Evaluation of Fluidized Bed Ashes from Animal Wastes, Properties, Environmental Impact and Valorization

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Abstract:

Use of secondary fuels for power production, such as animal and agricultural wastes, is becoming important nowadays, in view of the declining reserves of fossil fuels. Fluidized bed furnaces offer many advantages, such as fuel flexibility, high efficiency and low pollutant emissions. However, bottom or fly ashes produced from these appliances may create technical and environmental problems. In this study, agricultural wastes from the island of Crete (S. Europe) were co-fired in a fluid bed unit and bottom and fly ashes were characterized by mineralogical and chemical analyses. The effect of ash materials on system’s performance, as well as their environmental impact and valorization were assessed. The results showed that all ashes were enriched in Ca, Si, Mg, P, K. These elements were principally associated with calcite, anhydrite, quartz, dolomite, hydroxyapatite, fairchildite and arcanite minerals. Animal waste ashes contained whitlockite, calcium sodium phosphate and epsonite. Combustion of animal manure above 1000°C could lead to deposition problems in furnaces. Heavy metals Cu, Zn, Mn and Sr dominated in fly ashes. Toxic elements leached through alkaline soil of phyllitic and quartzitic natures were below legislation limits for land disposal. All ashes could be used for soil amelioration, liming or possibly fertilization.

Keywords:

Agricultural Wastes, Animal Wastes, Fluidized Bed, Ash Leaching

1. Introduction

Agricultural and animal wastes are readily available in large quantities in S. European countries. In Crete, excessive amounts of olive by-products are generated annually and animal breeding is intensive, whereas on the other hand there is an increased demand for power, due to the tourism industry. Therefore, the thermal treatment of these wastes is becoming important, given also the EU directives [1], which impose a reduction in the amount of biodegradable wastes in the landfills, as well as an increase in the share of biomass fuels for the primary energy consumption.
Among dedicated technologies, fluidized bed is regarded as the most versatile for biomass fuels, due to its advantages of fuel flexibility, high efficiency and low emissions [2,3,4]. However, even in such systems the bottom and fly ashes produced may create technical and environmental problems, which reduce the availability of the facilities and increase the power cost. These problems include slagging, fouling and corrosion of surfaces, or risk to the environment and health from heavy metals disposal [5,6].

The heterogeneous nature of biomass materials and the different operating conditions during their combustion, imply a thorough knowledge of ash properties, as well as investigation for their recycling and utilization in various applications, according to the environmental regulations. When mixtures of fuels are used for increasing supply options, final ash materials may have a different behavior than that of component fuels.

There are many studies in literature dealing with the characterization of fluid bed ashes from woody wastes, sewage sludge and municipal solid wastes. Sintering mechanisms and the factors influencing trace element partitioning have been discussed [7,8]. A considerable research has been carried out on the possible use of these ashes for soil amendment or for concrete manufacturing [9,10]. However, there is lack of literature data on ash blends from agricultural and animal wastes co-combustion in fluid bed systems. The only information is from raw poultry combustion or pig manure gasification [11,12]. Furthermore, leaching experiments to assess risk and select proper management and disposal strategies for such ash mixtures have not been conducted so far.

Based on the above, the aim of this work was to evaluate fluid bed ashes obtained from the co-firing of animal and agricultural wastes. Thus, fly and bottom ashes were characterized by mineralogical, chemical and fusibility analyses and their leaching behavior through a local soil was studied. Thus, the effect of ash materials on system’s performance, as well as their environmental impact upon disposal and valorization for industry or soil amelioration were assessed.

2. Materials and Methods

2.1. Production of Ash Materials

Three agricultural wastes were selected as the raw materials for this study, namely, MBM (Meat and Bone Meal) and untreated manure (AM) from swine breeding, as well as olive kernel (OK) from two local food and oil factories in the region of Crete. After grinding and riffling, representative samples from these wastes were characterized by proximate analysis, ultimate analysis and heating value, according to the European standards CEN/TC335.

For combustion tests, mixtures of fuels were prepared at ratios OK/MBM 90:10, OK/AM 70:30 and OK/AM 50:50 (wt%). Fly and bottom ashes were produced from the combustion of the fuels in a bubbling fluidized bed reactor system, described in a previous work [4]. The feeding rate of each raw material/mixture, of particle size 1-2.8mm, was 0.72kg/h, the excess air ratio was 1.4 and the air flow rate 4.7-5.1m3/h, depending on fuel. The inert bed material was a Na-feldspar NaAlSi3O8 with an average particle size of 421μm. Bed temperatures during the experiments ranged between 840 and 861°C and they will be reported for each case in the sections to follow.
The soil sample used for the leaching tests (mineralogical analysis in Figure 1) was collected from the area of Chania, Crete. After passing a 2mm sieve, it was subjected to particle size analysis and determination of the sand, silt and clay proportions, via the hydrometer method [13]. Cation-exchange capacity was measured by applying the ammonium acetate method [14].

2.2. Ash Analyses

Prior to any analysis, all ashes were weighed and burned in the oven at 300°C for not altering the mineralogical composition, in order to calculate combustion losses due to unburned carbon.

The fusibility test for laboratory ashes was conducted according to European standards DDCEN/TS 15370-1:2006, using a heating microscope type 789-900.

The mineral phases of crystalline compounds were detected by an X-ray diffractometer (XRD), model D8 Advance of Bruker AXS, with application of Cu Kα radiation and nickel filter. The JCPDS database in conjunction with the software DIFFRAC plus Evaluation were used for the identification of minerals.

After being dissolved with HNO₃ acid and digested in a microwave oven, ash materials were analyzed for major and trace elements in an inductive coupled plasma mass spectrometer type ICP-MS 7500cx (detection limits 0.4-34 ppb, depending on element). On the other hand, Li₂B₄O₇ fusion or acid digestion was used as the sampling preparation procedure, before silicon and phosphorous measurements. These were conducted in a spectrophotometer type UV-VIS Hach 4000V and an atomic absorption spectrometer Analyst-100 of Perkin Elmer.

2.3. Leaching Tests

Continuous column leaching experiments, simulating the release of components from a soil-ash mixture to a water phase, were adopted in this work, in order to get an estimate of long-term leaching behaviour. To maintain compatibility with field conditions, soil-ash mixtures were prepared at a ratio 95:5 and no extraction with strong acids was applied. Purified water instead, with an amount corresponding to the average annual quantity of rainfall in the area of Crete (~620mm), was percolating through the soil-ash mixture (100g) in a vertical column with an ID of 2.5cm and a height of 20cm. The hydraulic head was kept constant during each test and the ratio of solid to water was 1:0.7, so that to simulate the water saturation capacity of the soil. The column effluent was collected in seven equal volume glass flasks, filtered through a micropore membrane filter and the pH of each extract was measured. The filtered leachates were concentrated, transferred to 25mL plastic vials and prepared for chemical analysis.

3. Results and Discussion

3.1. Raw Materials Analyses

Proximate, ultimate and fusibility analysis results are presented in Table 1. Animal wastes had lower volatile and carbon contents than olive kernel, while higher ash content, resulting in lower calorific values. The sulphur and chlorine contents of all samples, which are related to emissions, fouling and corrosion in boilers, were low, however the nitrogen percentage of both animal wastes was high, revealing NOx emissions during combustion. Previous investigations by the author [4] have shown
that NOx emissions of OK/AM 50:50 blends, at a feed rate of 0.72kg/h and \( \lambda = 1.4 \), slightly exceeded legislation limits \([15]\), whereas those of OK/MBM 90:10 blends were extremely high (846mg/Nm\(^3\), limit 350mg/Nm\(^3\)).

The initial deformation and fluid temperatures of AM were lower than MBM and OK fuels. The former could be problematic for systems operating above 1000°C, causing deposition on furnace surfaces. Contrary, the fusion temperatures of MBM were quite high for most combustion processes. Such variations in fusibility behavior reflect the differences in mineralogical and chemical composition between woody and animal wastes.

![Figure 1. XRD spectra of soil.](image)

### Table 1. Proximate, ultimate, fusibility analyses and calorific value of the samples (% dry).

| Sample            | OK      | MBM     | AM      |
|-------------------|---------|---------|---------|
| **Proximate analysis** |         |         |         |
| Volatile matter   | 73.6    | 58.7    | 60.9    |
| Fixed carbon      | 19.3    | 9.3     | 11.7    |
| Ash               | 7.1     | 32.0    | 27.4    |
| **Ultimate analysis** |         |         |         |
| C                 | 49.7    | 35.0    | 43.3    |
| H                 | 6.6     | 5.2     | 6.5     |
| N                 | 2.0     | 8.7     | 4.3     |
| S                 | 0.33    | 0.51    | 1.15    |
| O                 | 34.2    | 18.6    | 17.3    |
| Cl                | 0.06    | 0.01    | 0.08    |
| HHV (MJ/kg)       | 20.8    | 15.6    | 18.0    |
| **Fusibility analysis** |         |         |         |
| Initial deformation temperature | 1026   | 1240    | 975     |
| Softening temperature | 1230   | 1440    | 1050    |
3.2. Mineralogical Analysis of Ashes

The crystalline mineral phases of fly and bottom ashes of olive kernel and its mixtures with the two animal wastes, as identified by XRD, are indicated in Table 2. Olive kernel ashes (produced at 854-861°C) were dominated by Ca-based minerals in the form of calcite, anhydrite, fairchildite and hydroxyapatite. Dolomite was concentrated only in bottom ash. Anhydrite was most probably formed by dehydration of gypsum, as the SO₂ content of flue gases was found to be extremely low [4]. Hydroxyapatite is associated with the use of fertilizers, such as NH₄H₂PO₄, during the cultivation of olive trees. Among silicates, quartz was abundant in both olive kernel ashes, whereas albite, muscovite and microcline were remnants of elutriated inert bed material in the cyclone during the tests. Periclase and hematite were detected in small amounts, in contrast to potassium minerals arcanite and sylvite, which were enriched in both fly and bottom ashes. These sulphate and chloride species were partly vaporized during combustion and collected in the cyclone ash.

When MBM was mixed with OK, Table 2 shows that two new mineral phases appeared in both fly and bottom ashes (produced at 845-854°C), calcium sodium phosphate and whitlockite magnesian, which obviously originated from MBM, due to its high concentration in bones.

On the other hand, the two mixtures of OK with AM (produced at 840-848°C), apart from the phases which were identified in OK ashes, presented also whitlockite magnesian, in accordance with other studies [6] and additionally epsonite (MgSO₄.7H₂O). The latter was probably formed by reaction of periclase (primary or secondary from partial decomposition of dolomite at temperatures higher than 800°C) with SO₂ of flue gas.

![Table 2. Mineralogical analysis of fluidized bed ashes.](image-url)

| Mineral phases | Inert bed material | OK | OK/MBM 90:10 | OK/AM 70:30 | OK/AM 50:50 |
|----------------|--------------------|----|--------------|-------------|-------------|
|                | Fly | Bottom | Fly | Bottom | Fly | Bottom | Fly | Bottom |
| Quartz SiO₂    | +   | +++    | +   | ++      | ++  |  +     | ++  | ++      |
| Calcite CaCO₃  | ++  | ++     | ++  | ++      | ++  | ++     | ++  | ++      |
| Anhydrite CaSO₄| ++  | +      | +++ | +++     | ++  | +      | ++  | ++      |
| Albite (Na, Ca)Al(Al,Si)₃O₈ | +++ | +  | ++  | ++      | +   | +      | +   | +       |
| Muscovite KAl₂(Si₃AlO₁₀)(OH)₂ | + | +   | +   | +       | +   | +      | +   | +       |
| Microcline KAlSi₃O₈ | +  | +    | +   | +       | +   | +      | +   | +       |
| Fairchildite K₂Ca(CO₃)₂ | ++ | +++   | ++  | ++      | +   | ++     | +   | ++      |
| Hydroxyapatite Ca₅(PO₄)₃(OH) | +  | ++   | ++  | +++     | +   | +      | +   | +       |
| Dolomite CaMg(CO₃)₂ | ++  |       |    |         |     |        |     |         |
| Hematite Fe₂O₃ | +   | +     | +   | +       | +   | +      | +   | +       |
3.3. Chemical Analysis of Ashes

The concentrations of major elements in fly ashes are compared in Figure 2. The common feature of these ash materials is that they were rich in Ca, P and Si, in accordance to the XRD analysis previously presented. The increased concentrations of Si, Al and Na observed were attributed to some elutriation of inert bed material in the cyclone. The higher amount of K in OK fly ash was due to the higher content of K originally found in this sample, as well as the partial vaporization of arcanite and sylvite under fluidized bed conditions identified in XRD spectra, which condensed on fly ash particles in the upper part of the reactor, where the flue gas was cooled. However, from Figure 2 it can be clearly seen that, when OK was mixed with either animal waste, the concentrations of Ca and P were significantly increased in the fly ashes, confirming the presence of calcium phosphates in these wastes (Table 2). Moreover, in the case of OK/AM blends the proportion of Mg was increased, due to the whitlockite magnesian, newberyite and epsonite minerals originating from the AM sample. Finally, it is interesting to note that, when the materials were mixed the fouling tendency due to potassium of OK was lowered and furthermore the sulphur of these materials was retained in ashes in the form of sulphates, supporting a previous work by the author [4], where no SO$_2$ emissions were found in flue gases.

![Figure 2. Chemical analysis of fly ashes in major elements.](image-url)
The analysis of fly ashes in trace elements is illustrated in Figure 3. Toxic heavy metals As, Hg, Cd, Co and Pb were not included in the graph, because they ranged from < 0.4ppb to 7ppm. All values were similar or lower to those reported in literature [7,8] and below the upper limit for disposal in landfills according to EU directives [16]. The fly ash of OK was enriched in Cu, Mn and Sr. When OK was blended with MBM material, trace elements, except Sr, were found in smaller amounts in fly ash particles, suggesting that they were associated with mineral phases (possibly phosphates) which concentrated in the bottom ash of the fluid bed configuration. However, when OK was blended with AM, apart from Sr, the concentrations of Mn and Zn, which are known to have a moderate volatility [17], were increased in fly ashes. As concerns the elevated amount of Sr in the presence of animal wastes, by comparing Figure 2 and Figure 3 it can be observed that this was most probably correlated with Ca, which was abundant in both wastes.

3.4. Analyses of the Leachates Through the Soil

The cumulative concentration of the elements leached through soil/fly ash mixtures, according to the column leaching tests previously described, are summarized in Table 3 and Table 4. All values were within the limits stipulated by the European Community directives [18]. However, Cr was leached in high amounts. Ti, Cd, Hg and Pb were not quantified in the extracts, because their concentration was below the instrument’s detection limit (1.96-10.76ppb depending on element). Table 3 shows that from major elements those which presented a higher mobility were Na and K, the former due to its high percentage in the soil, while the latter due to the solubility of carbonates, sulphates and chlorides of K incorporated in the fly ashes (Table 2). P showed an increased leachability (5.5% of the total) for olive kernel only, as it was incorporated in hydroxyapatite, partly extracted and kept in solution. In the case of animal waste ashes, P was identified in insoluble minerals, such as calcium sodium phosphate, whitlockite magnesian and newberyite. As concerns trace elements, Table 4 illustrates that shows that Cr presented the highest mobility from all samples, reaching levels up to 0.9ppm in the leachates. Sr, Cu and Zn were extracted in moderate amounts, whereas Ni, Co, As and Mn levels were the lowest in the leachates. It must be mentioned that when MBM was blended with olive kernel, the relative mass leached of As was increased, nevertheless the amount extracted was 5.6ppb. Finally, during the experiments it was observed that the highest concentrations of metals extracted from all samples occurred at the beginning of the tests and tended to decrease with time, as Figure 4 shows.
The above behaviour of ash elements through the soil is complex, since it is influenced by the mineralogical and chemical composition of the solid materials involved, reaction kinetics, permeability and cation exchange capacity of soil, as well as the pH of solid and liquid phases [19]. As previously shown, the cation exchange capacity of the soil was very low for adsorbing toxic substances, whereas all ashes were more alkaline than the soil ($\text{pH}_{\text{OK}}=10.3$, $\text{pH}_{\text{OK}/\text{MBM}}=10.4$, $\text{pH}_{\text{OK}/\text{AM}}=9.7$). Thus, as Figure 5 shows, addition of ashes to the soil increased the pH values of the water extracts initially up to 9.6. These high values were mainly attributed to the basic Ca-bearing minerals in the ashes, such as carbonates and hydroxides (Table 2), which were soluble in water. The drop of pH with time in the leachates, especially for animal waste mixtures, was most probably the result of the occurrence of considerable amounts of sulphates and magnesium hydrogen phosphate trihydrate in the ashes (Table 2). Consequently, these lower pH values as compared to the effluent waters from the soil-olive kernel sample increased the leaching rate of Cr, Sr and Mn from the soil-OK/MBM and soil-OK/AM samples.

The high extractability of Cr and As in the case of OK/MBM ash reveals their potential association with exchangeables, carbonates or sulphates [19]. On the other hand, the low percentages of Ni, Co and Mn released in the extracts, suggests that these were partly adsorbed on stable oxide surfaces, such as quartz and hematite, or bound in aluminosilicates, such as microcline.

**Table 3. Cumulative major element concentrations in the leachates and relative mass leached.**

| Sample                  | Na (mg/kg) | Mg (mg/kg) | Al (mg/kg) | K (mg/kg) | Ca (mg/kg) | P (mg/kg) |
|-------------------------|------------|------------|------------|-----------|------------|-----------|
| Soil                    | 40.1 (22.3) | 1.8 (0.18) | -          | 6.6 (7.4) | 15.0 (1.7) | 44.9 (5.5) |
| Soil-OK                 | 61.4 (3.9)  | 6.9 (0.32) | 4.8 (0.18) | 66.4 (1.6) | 17.9 (0.2) | 39.4 (1.03) |
| Soil-OK/MBM 90:10       | 45.0 (2.6)  | 15.2 (0.9) | 2.5 (0.11) | 48.0 (2.2) | 25.2 (0.15) | 39.4 (1.03) |
| Soil-OK/AM 50:50        | 42.0 (3.0)  | 46.5 (1.1) | 2.7 (0.10) | 57.0 (2.6) | 178.0 (1.6) | 35.5 (2.9) |

*Values in parenthesis represent cumulative mass leached (%)

**Table 4. Cumulative trace element concentrations in the leachates and relative mass leached.**

| Sample                  | Cr (µg/kg) | Ni (µg/kg) | Cu (µg/kg) | Zn (µg/kg) | Sr (µg/kg) | Co (µg/kg) | As (µg/kg) | Mn (µg/kg) |
|-------------------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Soil                    | -          | -          | -          | -          | 111.3 (1.3) | -          | -          | 0.4 (0.004) |
| Soil-OK                 | 927.0 (12.2)| 1.9 (0.02) | 23.6 (0.09) | 53.5 (1.1) | 115.1 (0.41) | 1.1 (0.07) | 1.4 (0.45) | 14.6 (0.05) |
| Soil-OK/MBM 90:10       | 780.0 (3.1) | 12.0 (0.22) | 76.0 (0.78) | 88.0 (1.1) | 219.0 (0.9) | -          | 5.6 (5.9)  | 27.0 (0.12) |
| Soil-OK/AM 50:50        | 518.0 (8.9) | 1.1 (0.02) | 21.5 (0.1)  | 43.7 (0.58) | 759.0 (2.3) | 0.5 (0.03) | 0.57 (0.2) | 71.0 (0.1)  |

*Values in parenthesis represent cumulative mass leached (%)*
3.5. Potential Utilization of Ashes

Concerning the potential utilization of the ash mixtures studied, the results indicate that the calcareous content of these ashes is quite elevated for hydraulic properties to develop, while their SiO$_2$ content is quite high, characteristic of pozzolanic materials. However, the minor amounts of aluminosilicate compounds, despite the low sulphur content, could not render these ashes as received suitable for the cement industry. On the other hand, their alkaline nature, the significant concentrations in nutrients such as Ca, Mg, P, K, Cu, Mn and Zn, along with the fulfillment for land disposal, could allow their use for soil amelioration or liming. The performance of all ash materials could be enhanced if they could be used as liming agents and fertilizers on acidic soils, where dissolution [20] of K and P-based minerals could occur, or if they could be blended with other organic or inorganic byproducts. In this case though, the leachability of Cr should carefully be examined.

![Figure 4. Concentrations of Cr and Sr leached from soil-OK/MBM as a function of time.](image)

![Figure 5. Variation of leachates pH as a function of time.](image)

4. Conclusions

Under fluidized bed conditions, fly and bottom ashes of animal and agricultural wastes were enriched in Ca, Si, Mg, P and K. The principal mineral phases identified were calcite, anhydrite, quartz, dolomite, fairchildite, hydroxyapatite and arcanite. When OK was mixed with MBM two new phases appeared in ashes, calcium sodium phosphate and whitlockite magnesian, whereas when mixed with AM whitlockite magnesian and epsomite. Combustion of AM above 1000°C could lead to ash deposition problems in furnaces. The trace elements which dominated in fly ashes were Cu, Zn, Mn and Sr, the latter presenting a correlation with Ca. Heavy metal
values leached through alkaline soil of phyllitic and quarzitic nature were below legislation limits for land disposal. Ash materials could be used for secondary building materials or for road construction, for soil amelioration, liming or fertilization on acidic soils.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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