TREATMENT FLY ASH OF AL MUSAYYIB THERMAL POWER PLANT TO BE USED AS A POZZOLANIC MATERIAL

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ABSTRACT

Crude oil ash is the residue that is produced during oil combustion for instance fly ash, bottom ash or boiler slag which was primarily produced from the combustion of coal. With growth in oil burning power station, huge amount of fly ash considered as organic materials which are normally disposed in an on-site disposal system without any commercialization purpose. Previous researchers have studied the extraction of silica from agricultural wastes such as palm ash and rice husk ash (RHA) and FA (fly ash) by using leaching treatment method. In this study, the weaker acid, citric acid solution was used to replace the strong acid in leaching treatment to process. Result showed that the loss on ignition materials can be decrease to 12%. Meanwhile the silica can be extracted up to 54.4% from FA using citric acid leaching treatment under the optimum reaction time of 60 minutes with solution temperature of 60°C and concentration of citric acid 5% receded by gradual combustion at 900°C for 3 hours.

KEYWORDS: Treatment fly ash; power plant; silica (SiO₂), strength activity index, compressive strength.
1. INTRODUCTION
The components of fly ash vary considerably, for instance many coal-bearing rock all fly ash includes substantial amounts of silicon dioxide (SiO$_2$), both amorphous and crystalline, and calcium oxide (CaO), both being endemic ingredients. The constituents depend upon the specific coal/oil bed makeup (Avwiri et al., 2012).

About 43% of fly ash in US is recycled (Davis et al., 1977), often used as a Pozzolan to produce hydraulic cement or hydraulic plaster or a partial replacement for Portland Cement in concrete production. Consequently, the treatment of fly ash is an essential process prior to storing it (Zacharczuk et al., 2003), to treat fly ash many methods have been developed. For example, fly ash was disposed in landfill after being stabilized or immobilized by hydraulic binder (Ghiloufi, and Baronnet, 2006).

Another technique used to treat the fly ash is thermal plasma, carried out in a plasma reactor and in two steps. In the first step, fly ash was treated in a pyrolysis/combustion plasma system to reduce the fraction of carbon. In the second step, the product obtained by the combustion of fly ash was vitrified in a plasma furnace. The leaching results show that the fly ash was detoxified by plasma verification and the produced slag is amorphous and glassy (Al-Mayman, 2017).

Previous researchers have studied the extraction of silica from by using leaching treatment method, silica can be extracted up to 44% from coal bottom ash using citric acid leaching treatment under the optimum reaction time of 60 minutes with solution temperature of 600°C and concentration of citric acid more than 2% (Yahya et al., 2017). Another method of treatment chemically treats fly ash with ferrous sulfate solutions to immobilize hazardous leachable trace elements after disposal (Bhattacharyya et al., 2008).

In the present work a sample of Al_Musayyib thermal power station fly ash in Iraq was treated at different condition and analyzed to control the SiO$_2$% and L.O.I%, the treatment was citric acid leaching to concentrate the silica and reduction percentage of loss on ignition materials (L.O.I) and study their change in chemical composition and their pozolanic activity index (ASTM C311, 2005).

2. EXPERIMENTAL WORK
2.1. Fly ash raw material
AL Musayyib is one of power plant in Iraq that used oil to produce electricity. It has been reported that, AL Musayyib power plant products about 5000 ton/ annual of fly ash. Due to the
large volume of waste material, the large quantity of fly ash will be considerable disposal concern because of the increase requirement for ash storage space. Hence, this will increase the expanses to obtain larger area (Jayaranjan and Annachhatre, 2013) and it could lead to the environmental problem to the future (Abdullah and Fazlul, 2014). Table 1 shows that FA has about 6.8% of silicon element and the list compounds that exist in fly ash.

| Compound | Concentration (%) |
|----------|-------------------|
| SiO₂     | 6.8               |
| LIO      | 48                |
| CaO      | 12.3%             |

Table 1. Chemical composition of untreated FA.

2.2. Leaching process
citric acid or lemon salt is a weak organic acid is a phrase and a white granules for a soft crystalline powder, which is very hydrolysis, twenty grams of FA was combusted at 600°C, 800°C and 900°C for 30 minutes in the furnace (Carbolite HTF Furnace, Model 1800). At different periods time (60, 120 and 180) min. The sample then it was put into beaker of 500 mL that contained citric acid solution using the hot plate magnetic stirrer for treatment, The concentration of the citric acid solution were controlled as 5%, (citric acid powder (EMORY, Purity > 99.5%) with distilled water and the solution temperature was 60°C with reaction time recorded within 60 minutes. After the acid leaching process, the treated FA was rinsed in distilled water at room temperature to remove of excessive citric acid content in the ash.

The treater ash was filtered by using vacuum filtered (GAST, MODEL:DOA-P504-BN) to obtain the retained treated ash. After that, the ash was dried at 60°C, then, the sample is weighed by a sensitive balance. The treated FA was tested by using X-ray fluorescence spectroscopy (Model XRF BRUKER S4 PIONEER) and the chemical analysis for specified sample. The details Experiments for treatment FA and chemical compositions shown in Table 2.

Fourth attempts of treatment was adopted with citric acid and, defined as P4 attempt the best results according to the requirements ASTM C3618 (ASTM C618, 2005).

2.3. Mortar Mixing and Preparation:

2.3.1. Materials

The cementitious materials were used ordinary Portland cement, the chemical compositions and physical properties are given in Table 3 (IQS No.5/1984) (Iraqi Specification, 1984). The
chemical compositions treated Iraqi fly ash is given in Table 4 and X-ray diffraction (XRD) pattern given in Fig.1. Graded river sand passing from sieve No. 20 (850µm) and retaining on sieve No. 30 (600µm) to complying the requirements of the Iraqi specification (IQS No. 2080/1998).

**Table 2. The details of treatment FA and chemical compositions.**

| Attempt | The amount of FA (g) | Ignition temp. (°C) | Period of ignition (min) | The amount of citric acid (mL) | Period of mix. (min) | Drying temp (°C) | SiO₂ % | LIO % | Loss of weight % |
|---------|---------------------|---------------------|--------------------------|-------------------------------|---------------------|----------------|--------|-------|-----------------|
| p1      | 20                  | 600                 | 60                       | 500                           | 60                  | 60             | 31     | 60    | 69              |
| p2      | 20                  | 800                 | 120                      | 500                           | 60                  | 60             | 45.4   | 25    | 72              |
| p3      | 20                  | 900*                | 180                      | 500                           | 60                  | 60             | 25     | 19.8  | 78              |
| p4      | 20                  | 900                 | 180                      | 500                           | 60                  | 60             | 54.4   | 12    | 77              |

*ignition after washing

**Table 3. Chemical analysis and physical properties of ordinary Portland cement used.**

| Oxide              | I.O.S. 5: 1984 Limits |
|--------------------|-----------------------|
| CaO                | 61.95 %                |
| SiO₂               | 20.92 %                |
| Al₂O₃              | 6.02 %                 |
| Fe₂O₃              | 3.12%                  |
| MgO                | 3.33%                  |
| SO₃                | 2.57%                  |
| Loss on Ignition (L.O.I) | 1.71 %  |
| Lime Saturation Factor (L.S.F) | 0.87%  |
| Insoluble residue (I.R) | 0.66 %  |
| Free lime (F.L)    | 1.23%                  |
| C₃S                | 33.96 %                |
| C₃S                | 32.84 %                |
| C₃A                | 10.67 %                |
| C₄AF               | 9.49 %                 |

**Compressive Strength MPa 3-**

| days    | 21.0 | ≥15 |
|---------|------|-----|
| 7-days  | 27.0 | ≥23 |
| 28-days | 40.0 | ≥35 |
Table 4. Chemical properties of the treated fly ash (%).

| Chemical | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | H₂O | LOI |
|----------|------|-------|-------|-----|-----|-----|-----|-----|
|          | 54.4 | 14.96 | 5.84  | 18.6| 3.2 | 1.2 | 1.4 | 12  |

Fig. 1 X-Ray pattern of treatment FA.

2.3.2. Test procedure

Details of the mix proportions for mortars are given in Table 5. The control mix was cast using ordinary Portland cement, while the test mix was prepared by replacing 20% of the cement by treated FA on mass-for-mass basis. All mortars were mixed in a mixer using change water/binder ratio to dive the same flow for both mixtures and sand/binder ratio of 2.75. Graded sand, cement and fly ash are mixed first for approximately 3 min. Water is added and mixed for 2–3 min. The flow values of mortars were determined according to ASTM C 1437 (ASTM C 1437, 2001). The cube samples of mortar with size (50 x 50 x 50) mm are cast and demoulded after 24 h.

The mortar specimens were cured in water at room temperature for 28 days. Compressive strength of mortar specimens were tested according to ASTM C109 (ASTM C 109/C 109M – 2007) using a loading rate of 0.7 MPa/s.

In these tests three cubes (50 x 50) mm of control mixture, the strength activity index at age of 28 days using the following relation (S.A.I)% :-

\[ \text{Strength activity index with portland cement} = \left( \frac{A}{B} \right) \times 100 \quad \ldots \ldots (\text{S.A.I})\% \]

where:
A = average cube compressive strength of test mix, MPa
B = average cube compressive strength of control mix, MPa
In all mortars the w/c or w/cm ratio were adjusted to maintain equal flow of 135±5 mm in 25 drops of the flow Table 5.

### Table 5. w/c or w/cm ratio for mixture.

| mix       | OPC | FA   | sand | w/c or w/cm ratio to give flow of 135±5 |
|-----------|-----|------|------|---------------------------------------|
| Control   | 500 | ---- | 1375 | 0.484                                 |
| FA treated| 400 | 100  | 1375 | 0.463                                 |

3. RESULTS AND DISCUSSIONS
The result shows that, citric acid seems to be as a good alternative to substitute strong acid in leaching process. The temperature and time was an important parameter in leaching process.

3.1. The effect of different time and temperature on SiO\(_2\) and L.O.I
Table 4 shows the chemical composition of FA after leaching treatment done under different time and temperature of ignition. From the result, the increased temperature tends to vaporize organic acids and water (Sarode et al., 2010). Experimental result from Table 5 shows that the L.O.I content shows some decrement compared to the untreated FA specimen and increased in SiO\(_2\) content up to 54.4% when burning 900 degree, time ignition of 3 hr. The color of pulverized coal bottom ash after citric acid leaching treatment was changed from black to brown color as shown in Fig. 2.

![Fig. 2. Image of FA (a) before leaching treatment (b) after leaching treatment.](image)

3.2. Chemical compositions
Table 6 illustrates the results show that treated FA are acceptable according to the Chemical Requirements ASTM C618-05 (Pedrazaa et al., 2014) as a pozolanic material.
Table 6. Proposed ASTM chemical requirements for fly ash.

| Requirements of ASTM                        | Class of fly ash | Result of FA treatment |
|--------------------------------------------|------------------|------------------------|
|                                            | N    | F    | C      |                  |
| Silicon dioxide (SiO_2) plus                | 70.0 | 70.0 | 50.0   | 76.2             |
| Aluminum oxide (Al_2O_3) plus               |      |      |        |                  |
| Iron oxide (Fe_2O_3), min, %                | 4.0  | 5.0  | 5.0    | 1.2              |
| Sulfur trioxide (SO_3), max, %              | 10.0 | 12.0 | 12.0   | 12               |

3.3. Strength

The results of the strength of mortar are given in Fig. 3.

It can be seen the strength of test mixture decreases compared with control mixture, replacing 20% of the cement with treatment FA would have lower strength at 28 day due to the decreased cement available for reactions and the organic materials not remove all which may be give a negative effect on the strength of the mortar in 30% of required value.

![Fig. 3. Compressive strength of different mortar mixes.](image)

3.4. Strength activity index (S.A.I)

The result of S.A.I for treated FA with Portland cement was (77.2%) at 28 days which depend on the result of compression strength at the same time of curing, At least Strength Activity Index with Portland cement, at 7 or 28 days was 75 percent of control according to physical requirements (ASTM C618-2005).

3.5. X-ray Diffraction (XRD)
Fig. 1 represents the XRD diffraction pattern for treated FA. Two phases can be observed; an amorphous phase (reactive material), a larger percentage of a crystalline phase, comprised of quartz and mullite (silicates), low phase for Calcium as anthracites and subbituminous carbon.

3.6. Scanning electron microscope (SEM) results

The scanning electron microscope imaging as can be seen in Fig. 4 reveals that the majority of treated FA particles are glassy in appearance and hexagon in shape. The treated FA fineness was very close to OPC. The chemical composition, as illustrated in Table 5, reveals that fly ash is moderately rich in silica content (54.4%) as compared to that of OPC (20.92%). The CaO content, however was very low i.e. about 18.6%. The sum of silica, alumina and iron oxide is 76.2%, that satisfies the requirement to be classified as Class F according to the standard specified in ASTM C618, (2005). The silica content gives the fly ash a large amount opportunity to react with the Ca(OH)$_2$ that is expected from the cement hydrations. The ecospheres present in fly ash formed by the surface tension generated by the heat of combustion. Porous particles of irregular shape are also recognized, which are what is called “unburned residue” (Pedrazaa et al., 2015).
4. CONCLUSION

The experimental studies show that there is a possibility to extract silica and at the same time reduce the loss on ignition materials from FA by using acid leaching method. From the result, it shows that the silica was increased up to 54.4% with the increasing of temperature of ignition at 900°C and optimum reaction time of 180 minutes. Moreover, although the organic materials content are not fully eliminated, but it can be reduce with higher temperature of ignition. Therefore, it can be conclude that by increasing degree of ignition temperature and time of reaction may lead to the better result for some limits.

Pozzolanic activity is evaluated using an accelerated method that establishes the reaction speed of the different materials considered. While replacement of part of the cement in a mortar typically reduces the overall heat of hydration, it is shown that, compared to a control cement much less reactive fly ash decreased early heat output, compared to the control cement, a good correlation of between pozzolanic activity and hydration heat found.

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