Multicomponent Utilization of Fly Ash: Dream or Reality

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ABSTRACT

The present work characterizes various products recovered from fly ashes (FAs) at coal-fired thermoelectric power stations (TPSs) in an attempt at their multicomponent utilization. A combination of conventional methods including sink-float, magnetic, sieving and froth flotation separations, leaching and crystallization procedures, as well as different routine physical and chemical analyses were used to separate and characterize the products derived from FAs at some Spanish TPSs. Both potentially useful and hazardous fractions were sequentially recovered. These include: 1) ceramic cenospheres; 2) water-soluble salts containing some trace elements; 3) a magnetic concentrate enriched in siderophile and certain chalcophile trace elements; 4) a char concentrate with some volatile trace elements; 5) a heavy concentrate containing various trace elements; and finally 6) an improved FA residue suitable for construction materials. The study shows how a waste product can be transformed into useful, high-grade and expensive materials, which may find numerous advanced applications. The preliminary results could be used as an initial basis for the multicomponent, wasteless and environmentally friendly utilization of various FAs.

INTRODUCTION

The present investigation is a characterization of different products recovered from fly ashes (FAs) at coal-fired thermoelectric power stations (TPSs) in an attempt at their multicomponent utilization. Similar FA utilization efforts have been conducted extensively before[1-3]. However, fundamental knowledge about the bulk composition and modes of element occurrence in feed coals and FAs produced in TPSs was insufficient for the advanced and effective application of FA. These relatively unsuccessful attempts are an example of why both basic and applied investigations should be intimately combined in solving FA utilization problems.

The multicomponent utilization of FA is a necessary and unavoidable process due to the complex, heterogeneous and unique polycomponent composition of FA. This waste product originates from the combustion of organic-mineral

rocks, which contain a variety of biogenic, detrital and authigenic (syngenetic and epigenetic) constituents. These constituents are bearing phases and a favorable environment for the capture, fixation and accumulation of various valuable and/or hazardous trace elements. Hence, the bulk utilization of low-cost FA in specific directions without the preliminary recovery of the valuable components is an archaic, unattractive and less effective approach. On the other hand, bulk FA utilization without the preliminary elimination or reduction of some potentially hazardous components is also an environmentally harmful approach.

Why is there seemingly no alternative to the multicomponent FA utilization? A rough estimate may give the answer to this question. From the data available[2-5], it can be calculated that the annual worldwide production of solid combustion waste products (FAs and bottom ashes/slags) from coal-fired TPSs during the last 30 years between 1971 and 2000 was about 500 million tonnes, and optimistically about 33 % of these were utilized. A huge amount of about 10 milliard tonnes therefore must have been deposited unused in disposal ponds, landfills and restored sites. Certainly, some proportions of mobile elements such as As, Bi, Hg, Pb, S, Sb, Se, Sr, U, V, halogens and others were not captured or remained in the waste because they were emitted by the stack emissions of TPSs, washed out or even blown away from the weathered lagooned ashes. According to the mean values of elements in coal ashes worldwide[6], US coal ashes[7] and some components in these wastes[8-9], it can be seen that a great amount of numerous valuable components remain unused in the lagooned ashes/slags (Table 1). Another question is what percentage of these might be recoverable and utilizable, but this is the work of scientists and technologists.

FA is the main waste residue produced during the pulverized coal combustion in TPS. This residue is generated from both inorganic and organic constituents in coal, and from the fluid components associated with them. FA is a complex mixture of various amorphous and crystalline inorganic constituents, and to a lesser extent, organic (char) constituents, containing intimately mixed solid, liquid and gaseous phases. These phases have an original (natural) and/or newly formed technogenic (anthropogenic) genesis. The complex, heterogeneous and variable composition of FAs is the main reason why bulk FA utilization in many fields has limited potential. Each component in FA may be useful or inert in one specific case of application, but harmful in another. For instance, the production of construction materials from FA (as an additive in cement, concrete, bricks, etc.) in many cases cannot possibly be an attractive approach when the FA is enriched in char, magnetite-hematite, water-soluble salts, radionuclides and other toxic and potentially toxic elements. FAs abundant in water-soluble heavy metals are also unsuitable for agricultural uses. On the other hand, these phases and elements have potential for other useful applications. Additionally, sintering, hydrothermal, acidic, alkaline and some physical separation technologies for bulk FA treatment are commonly ineffective, quite expensive or environmentally harmful[2,3,10]. For example, there are fewer perspectives for bulk FA utilization because of: - the application of a large amount of additives for FA sintering; - the chemical leaching of "unleachable" components by a

huge volume of dangerous acid or alkaline solvents; - the synthesis of zeolites from char, Fe oxides, mullite and heavy metal accessory phases after alkaline activation; - the physical separation of "inseparable" aggregates, agglomerates, particles or components by unsuitable procedures. Even if a successful recovery or synthesis of one component from FA occurs the technology is normally not effective and the recovery of other components or the production of additional materials are required for economic reasons. All the above listed problems are related to some limited basic knowledge of the phase-mineral and chemical composition of FAs and their products.

As a result of detailed mineralogical and geochemical studies conducted simultaneously on feed coals and their combustion wastes, the presence and behavior of various noncrystalline, crystalline and organic constituents in FAs was elucidated at a later period[8,9,11-16]. Despite the complex, heterogeneous and variable composition of FAs, the above-mentioned constituents always contain more or less separable glass, quartz-mullite, char, Ca silicate-oxyhydroxide, spinel and salt matrices with various minor and accessory minerals included in the matrices or as discrete phases and particles. These components, occurring in different proportions, are bearing phases of various major, minor and trace elements and are the main useful and/or harmful products that could be initially recovered. Subsequently, if there is a need for additional product treatment this can be applied more successfully to the fractions with well-known and similar compositions or properties rather than to the highly heterogeneous bulk FAs. The conventional, inexpensive and environmentally friendly procedures for FA separation and beneficiation are an additional great advantage for making FA processing more attractive.

The purpose of the present work is to describe the preliminary results of the application of one approach and a combination of conventional methods for separating and characterizing the major useful and/or harmful products recovered from FAs at some TPSs. The study aims to demonstrate how a low-cost waste subjected to detailed basic investigations can be transformed into useful, high-grade and expensive materials, which may find various applications.

MATERIAL AND METHODS

Five FA samples generated from the pulverized combustion of 6 coal blends from national and imported fuels in 4 Spanish TPSs were investigated. A combination of conventional methods including sink-float, magnetic, sieving and froth flotation separations, as well as leaching and crystallization procedures were used to recover sequentially the useful or harmful products from these FAs. The separated fractions include: 1) a ceramic cenosphere concentrate (CCC); 2) a water-soluble salt concentrate (WSC); 3) a magnetic concentrate (MC); 4) a char concentrate (CC); 5) a heavy concentrate (HC); and finally 6) an improved FA (IFA) residue. Routine methods such as optical microscopy, SEM-EDX, XRD, DTA-TGA, XRF, ICP-MS and some other physical and chemical analyses were used to characterize the products recovered. The investigations on trace elements are still in progress and they will be reported in the near future.

RESULTS AND DISCUSSION

1. Coal characterization

The feed fuels used are high to low volatile bituminous coals and anthracites. These coals or their high-temperature ashes (HTAs) are relatively enriched in ash yields, Al_2O_3, Fe_2O_3, K_2O, MgO, and Na_2O, and depleted in SO_3, CaO, and MnO (Table 2), when compared to the Clarke values or mean contents for a set of coals or coal ashes worldwide[6-7,17]. The coals studied have high detrital mineral abundance with mixed carbonate and sulphide-sulphate authigenic mineral tendencies[18]. The mean mineral composition (in decreasing order of abundance) of the coal samples shows that the major minerals (>1-10 %) include quartz, kaolinite, illite-muscovite, and pyrite, while the minor minerals (0.1-1 %) are chlorite, plagioclase gypsum, calcite, dolomite, marcasite, montmorillonite, K-feldspar, jarosite, siderite, and ankerite. The HTAs (500°C) belong to the sialoferricalcic chemical type with a high silicate mineral abundance and oxyhydroxide mineral tendency[18]. The mean phase-mineral data for these HTAs reveal that the ash-forming minerals and phases (>10 %) include quartz > amorphous matter; the major minerals are kaolinite > calcite > illite + muscovite > hematite > anhydrite > plagioclase > K-feldspar; while the minor minerals include montmorillonite, lime, periclase, siderite, dolomite, ankerite and corundum. Hence, these minerals and phases plus unburned char are the most important components that take part in the formation of FAs at the TPSs studied. The common phase-mineral transformations during coal burning and FA formation have been described before[8-9,15,17].

2. Fly ash characterization

Despite the different origin of the samples (various TPS and coals used) most of the FA characteristics reveal a similar qualitative composition and relatively limited quantitative variations (Table 3). These products are finely dispersed materials with a grain size predominantly <100 μm and for some FAs even <20 μm. Their bulk chemical composition (ash basis) does not differ significantly from the composition of HTAs, excluding MnO and SO_3 (Tables 2 and 3). The mean phase-mineral composition (in decreasing order of abundance) of the FAs studied shows that the ash-forming phase is glass; the major minerals and phases include mullite, quartz, char, kaolinite, and hematite; while the minor minerals are cristobalite, plagioclase, K-feldspar, melilite, anhydrite, wollastonite, magnetite, and corundum (Table 4). Another 39 additional minerals, mineral groups or phases identified are accessory (<0.1 %), but very important components in these FAs (Table 4). They include different minerals mostly from oxide and to a lesser extent from silicate, sulphate, phosphate and carbonate classes. A characteristic phase feature of the FAs studied is the abundance of glass, mullite, quartz, kaolinite, Ca silicates, hematite-magnetite, corundum, spinels, char and various accessory minerals of Ba, Ce, Cl, Cr, Cu, F, La, Mn, P, Pb, Th, Ti, Y, and Zr, which is of considerable importance for the multicomponent utilization of FAs. Most of the above listed minerals have also been found in FAs from different Bulgarian

TPSs and their occurrence and probable genesis have been described elsewhere[8].

3. Characterization of the products recovered from fly ash

The characterization includes the composition, certain properties and potential utilization directions of 6 major and some minor products/fractions separated from FAs.

3.1. Ceramic cenosphere concentrate

The CCCs were recovered by the sink-float separation of FAs in distilled water. Their yields (Table 3) are in the range 0.2-1.1 % (mean 0.5 %) and their size is mostly between 20 and 300 μm (74.2-93.0 %, mean 82.8 %). CCCs are composed predominantly of light ceramic cenospheres and to a lesser extent plerospheres, and porous char. The mean phase-mineral composition (in decreasing order of abundance) of CCCs shows that the forming minerals and phases are aluminosilicate glass, calcite, and mullite; the major minerals and phases include quartz, cristobalite, and char; and the minor or accessory minerals are plagioclase, K-feldspar, dolomite, and gypsum (Table 4). CCCs are more abundant in mineral matter, cristobalite, mullite and calcite than the bulk FA samples. The surface occurrence of calcite, dolomite and gypsum on the CCC particles is a result of later crystallization due to the reaction of lime and periclase in FAs with S and C oxides, and water from stack emissions, air and sink-float treatment. The mean phase-mineral composition of CCCs includes 76 % glass, 22 % mineral matter (14 % mullite, 6 % quartz, and 2 % cristobalite and feldspars), and 2 % char if it is normalized without calcite.

The chemical data show that CCCs are more abundant in Al and occasionally in Si, Ca and K+Na oxides in comparison with the respective FAs. These enrichments are connected with the original minerals in coal, namely kaolinite, quartz, calcite, illite and feldspars, and the preferable formation of CCCs from the melting of such minerals. The SiO_2/Al_2O_3 ratio reveals that CCCs have lower values (1.6-1.8, mean 1.7) than FAs (1.8-2.1, mean 1.9). This is a geochemical indication that the major melt composition responsible for cenosphere formation is a result of mixed illite-chlorite-kaolinite (with 2.2, 1.3 and 1.2 SiO_2/Al_2O_3 ratios, respectively) occurrence in coal. The strong influence of illite originally present in coal for the favorable formation of cenospheres in FA has also been emphasized earlier[8].

The char value is lower in CCCs than in the bulk FAs due to the limited occurrence of CCCs and char in agglomerates. The chemical composition for 8 size fractions (in the interval 600-20 μm) separated from two CCCs shows a gradual enrichment of K_2O, and a gradual depletion of Mg and Na oxides with decreasing CCC size. Probably, the coarser grained CCCs are a result of melts originated from coal particles relatively enriched in montmorillonite, chlorite and acid plagioclase, while the finer grained CCCs are due to melts produced preferentially from coal particles abundant in illite and K-feldspar. No generalized trends for mineral distribution in the size fractions of these

CCCs were found. CCCs fusion probably starts at 1300-1330°C and is completed at 1365-1450°C according to the DTA-TGA investigations conducted.

A CCC sample etched by HF reveals that the phase-mineral composition of the residual material includes mullite > aluminosilicate glass > cristobalite > char > quartz. The cenosphere skeleton is built up of intimately growing fine mullite, cristobalite and quartz needle crystals, whereas the skeletal interstices and surfaces are represented by aluminosilacate glass relicts. This sample also shows that the dominant parts of K > Ca > Mg > S > Na and significant amounts of Cl > Fe > P > Si > Ti were leached by the HF treatment. On the other hand, high relative concentrations of insoluble Al with an enrichment factor (EF) = 1.9 and char with EF = 8.1 were detected in this residue. The SiO_2/Al_2O_3 ratio in the residue is 0.7 and this value is considerably lower than that of kaolinite (1.2) and close to that of refractory andalusite - silimanite - kyanite (0.6) and even mullite (0.4). The CCCs recovered could find various applications as special ceramics (fire-, heat- and sound-insulating materials), fillers, sorbents, catalyst supports, etc.

3.2 Water-soluble salt concentrate

The WSCs were recovered by the evaporation and crystallization of the water-soluble alkaline and highly alkaline solutions leached from FAs after the CCC isolations. Their yields (Table 3) are in the range 0.2-0.6 % (mean 0.4 %). The mean phase-mineral composition (in decreasing order of abundance) of the WSCs shows that the forming minerals are gypsum, calcite and bassanite; the major minerals and phases include inorganic amorphous matter, anhydrite, alunite and halite; and the minor minerals are opal, zeolite, dolomite, ankerite, and jarosite (Table 4). The WSCs are more enriched in mineral matter, sulphates, carbonates and chlorides than the bulk FA samples. The WSCs are abundant in S and Ca, and to a lesser extent in Al, Si, Na, K, Mg, Cl, Fe, P and Ti (Table 3). The leaching of these elements is due to their occurrence in water-soluble oxides, sulphates and carbonates, and to a lesser extent chlorides, silicates and phosphates with predominant surface deposits on FA particles. The results show that significant parts of the above listed elements plus some trace elements associated with them also occur in mobile and dangerous water-soluble forms that may contaminate the water, soil and plants. These modes of element occurrence are bioavailable and could penetrate easily into the nutritious chain. On the other hand, the wastewaters from FA processing may be of interest in terms of some element extractions and utilization, in particular for certain trace elements.

3.3. Magnetic concentrate

The MCs were recovered by the dry magnetic separation of FAs after the CCC and WSC isolations. Their yields (Table 3) are in the range 0.7-4.1 % (mean 2.7 %), while their most important size is <100 μm (63.4-94.0 %, mean 79.4 %). The mean phase-mineral composition (in decreasing order of abundance) of the MCs shows that the forming minerals and phases are aluminosilicate glass, magnetite, quartz, and hematite; the major minerals and

phases include mullite, plagioclase, ferrian spinel, and char; the minor minerals are K-feldspar, wollastonite, anhydrite and larnite; while the accessory minerals include different oxides and to a lesser extent silicates (Table 4). The MCs are more abundant in mineral matter, magnetite, maghemite, hematite, ferrian spinel, larnite, and to a lesser extent quartz, plagioclase, and wollastonite than the bulk FA samples.

The bulk chemical composition of the MCs shows that they are relatively more abundant in Fe_2O_3 (EF = 4.2-6.4, mean 5.1), MnO (EF = 3.3-5.9, mean 4.0), and to a lesser extent in MgO (EF = 1.1-1.3, mean 1.1) than the bulk FAs (Table 3). The abundance of these elements is due to their occurrence mainly in the relatively less oxidized ferro-ferrimagnetic and paramagnetic Fe, Mn, Mg and Cr oxides and glasses. Hence, the major source responsible for the formation of MCs is the original coal minerals such as Fe and Mn sulphides-sulphates-carbonates, montmorillonite, chlorite and biotite. Despite these enrichments, MCs are contaminated by Si-, Al-, and Ca-containing phases and to a lesser extent char due to Fe oxide crystallization in the aluminosilicate glass and char particles.

Samples with higher MC yields normally show lower Fe and Mn contents. The enrichment and recovery of these elements from FAs could be improved by several magnetic separations in regulated magnetic fields, under wet conditions and by treatment in solvents. Such Fe-Mn concentrates enriched in siderophile and certain chalcophile trace elements could be used as catalysts or in metallurgy for producing steel abundant in such trace elements or even for their recovery. If the enrichment of Fe and Mn phases and trace elements associated with them are not enough for their above-mentioned utilization, the MCs may be successfully used in the preparation of heavy suspensions in ore or coal washing plants. On the other hand, the thermal treatment of the MC causes the transformation of Fe^{2+} spinels into hematite with a potential application as pigments.

3.4. Char concentrate

The major CCs were recovered by the sieving (>100 μm) of FAs after the CCC, WSC and MC isolations. The CC yields (Table 3) are in the range 1.6-22.8 % (mean 10.0 %) and the most important size of CCs is 100-200 μm (75.5-92.6 %, mean 83.5 %). The char contents in CCs (Table 3) are in the range 5.3-46.8 % (mean 18.6 %) and the EF is 2.1-4.3 (mean 3.4) in comparison with the bulk FAs. A froth flotation procedure was applied to two CCs in order to increase the quantity of char. This beneficiation procedure isolated flotation CCs with 14.8-17.6 % yields and the char material in them is 41.6-92.6 %. The EF for char in these flotation CCs is 2.0-3.1 in comparison with the CCs and 8.4-9.0 in comparison with the bulk FAs, respectively. Hence, a high purification effect can be achieved for CCs after FA sieving >100 μm and froth flotation.

However, limited amounts of char in these CCs (7-48 %, mean 28 %) were recovered from the bulk char material in FAs. For an increase of char yield from FAs, two additional CCs were separated from FAs after the CCC, WSC,

MC and size (<20 μm) isolations. The experiment reveals that 78-91 % of the bulk char material in FAs was derived in this case. So, higher char yields are achieved by sieving >20 μm (mean 85 % char recovery) than by >100 μm (mean 25 % char recovery) for these samples. Additionally, the purification effect for both IFAs is also high because the char value from 10.2 and 4.1 % in bulk FAs decreases to 5.1 and 1.3 % in IFAs, respectively. However, the char quantity in CCs >20 μm is lower (9.1-24.3 %) than in CCs >100 μm (13.5-46.8 %). For this reason two additional flotation CCs were also recovered from the former CCs. The beneficiation procedure isolated flotation CCs with 8.1-14.3 % yields and the char material in them is 29.6-31.8 %. The EF for char in these flotation CCs is 1.3-3.3 in comparison with CCs >20 μm and 2.9-6.4 in comparison with bulk FAs. Hence, a high char yield and significant purification effect can also be achieved for CCs after sieving >20 μm and froth flotation.

The mean phase-mineral composition (in decreasing order of abundance) of CCs shows that the forming minerals and phases are aluminosilicate glass, char, quartz, and mullite; the major minerals include magnetite; while the minor minerals are cristobalite, plagioclase, K-feldspar, wollastonite, hematite, anhydrite, calcite, kaolinite, larnite, and lime (Table 4). The CCs are more abundant in char, mineral matter, quartz, mullite, wollastonite, larnite, magnetite, lime, and calcite than the bulk FA samples. The char in CCs is mainly derived from the highest ranked coals in the blends[19]. It is dominantly formed by anthracite-derived particles and other anisotropic materials either porous or massive, and to a lesser extent, by unfused inertinite and porous isotropic materials. The flotation CCs are relatively enriched in Fe, Ca, S, Ti, P and Cl oxides in comparison with the CCs and flotation wastes (ash basis). Hence, there is an association between the organic matter and some phases (Fe spinels, anhydrite, rutile, phosphates and chlorides) in agglomerates.

The specific surface area (SSA) for the flotation CCs is 3.6 and 9.2 m^2/g, while for the respective FAs used it is 1.5 and 1.9 m^2/g. So, EF = 2.4 and 4.8 for SSA were achieved, respectively. The observations reveal that a significant amount of glass and silicates, and to a lesser extent salts, fill or coat the organic particles. This inorganic material has an increased blockage effect for gas access in the char pores. Acid treatments and steam activation procedures should remove this inorganic material and could increase the SSA. These procedures may cause some microtextural and microstructural rearrangements in char and increasing SSA, but not dramatically for the chars studied. The recovered major and minor CCs enriched in some volatile trace elements could find various applications as fillers, pigments, carbon matrix, catalyst supports, fuel, fertilizers and precursors for sorbents, catalysts and activated carbons.

3.5. Heavy concentrate

The HCs (≥2.9 g/cm^3) were recovered by the sink-float separation of FAs in bromoform after the CCC, WSC, MC and CC isolations. Their yields are in the range 0.02-0.28 % (mean 0.14 %). The mean phase-mineral composition (in decreasing order of abundance) of HCs shows that the forming minerals and

phases are aluminosilicate glass, hematite, and magnetite; the major minerals and phases include larnite, quartz, periclase, mullite, corundum, lime, char, melilite, and rutile; and the minor minerals are plagioclase, wollastonite, ferrian spinel, and anhydrite. The accessory minerals and phases include various species (Table 4). The HCs are more abundant in mineral matter, wollastonite, larnite, melilite, magnetite, hematite, ferrian spinel, lime, periclase, corundum, rutile, and accessory minerals than the bulk FA samples.

The HCs (Table 3) are relatively more enriched in CaO (EF = 1.4-5.0, mean 2.8), Fe_2O_3 (EF = 1.3-3.6, mean 2.3), MgO (EF = 1.6-3.6, mean 2.3) and occasionally in Ti (EF = up to 2.6) and P (EF = up to 1.4) oxides than the bulk FAs (ash basis). They occur mainly in higher density and nonmagnetic or less magnetic Fe oxides and spinels, Ca-Mg-Fe silicates, rutile, phosphates and glasses. Hence, the major source responsible for the formation of HCs is similar to that for MCs plus some Ca-Mg-Fe carbonates and sulphates, phosphates and Ti oxides. Such original minerals were transformed during the combustion process into the above listed newly formed phases, but under more oxidized conditions than those for MCs. Certainly, some parts of the accessory minerals could also be original coal minerals or products from organically bound elements liberated during coal combustion. Despite these metal enrichments, HCs are contaminated by Si- and Al-containing phases and to a lesser extent char due to some crystallization of the Ca-, Fe- and Mg-bearing minerals in the glass and char particles. Samples with lower HC yields normally show higher Fe, Ti and P concentrations. The recovered HCs containing various trace elements could find different applications as raw materials for metallurgy, catalysts, pigments, fertilizers, etc.

3.6. Improved fly ash

These are the final FA residues (IFAs) after the CCC, WSC, MC, CC and HC isolations. The IFA yields (Table 3) are in the range 71.5-97.1 % (mean 86.2 %). The mean phase-mineral composition (in decreasing order of abundance) of IFAs shows that the ash-forming minerals and phases are aluminosilicate glass, mullite, and quartz; the major minerals and phases include char, kaolinite, and plagioclase, while the minor minerals are cristobalite, wollastonite, hematite, anhydrite, K-feldspar, melilite, and corundum (Table 4). The IFAs are commonly abundant in SiO_2, Al_2O_3, mineral matter, quartz, kaolinite, mullite, plagioclase, and wollastonite, but are more depleted in Fe_2O_3, SO_3, Cl_2O, aluminosilicate glass, char, K-feldspar, melilite, magnetite, hematite and accessory minerals than the bulk FA samples (Tables 3 and 4). These FA residues have an improved composition in comparison with the bulk FAs because they have more homogeneous and finer-grained constituents. They also contain favorable components (aluminosilicate glass, mullite, quartz, kaolinite, plagioclase, cristobalite, wollastonite, K-feldspar, melilite, corundum) and few harmful components (water-soluble salts, Fe oxides, unburned organic material, toxic and potentially toxic elements) for construction and other materials. The IFAs could find various applications for construction materials, ceramics, fillers, fertilizers, soil amendment, synthesis of different zeolites, etc. Based on the phase-mineral and chemical

composition, size and pH of IFAs, their agricultural uses as plant nutrients and amendments to acidic soils, and to improve soil physical properties (grain size, aggregation, compaction, water infiltration, stability) are also possible. However, in this case a monitoring of the behaviour of certain toxic or potentially toxic trace elements is required.

CONCLUSIONS

According to the reference data on the multicomponent utilization of FAs the following points should be emphasized:
1) The multicomponent utilization of FAs is a necessary and unavoidable process due to their complex, heterogeneous and unique polycomponent composition, and the great amount of valuable components occurring in FAs.
2) The fundamental knowledge available on the bulk composition and modes of element occurrence in FAs is sufficient for starting and carrying out an advanced, effective and environmentally sound multicomponent FA utilization programme.

A detailed description of the results (some of them are still in progress) from the present work will be reported in the near future. However, some preliminary concluding remarks about the multicomponent utilization of FA can be made:
1) FAs subjected to detailed basic investigations can be transformed into useful, high-grade and expensive materials.
2) Both basic and applied investigations should be intimately combined in solving multicomponent FA utilization problems.
3) Six initial and potentially useful or hazardous products from different FAs, namely ceramic cenospheres, water-soluble salts, a magnetic concentrate, a char concentrate, a heavy concentrate, and finally an improved FA residue can be sequentially and successfully recovered by conventional separation procedures.
4) The above listed 6 products (with or without additional treatments) could find various applications as special ceramics (fire-, heat- and sound-insulating materials), fillers, pigments, raw materials for metallurgy, synthesis of minerals, heavy suspensions for ore and coal preparation, sorbents, catalysts, carbon matrix, activated carbons, catalyst supports, fuel, fertilizers, soil amendments, etc.
5) The present results could be used as an initial basis for the multicomponent, wasteless and environmentally friendly utilization of various FAs.

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Table 1. Rough estimates of the total deposited and unutilized quantities of components in lagooned ashes/slags from coal-fired TPSs worldwide (for a 10 milliard tonnes basis)

Component	Clarke or mean value for coal ashes and lagooned ashes/slags (ppm)	Total deposited and unutilized quantity of components in lagooned ashes/slags (t)
Ag	1.7[a]	17 000
Al	114500[b]	1 145 000 000
As	75[a]	750 000
Au	0.02[a]	200
B	620[a]	6 200 000
Ba	910[a]	9 100 000
Be	16[a]	160 000
Bi	<7.6[b]	<76 000
Br	130[b]	1 300 000
Ca	35100[b]	351 000 000
Cd	5[a]	50 000
Ce	160[b]	1 600 000
Cl	4687[b]	46 870 000
Co	27[a]	270 000
Cr	78[a]	780 000
Cs	8.4[b]	84 000
Cu	64[a]	640 000
Dy	14.5[b]	145 000
Er	7.6[b]	76 000
Eu	3.1[b]	31 000
F	748[b]	7 480 000
Fe	99200[b]	992 000 000
Ga	43[a]	430 000
Gd	13.7[b]	137 000
Ge	14[a]	140 000
Hf	5.6[b]	56 000
Hg	1.3[b]	13 000
Ho	2.7[b]	27 000
I	<7.6[b]	<76 000
In	0.08[a]	800
Ir	<0.008[b]	<80
K	13700[b]	137 000 000
La	92[b]	920 000
Li	115[a]	1 150 000
Lu	1.1[b]	11 000
Mg	8000[b]	80 000 000
Mn	485[a]	4 850 000
Mo	19[a]	190 000
Na	6100[b]	61 000 000
Nb	8[a]	80 000
Nd	72.5[b]	725 000
Ni	70[a]	700 000
Os	<0.008[b]	<80
P	1150[a]	11 500 000
Pb	110[a]	1 100 000
Pd	<0.008[b]	<80
Pr	18.3[b]	183 000
Pt	<0.008[b]	<80
Rb	83[a]	830 000
Re	<0.008[b]	<80
Rh	<0.008[b]	<80

Component	Clarke or mean value for coal ashes and lagooned ashes/slags (ppm)	Total deposited and unutilized quantity of components in lagooned ashes/slags (t)
Ru	<0.008[b]	<80
S	6000[c]	60 000 000
Sb	9.2[b]	92 000
Sc	17[a]	170 000
Se	21.4[b]	214 000
Si	206100[b]	2 061 000 000
Sm	13.0[b]	130 000
Sn	6[a]	60 000
Sr	780[a]	7 800 000
Ta	1.7[b]	17 000
Tb	2.3[b]	23 000
Te	<0.8[b]	<8 000
Th	21[a]	210 000
Ti	3600[a]	36 000 000
Tl	9.2[b]	92 000
Tm	1.2[b]	12 000
U	16.0[b]	160 000
V	150[a]	1 500 000
W	7.6[b]	76 000
Y	42[a]	420 000
Yb	6[a]	60 000
Zn	125[a]	1 250 000
Zr	210[a]	2 100 000
Char	88000[c]	880 000 000
Cenospheres	5000[c]	50 000 000

[a]Clarke for coal ashes worldwide according to Yudovich et al., 1985[6]
[b]Clarke for US coal ashes according to Finkelman, 1994[7]
[c]Mean value based on Vassilev and Vassileva, 1996; 1997[8-9]

Table 2. Common characteristics of 6 feed coal blends used in 4 Spanish TPSs, wt. %

Component	Minimal value	Maximal value	Mean value
Proximate analysis and calorific value (as received basis)			
FC	45.6	70.4	54.8
A (815°C)	12.1	30.8	24.1
VM	6.2	33.6	19.3
W	1.1	2.5	1.9
Calorific value (kcal/kg)	5521	6954	6066
Ultimate analysis (dry ash-free basis)			
C	82.3	89.4	86.1
O	4.9	9.6	7.2
H	2.5	5.3	3.9
N	1.0	2.3	1.6
S	0.8	1.6	1.3
High-temperature (500°C) ash analysis (XRF data)			
SiO_2	50.5	55.1	52.7
Al_2O_3	22.0	30.7	26.1
Fe_2O_3	6.0	8.3	7.1
CaO	3.4	5.1	4.1
K_2O	1.7	4.0	3.2
MgO	1.8	3.2	2.7
SO_3	1.4	2.6	2.0
Na_2O	0.9	1.3	1.1
TiO_2	0.8	1.6	1.0
P_2O_5	No data	No data	No data
Cl_2O	No data	No data	No data
MnO	0.01	0.02	0.02

Table 3. Some common characteristics of 5 FAs and separated FA fractions from 4 Spanish TPSs, as received basis, wt. %

Component	Minimal value	Maximal value	Mean value
Common characteristics of bulk FAs			
Inorganic constituent	89.0	98.7	94.6
Glass material	60.7	79.5	68.3
Mineral matter	17.0	33.1	26.4
Organic constituent (815°C)	1.2	10.9	5.3
Carbon	1.1	9.8	4.7
Volatile matter	0.5	1.0	0.8
Moisture	0.1	0.2	0.1
Calorific value (kcal/kg)	122	875	412
Particle size (<100 µm)	75.0	97.8	87.9
Particle size (<20 µm)	31.2	64.6	52.1
pH for FA (1:10 FA-water ratio)	9.9	10.9	10.5
Ceramic cenospheres	0.2	1.1	0.5
Water-soluble salts	0.2	0.6	0.4
Magnetic concentrate	0.7	4.1	2.7
Char concentrate	1.6	22.8	10.0
Heavy concentrate	≤0.1	0.3	0.1
Improved FA residue	71.5	97.1	86.2
Chemical composition of bulk FAs (XRF data, in brackets EDX data)			
SiO_2	47.7 (48.9)	54.2 (55.5)	50.5 (51.3)
Al_2O_3	24.4 (25.5)	26.6 (27.8)	25.5 (26.4)
Fe_2O_3	6.0 (4.9)	8.0 (6.6)	6.8 (5.9)
LOI (500°C)	1.2	9.7	4.9
CaO	3.3 (3.0)	4.0 (3.5)	3.8 (3.3)
K_2O	2.4 (1.7)	4.0 (2.8)	3.4 (2.5)
MgO	2.5 (2.1)	3.2 (2.9)	2.8 (2.4)
TiO_2	0.8 (0.8)	1.1 (1.1)	1.0 (1.0)
Na_2O	0.8 (0.7)	1.1 (0.8)	0.9 (0.8)
SO_3	0.3 (0.7)	0.6 (1.3)	0.4 (1.0)
P_2O_5	(0.4)	(0.8)	(0.7)
MnO	0.06	0.07	0.07
Cl_2O	(0.02)	(0.04)	(0.03)
Chemical composition of ceramic cenosphere concentrates (EDX data)			
SiO_2	48.1	56.0	52.4
Al_2O_3	29.6	33.2	30.9
CaO	0.7	10.5	4.2
Fe_2O_3	2.1	5.4	3.8
K_2O	2.3	3.0	2.6
MgO	1.5	2.6	2.3
LOI (500°C)	0.7	3.9	1.6
Na_2O	0.6	1.0	0.8
TiO_2	0.7	0.8	0.7
SO_3	0.3	0.7	0.5
P_2O_5	0.1	0.3	0.2
Cl_2O	<0.02	0.05	≤0.03
MnO	No data	No data	No data
Chemical composition of water-soluble salt concentrates (EDX data)			
SO_3	28.7	46.6	36.2
CaO	24.3	40.2	32.2
Al_2O_3	5.8	23.2	12.2
SiO_2	2.9	7.9	6.3
Na_2O	3.2	5.7	4.8
K_2O	3.2	5.9	4.2

Component	Minimal value	Maximal value	Mean value
MgO	1.5	3.7	2.5
Cl_2O	0.6	2.4	1.2
Fe_2O_3	≤0.1	0.6	≤0.3
P_2O_5	0.1	0.4	0.2
TiO_2	0.1	0.3	0.2
MnO	No data	No data	No data
Chemical composition of magnetic concentrates (XRF data, in brackets EDX data)			
Fe_2O_3	28.3	40.8	36.3
SiO_2	29.8	39.1	33.7
Al_2O_3	15.9	20.3	17.6
CaO	3.2	4.0	3.5
MgO	3.0	3.8	3.3
K_2O	1.3	2.6	1.9
LOI (500°C)	0.5	4.1	1.8
TiO_2	0.6	0.8	0.7
Na_2O	0.5	0.8	0.6
P_2O_5	(0.2)	(0.8)	(0.6)
SO_3	0.2	0.4	0.3
MnO	0.20	0.41	0.28
Cl_2O	(<0.02)	(0.02)	(≤0.02)
Chemical composition of char concentrates (EDX data)			
SiO_2	26.3	52.2	42.1
Al_2O_3	15.8	27.9	24.7
LOI (815°C)	5.3	46.8	18.6
Fe_2O_3	2.6	5.4	4.4
CaO	1.8	2.9	2.6
MgO	1.4	2.7	2.3
K_2O	1.0	2.3	1.8
SO_3	0.9	2.0	1.5
Na_2O	0.5	1.0	0.7
TiO_2	0.6	0.9	0.7
P_2O_5	0.3	0.5	0.4
Cl_2O	<0.02	≤0.04	≤0.03
MnO	No data	No data	No data
Chemical composition of heavy concentrates (EDX data)			
SiO_2	34.4	45.1	40.5
Al_2O_3	18.8	26.6	22.7
Fe_2O_3	8.5	18.9	13.8
CaO	4.9	18.4	9.6
MgO	3.4	9.0	6.0
LOI (500°C)	0.6	4.3	2.4
K_2O	1.2	2.1	1.7
TiO_2	0.7	3.0	1.3
SO_3	0.4	1.1	0.8
Na_2O	0.6	0.8	0.7
P_2O_5	0.2	1.1	0.7
Cl_2O	<0.02	0.08	≤0.04
MnO	No data	No data	No data
Chemical composition of improved FA residues (XRF data, in brackets EDX data)			
SiO_2	48.5	55.2	51.8
Al_2O_3	25.0	27.2	25.5
Fe_2O_3	5.6	6.9	6.2
LOI (500°C)	1.2	9.1	4.2

Component	Minimal value	Maximal value	Mean value
CaO	3.2	4.3	3.8
K_2O	2.4	3.9	3.5
MgO	2.3	3.2	2.7
TiO_2	1.0	1.2	1.1
Na_2O	0.7	1.2	0.9
P_2O_5	(0.3)	(1.1)	(0.8)
SO_3	0.3	0.4	0.3
MnO	0.05	0.07	0.06
Cl_2O	(0)	(<0.04)	(<0.01)

Table 4. Forming (F) (>10 %), major (M) (>1-10 %), minor (Mi) (0.1-1 %) and accessory (A) (<0.1 %) minerals and phases identified in 5 FAs and separated FA fractions (CCC – ceramic cenosphere concentrate, WSC – water-soluble salt concentrate, MC – magnetic concentrate, CC – char concentrate, HC – heavy concentrate, and IFA – improved FA residue) from 4 Spanish TPSs. The data are based on mean contents.

Mineral, phase	FA	CCC	WSC	MC	CC	HC	IFA
Silicates							
Quartz	M	M		F	F	M	F
Cristobalite	Mi	M			Mi		Mi
Opal	A?		Mi				
Kaolinite	M				Mi		M
Mullite	M	F		M	F	M	F
Plagioclase	Mi	Mi		M	Mi	Mi	M
K-feldspar	Mi	Mi		Mi	Mi		Mi
Celsian	A					A	
Wollastonite	Mi			Mi	Mi	Mi	Mi
Larnite	A			Mi	Mi	M	
Melilite	Mi					M	Mi
Zircon	A					A	
Zeolite	A?		Mi				
Ca-Fe silicate	A			A		A	
Ca-Fe aluminosilicate	A			A		A	
Fe-Mg aluminosilicate	A			A		A	
Ca-Fe-Mg aluminosilicate	A			A		A	
Oxides							
Magnetite	Mi			F	M	F	
Maghemite	A			A		A	
Hematite	M			F	Mi	F	Mi
Ilmenite	A			A		A	
Spinel	A					A	
Ferrian spinel	A			M		Mi	
Magnesioferrite	A			A		A	
Hercynite	A			A		A	
Ulvospinel	A			A		A	
Chromite	A			A		A	
Chromspinel	A			A		A	
Lime	A				Mi	M	
Periclase	A					M	
Corundum	Mi					M	Mi
Rutile	A					M	
Tenorite - Cuprite	A					A	
Pyrolusite	A					A	
Baddeleyte	A					A	
Ba oxide	A					A	
Ba-Ca oxide	A					A	
Sulphates							
Gypsum	A	A	F				
Bassanite	A?		F				
Anhydrite	Mi		M	Mi	Mi	Mi	Mi
Jarosite	A?		Mi				
Alunite	A?		M				
Barite	A					A	

Mineral, phase	FA	CCC	WSC	MC	CC	HC	IFA
Anglesite	A					A	
Fe sulphate	A						
Carbonates							
Calcite	A	F	F		Mi		
Dolomite	A?	A	Mi				
Ankerite	A?		Mi				
Phosphates							
Apatite	A					A	
Monazite	A					A	
Chlorides							
Halite	A?		M				
Others							
Glass or amorphous matter	F	F	M	F	F	F	F
Char	M	M		M	F	M	M

Multicomponent Utilization of Fly Ash: Dream or Reality

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EXTENDED ABSTRACT

The present investigation is an attempt at the multicomponent utilization of fly ashes (FAs) obtained from coal-fired thermoelectric power stations (TPSs). The experiments carried out are based on detailed chemical and mineral characterizations of these complex combustion residues. A combination of methods including sink-float, magnetic, sieving and flotation separations, leaching and crystallization procedures, as well as various physical and chemical analyses were used to separate and characterize the products recovered from FAs at some Spanish TPSs. Both potentially useful and hazardous fractions were sequentially derived. The products recovered included ceramic cenospheres, water-soluble salts containing some trace elements, a magnetic concentrate enriched in siderophile and certain chalcophile trace elements, a char concentrate with some volatile trace elements, a heavy concentrate containing various trace elements, and finally an improved FA residue for construction materials. The data provide information on the composition and certain properties of the fractions and components separated from the combustion waste products. The preliminary results could be used as an initial basis for a multicomponent, wasteless and environmentally friendly utilization of fly ash. The study shows how a waste product can be transformed into useful and high-grade materials which could find various applications as special ceramics (fire-, heat- and sound-insulating materials), fillers, pigments, raw materials for metallurgy, heavy suspensions for ore and coal preparation, carbon matrix, sorbents, activated carbons, catalysts, catalysts support, fuels, fertilizers, etc.