band 560 cm\(^{-1}\) indicates the presence of mullite (octahedral formation). In XRD analysis these results are confirmed with the presence of crystalline peaks of mullite in figures 4, 5 and 6.

Characteristic bands cited above (796, 779, 693, 559 e 461 cm\(^{-1}\)) were identified both in original fly ash and in alkali-activated fly ash samples (Figures 7 and 8). As these bands are related to Si-O-Si e Si-O-Al bonds, FTIR results confirm XRD analysis, thus demonstrating the chemical stability of crystalline quartz and mullite in a strong alkali environment.

Band 1090 cm\(^{-1}\) from original fly ash is altered to regions near to 1000 cm\(^{-1}\) in alkali activated samples. This is proposed to be related with vibrations in Si-O and Al-O bonds, and reducing the frequency in this region suggests that vitreous components of fly ash are reacting with the alkali-activator and that different products are being formed – namely the aluminosilicate gel (FERNÁNDEZ-JIMENEZ et al., 2005).

Comparisons of alkali-activated fly ash samples and samples with EAFD additions show no difference in frequencies of bands in FTIR analysis. These results indicate that alkali-activation is successful in all samples and that EAFD additions have no harmful interference in the formation of aluminosilicate gel and the in the polymerization reactions.

CONCLUSIONS
Results demonstrate potentiality of binder proposed here, especially for precast concrete production. Low carbon emission to atmosphere, sustainable characteristics, reduced energetic demand and the use of wastes and by-products are valuable positive aspects for society and scientific communities. Mechanical properties of this binder can be improved using fly ash containing a higher level of SiO₂ and using processes for reducing the fly ash mean particle size. Microstructural XRD analysis suggests that albite, natron and characteristic EAFD crystalline peaks decrease intensity according to EAFD addition ratio, indicating the occurrence of reactions with the crystalline material. FTIR analysis indicates that original fly ash is successfully alkali-activated and that no significant difference is found among the EAFD addition ratios, proving that the additions have no interference in polymerization and aluminosilicate gel formation.

REFERENCES


