Leachability of Heavy Metals from Autoclaved Fly Ash-Lime Building Bricks

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Abstract

The fly ash as a byproduct of coal-fired power plants constitutes vital ecological problems. In Turkey, approximately 15 million tons of ashes are generated via the combustion of 40 million tons of lignite yearly. Worldwide, a number of investigation and applications were undertaken to utilize fly ash in order to overcome the environmental problems. One of the application area of fly ashes is the production of building bricks. Characterization of fly ash samples from Seyitomer and Yatagan coal-firing power plants were conducted in this study. TCLP 1311, ASTM3987-85 and EN 12457-2 leaching tests on the cylindrical fly ash/lime brick (FA/LB) samples which were produced from Seyitomer and Yatagan thermal power plant fly ash-lime mixtures were performed to determine the leachability of some chosen trace elements. The results show that the release of all trace elements was lower than the hazardous material limit values of waste acceptance. Thus, non-fired fly ash bricks are an advantageous way to solving environmental effect of disposal of fly ashes.

Keywords: coal fly ash, fly ash/lime brick, leaching, trace elements

1. Introduction

According to the statistical data, Turkey is in the first ten ranking major countries of the world with coal and lignite production and consumption (http://www.enerji.gov.tr/tr-en-US/Pages/Coal). The hard coal and lignite reserves of Turkey are 1.3 billion tonnes and 13.9 billion tonnes respectively. Approximately 68% of the total lignite coal reserves in our country are low calorie and 23.5% of them are 2000-3000 kcal/kg (http://www.enerji.gov.tr/tr-en-US/Pages/Coal).

Turkey's primary energy production totaled 41.8 Mtoe in 2016, of which domestic coal provided 52.7%. Most of the lignite coal is used in energy production. Energy demand of Turkey has increased twofold over the last two decades, and this trend seems to continue in the future with an average increase of 4% per year. In the first half of 2018, 33% of Turkey's electricity production of 53,9TWh was generated in coal-fired thermal power plants (https://euracoal.eu/info/country-profiles/turkey).

In 2017, power plants created about 10 million tons of residual product. The amount of fly ash ponded near the power plants has reached already 150 million tonnes (Akar, 2003; Akar et al, 2010). Therefore, fly ash (FA) destruction, poses a major problem in Turkey. Fly ash is generally classified as hazardous waste because it is contaminated with a small amount of contaminants; including heavy metals. The assessment of the risk arising from FA is of particular importance during its utilization (Liu et al, 2009; Kosson et al., 2000; Ural, 2005; Carlson and Andriano, 2005; ASTM C20-11, 2005)

Most of the FA derived buildings materials such as concrete, cellular aerated concrete, foam concrete, building bricks, FA stabilized soil and many others will be exposed to rain. Therefore, it is significant to determine the leachability of pollutants such as toxic metals from FA derived materials. Laboratory leaching tests are usually conducted to assess the long-term effect of possibly hazardous constituents on soil, surface and groundwater. They define leach potential of pollutants during the use or discarded mate-rials (Getin et al., 2012; Cinquepal-mi et al., 2008). Unfortunately, there is no standard or accepted method for testing the effect of rain on pollutant leachate from FA and FA derived building materials. Therefore, researchers developed different leaching tests to describe and evaluate the pollutants that could be released from FA. There is a variety of leaching tests with different varia-bles such as solid to liquid ratio (S/L), chemical reagents, temperature and contact time (Terzic et al., 2012; Johnson et al., 1999). The procedures simulate leaching behavior of coal ash and the results obtained are generally not directly comparable; However, they can show the general mobility of toxic elements in fly ash (Cappuyns and Swennen, 2008; Vitkoca et al., 2009).

The number of the research on description and industrial application of fly ash have enlarged significantly over the years. Consequently, nowadays fly ash can useable in many different sectors (Kosson, 2000, Lea, 1980; Kouskouzas et al., 2010; Lee et al., 2017). Limited amount of FA, primarily for cement and concrete production, is being employed in Turkey. Using FA as a main raw material to make light-weight building bricks is recently investigated with encouraging results (Prinya and Ubol-luk, 2018; Çiçek and Cincin, 2015). Re-cently, tests have been done on determining the leachability of heavy metals from FA and FA derived materials (Tanrverdi, 2006; Zermeno et al., 2013; Hjelmelmar et al., 2007; Lidelöw and Lagerkvist 2007; Ferreira et al., 2003)).

The objective behind conducting this research work was to study chemical, mineralogical and morphological characteristics of fly ashes and evaluate the extent to which pollutants leach from the autoclaved fly ash/lime bricks (FA/LB). For this purpose, TCLP-1311 method (US-EPA 1992), ASTM D3987-85 (ASTM 2004) (ASTM, 2004) and one stage water batch test
EN-12457-2 (CEN 2002) (CEN, 2002) were applied on the FA/LB samples.

2. Materials and Method

2.1 Fly ash and fly ash/lime brick samples and characterization

Fly ash samples were taken from two different lignite fired power plants from the western Turkey. The Seyitomer (SO) and Yatagan (Y) power plants use low quality lignite and generate about 0.9 million and 1.1 million ton of fly ash, respectively. Seyitomer fly ash (SOFA) and Yatagan fly ash (YFA) can be categorized as F-class low-lime FA according to ASTM C 618 standard (ASTM 2000). Using a fly ash and quenched lime, a cylindrical fly ash-lime brick (FA/LB) of 45 mm diameter and 100 mm length was made at 12-bar pressure with laboratory size steam autoclave as described by Cicek & Cincin (2015).

In this work, particle size analysis of the SOFA and YFA were determined using Horiba brand LA 950 V2 laser diffraction particle size analyzer. The specific surface area of both fly ashes were determined in accordance with ASTM C 204-11 (ASTM, 2005). The chemical analysis results of the fly ash samples was conducted using Analytic Jena NovaA 300 AAS. Agilent Technologies 7700 series ICP-MS was used to determine the trace element concentrations. Physical and chemical properties of the SOFA and YFA are tabulated in Table 1. The particle size distributions are shown in Figure 1.

The mineralogical compositions were recognized using Rigaku Miniflex-2 X-ray diffractometer (XRD) at Cu–Kα radiation.
Morphological investigations were conducted with Jeol JXA 733 microprobe, scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS).

2.2 Batch leaching tests

Mobility of trace elements in fly ash/lime bricks was determined by using serial leaching test, TCLP-1311 method, ASTM D3987-85 and one stage water batch test (EN-12457-2). Each procedure needs the application of specific test conditions. TCLP-1311 method and ASTM D3987-85 were applied on FA/LB samples as described by Akar et al. (Akar et al., 2012). The EN 12457-2 leaching test was carried out at a ratio of L/S=10 L/kg. A mixed samples, 40g FA/LB samples and 400 ml deionized water, was placed in 500 ml polyethylene bottles. The mixture in the bottles was then shaken for 24±0.5 h at 10 rpm in a horizontal oscillating shaker. All the mixtures were kept for 5 minutes, and then the aqueous phase separated by decantation. After the pH of the leachate was measured, it was filtered through a 0.45 mm membrane filter paper with a vacuum filtration system and then acidified to pH<2 using high purity nitric acid for analysis. The leached amount of the components was matched with the leaching limit values suggested by the European Council decision 2003/33/EC (C. Decision, 2003).

3. Results and Discussions

3.1 Physical/chemical and mineralogical characterization of Seyitomer and Yatagan fly ashes

Specific gravities, particle size, specific surface area and pH are the most important physical and chemical factors for determining the leaching behavior of the pollutants from fly ash (Koukouzas et al., 2011; Akar et al., 2012). Figure 1 depicts size distributions for SOFA and YFA. The graph shows that particle size of SOFA is below 0.800 mm and 0.212-0 mm fraction makes up 76.06% of the ash. YFA is below 0.300 mm and 0.212-0 mm fraction makes up 84.14% of the ash. SOFA has a triple modal particle size histogram (Figure 1a), while YFA has a monomodal distribution (Figure 1b). Some physical properties of SOFA and YFA tabulated in Table 1.

Behavior of trace elements in aqueous environment is related to the natural pH value of fly ash. The pH of the slurry obtained by adding 200 ml deionized water and 10 g fly ash was measured and recorded at 1 hour intervals over a 24 hour period using a WTW brand pH/Cond. 320 portable water meter (Akar et al., 2012). Both fly ashes have the alkaline character, which can be explained by the calcium content being mainly in the form of lime and soluble metal salts, oxides and carbonates. Chemical analysis and trace element concentrations are given in Tables 2.

Mineralogical properties are another important factor for the leachability of trace elements from fly ash. The XRD analyses on SOFA and YFA in comparison with SOFA/LB and YFA/LB were performed to determine the mineralogical properties (Figure 2a, Figure 2b). The crystalline phases were identified by powder X-ray diffraction (XRD) using RIGAKU-Dmax-2200 PC equipment, operating at 30 kV and 15 mA with Cu–Kα radiation. Both fly ash samples contained both the crystal and the amorphous phase. The crystalline phases generally consist of quartz, mullite, lime, iron oxides, etc. The amorphous phases are predominantly made of aluminum. However, some phases contain silica and silicates containing calcium, magnesium and iron at various concentrations. X-ray patterns and assignment of the peaks of the FA and FA/LB are given in Figure 2a and Figure 2b.
jor crystalline phase of the Seyitömer fly ash was determined as quartz (Figure 2a). Magnesioferrite is the second dominating mineral. It has small amounts of anorthite, anhydrite, hematite, mullite and lime.

Quartz is found as the major component in the autoclaved SOFA/LB samples. Mullite and lime peaks have disappeared and new phases was occurred such as katoite (Ca$_3$Al$_2$(Si$_{0.64}$O$_{2.56}$)(OH)$_{9.44}$), tobermorite Ca$_4$(Si$_6$O$_{15}$)(OH)$_2$(H$_2$O)$_5$ and calcium silicate hydrate 2CaO(SiO$_2$)$_2$.4(H$_2$O) (Fig 2a).

As can be seen from Fig. 2b, high content of Quartz (SiO$_2$) and anorthite (CaAl$_2$Si$_2$O$_8$) were found in YFA. Furthermore, minor amounts of hematite (Fe$_2$O$_3$), lime (CaO), gehlenite (Ca$_3$Al$_2$SiO$_7$), anhydrite (CaSO$_4$), hematite (Fe$_2$O$_3$) and mullite (Al$_6$Si$_2$O$_13$) were observed. Quartz (SiO$_2$) was determined as the main crystalline phase of the YFA/LB like SOFA/LB. Similarly, mullite and lime peaks have disappeared in autoclaved YFA/LB samples. Katoite (Ca$_3$Al$_2$(SiO$_4$)$_{1.5}$(OH)$_6$), tobermorite and calcium silicate hydrate (CSH) were detected in YFA/LB. The formation of calcium silicate hydrates (CSH), and calcium alumino-silicate hydrates (CASH) occurs as a result of pozzolanic reaction of fly ash with lime. Low alkalinity helps the formation of C-S-H phase while the high alkalinity encourages the poorly crystalline C-(A)-S-H phase formation.

Hollow and spherical particles, which are called as cenospheres and small spherical particles within a large glassy sphere, called plesospheres can be seen in Fig. 3. Some clathro sphere particles with partial melting or eroding on their surface can also be seen in Fig. 3a and 3c.

SOFA, generally composed of irregularly shaped particles and agglomerates, also contains in small amount and different sizes of microspheres and irregularly shaped unburned carbon particles. (Fig. 3a). Particle sizes were observed ranged from submicron to greater than 100 μm. These findings are well matched with the triple modal size distribution plot of SOFA (Fig 1a). Results of SEM showed that SOFA also contains many porous particles that the particles contain CAS, anhydrite and kaolinite. As seen from the Figure 1a irregular agglomerated form of SOFA composed mainly of CaSO$_4$, lime and alkali alumin silicate composites.

It is very different from the structure of SOFA with the individual spherical particles of YFA. Larger parts of the YFA particles consist of spherical and partially agglomerated particles (Figure 3c). In addition, particle size distributions are in the middle narrow range. This finding is consistent with the size distribution given in figure 1b. SEM photos of FA/LB brick are shown in figure 3b and figure 3d. It is observed that after hydrothermal treatment of FA/LB new crystalline phases were formed. The crystalline phases are shaped on the surface of fly ash particles. They cover the surface of fly ash particles in form of short and long needles. These phases are mainly C-S-H in the form of tobermorite and small amount of katoite as determined also by XRD analyses.

3.2. Results of leaching potential of the trace elements in the fly ash/lime brick samples

In this part of the experimental study, typical leaching tests (TCLP 1311, ASTM3987-85 and EN-12457-2) were conducted to determine the solubility of the trace elements in FA/LB under a weak acid and water environment.
There were a number of previous studies indicating that leaching behavior of the elements from fly ash samples can change depending on the pH of the leach solution (Dahl et al., 2008; Iyer, 2002; Valentin et al., 2009; Sasmita et al., 2017). Therefore, the pH values of the samples were continuously monitored during the test. pH variations measured during toxicity tests are illustrated in Figure 4.

During the TCLP tests, pH values of all samples were measured as ranging between 3-5.5 (Figure 4a). The initial pH of SOFA, YFA and their FA/LBs are found as lower than final pH under TCLP test conditions. Initial pH values of SOFA and YFA under ASTM D3987 and EN-12457-2 test conditions were found as slightly higher than the final pH values. Both initial and final pH values of samples for ASTM D3987 test were lower than those of EN-12457-2 mainly due to L/S ratio. As seen from Figure 4b and 4c, the final pH values of the leachate are changing between 12 and 13.5 for both FA in agreement with the free lime content. Final pH of YFA and YFA/LB was slightly higher than that of SOFA and SOFA/LB due to free CaO content of YFA and YFA/LB. Secondary precipitation reactions can occur in the presence of soluble alkali phases (free calcium oxide, soluble metal salts, oxides and hydroxide) in the test sample. This may bound the solubility of some metals (Akar, 2012; Kim, 2006).

### 3.2.1 pH measurements

The leached element ratios (%) from the fly ash lime brick samples under TCLP (in TCLP test procedure sodium acetate buffer was used at pH 4.99), ASTM D3987 and EN-12457-2 test conditions were given in Figures. 5-6.

Leaching test was performed on FA/LBs showed no presence of Hg, Ti, Ar, Se in investigated samples. Because, in alkaline FA/LB, as release decline with rising pH. In leaching conditions of the method, it was seen that the elements were higher in TCLP test conditions. Most of the selected trace elements were leached at higher proportions under TCLP test conditions (Figure. 5 and Figure 6).

It can be seen from the Figure 5, Ba, Co, Mo, Zn and Cu leached in weakly acidic media and were solved at higher amounts in SOFA/LB. Cd, Cr, Ni, Sr, and Pb also show solubility but at very little percentages for SOFA/LB. The solubility ratio of metals in TCLP was greater than the solubility ratio of metals in batch leach test (ASTM and EN) due to the metal solubility generally decreases with increasing pH. The leached elements in deionized water because of the batch leaching tests (ASTM and EN) also shown in Figure 5. Ni, Pb, Cu and Cd did not leach from the SOFA/LB. Most of selected elements dissolved relatively low amounts under ASTM and EN test conditions due to the high pH of the medium. The leachability of Pb was found to be very low due to the internal glassy matrix form in the sample therefore not readily leached. It is insoluble and constant, independently from the type of leaching test applied. Cadmium is consistently inert in neutral and alkaline mediums. Even though Cd is connected with the fly ash particles surface, the concentrations leached in water not often exceed the limits (Gould et al., 1989). The leach-ability of Zn is relatively high for SOFA/LB under TCLP test conditions while, in general, Zn mobility for both FA/LB is very low (Figure 5 and 6). Copper (Cu) is present within the glassy phase and not easily released. Leachability of Cu was in between 1.2% and 5.39% under TCLP test conditions while it was not leached in both ASTM and EN (Figure. 5 and 6). Nickel (Ni) is dispersed between the silicate fraction and the magnetic fraction of FA during burning process. The majority of the leachable Ni is released from the non-magnetic fraction. Leached Ni were present in SOFA/LB and YFA/LB under TCLP test conditions, but not present in ASTM and EN.

# Table 3. The concentration of heavy metals in SOFA/LB and YFA/LB leachate (mg/kg)

<table>
<thead>
<tr>
<th>Element</th>
<th>SOFA/LB</th>
<th>YFA/LB</th>
<th>ASTM</th>
<th>EN</th>
<th>EPA max mg/kg</th>
<th>Waste acceptance criteria, mg/kg at L/S20</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ba</td>
<td>15.370</td>
<td>0.193</td>
<td>0.206</td>
<td>28.176</td>
<td>11.986</td>
<td>17.843</td>
</tr>
<tr>
<td>Ca</td>
<td>25.590</td>
<td>4.220</td>
<td>3.060</td>
<td>82.870</td>
<td>6.880</td>
<td>5.282</td>
</tr>
<tr>
<td>Cd</td>
<td>0.035</td>
<td>0.007</td>
<td>0.072</td>
<td>0.045</td>
<td>0.020</td>
<td>20</td>
</tr>
<tr>
<td>Co</td>
<td>2.942</td>
<td>ND</td>
<td>1.3</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cu</td>
<td>5.447</td>
<td>ND</td>
<td>0.864</td>
<td>ND</td>
<td>300</td>
<td>4</td>
</tr>
<tr>
<td>Cr</td>
<td>8.924</td>
<td>0.244</td>
<td>0.629</td>
<td>1.927</td>
<td>0.101</td>
<td>100</td>
</tr>
<tr>
<td>Mo</td>
<td>0.050</td>
<td>0.027</td>
<td>0.085</td>
<td>1.009</td>
<td>0.498</td>
<td>0.391</td>
</tr>
<tr>
<td>Ni</td>
<td>1.257</td>
<td>ND</td>
<td>0.72</td>
<td>ND</td>
<td>40a</td>
<td>0.8</td>
</tr>
<tr>
<td>Zn</td>
<td>10.391</td>
<td>0.940</td>
<td>0.314</td>
<td>0.430</td>
<td>0.141</td>
<td>0.376</td>
</tr>
<tr>
<td>Pb</td>
<td>0.1917</td>
<td>ND</td>
<td>0.250</td>
<td>ND</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>Sr</td>
<td>0.30</td>
<td>1.497</td>
<td>1.117</td>
<td>23.371</td>
<td>11.394</td>
<td>9.879</td>
</tr>
<tr>
<td>Fe</td>
<td>872.381</td>
<td>0.45</td>
<td>97.027</td>
<td>0.256</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Hg</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.02</td>
</tr>
<tr>
<td>Se</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.4</td>
</tr>
</tbody>
</table>

* 100x drinking water max, since an EPA-TCLP max has not been established, ND – Not Detected
4. Conclusion

Based on the findings, Seyitomer fly ash sample contains particles below 0.800 mm particle size and 0.212-0 mm fraction makes up 76.06% of the ash. Particle size of Yatagan fly ash sample is found below 0.300 mm and 0.212-0 mm fraction makes up 84.14% of the ash. It is found that both fly ashes have the alkaline character due to lime and soluble metal salts, oxides, hydroxides, and carbonates contents. Quartz (SiO$_2$) is found as the main crystalline phase, magnesioferrite (Mg$_2$Fe$_2$O$_4$) is the second dominating mineral and small amounts of anorthite (CaAl$_2$Si$_2$O$_8$), anhydrite (CaSO$_4$), hematite (Fe$_2$O$_3$), mullite (Al$_2$Si$_2$O$_13$) and lime (CaO) was detected in SOFA samples. Quartz is found as the major component in the autoclaved SOFA/LB samples. Katoite (Ca$_3$Al$_2$(Si$_{0.64}$O$_{2.56}$)(OH)$_{9.44}$), tobermorite Ca$_4$(Si$_6$O$_{15}$)(OH)$_2$(H$_2$O) and calcium silicate hydrate 2CaO(SiO$_2$)$_2$:4(H$_2$O) were found in brick samples while mullite and lime peaks in fly ash have disappeared. High content of Quartz (SiO$_2$) and anorthite (CaAl$_2$Si$_2$O$_8$) were found in YFA with minor amounts of hematite (Fe$_2$O$_3$), lime (CaO), gehlenite (Ca$_2$Al$_2$SiO$_7$), anhydrite (CaSO$_4$), hematite (Fe$_2$O$_3$) and mullite (Al$_2$Si$_2$O$_13$). Quartz (SiO$_2$) was detected as the main crystalline phase of the YFA/LB like SOFA/LB.

Both FA/LB showed no presence of Hg, Ti, As and Se in investigated samples. In leaching tests for SOFA / LB and YFA/LB, the highest solubility was observed in Ba, Cr, Mo, Cd and Co that is the elements with environmental importance. Most of the selected trace elements were leached at higher proportions under TCLP test conditions due to lower pH of the eluate. Using lime in production of fly ash bricks helps to establish an alkaline matrix so that the solubility of many toxic elements are prevented. The release of all trace elements was lower than the hazardous material limit values of waste acceptance for land filling stated in the Annex 2 of the 2003/33/CE Council Decision (based on 1999/31/EC Directive) and TCLP-EPA max directive. The study revealed that there would be no environmental risk posed by the presence of pollutants when SOFA and YFA are used as raw materials in FA/LB-making.

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Literatura – References


**Wymywalność metali ciężkich z autoklawizowanych cegieł z popiołu lotnego i wapna**


Wyniki pokazują, że uwalnianie wszystkich pierwiastków śladowych było niższe niż dopuszczalne wartości dla materiałów niebezpiecznych. Zatem niewypalane cegły z popiołu lotnego są korzystnym sposobem rozwiązania problemu środowiskowego wpływu usuwania popiołów lotnych.

**Słowa kluczowe:** popioł lotny z węgla, popioł lotny/cegła wapienna, ługowanie, pierwiastki śladowe