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Recycling potential of coal fly ash and titanium waste as new fireproof products

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Abstract

This paper studies the possibilities for joint recycling of fly ash (FA) from the combustion of coal in power plants and the waste of the first attack on ilmenite in the production of titanium dioxide (RTi). Studies have been made of the insulating properties of plates composed mainly of FA, together with RTi waste, subjecting them to thermal exposure using standardized fire-resistance tests, with a view to potential use as insulating and fireproof components of fire-resistant items such as fireproof doors and firewalls. Other physical and chemical properties of these products have also been determined in order to characterize their mechanical properties. In addition, given the nature of the raw materials used in the manufacture of the product, an environmental study has been carried out to assess their environmental impact and to compile an ecotoxicological report on the material prepared.

Keywords: Coal fly ash; Titanium waste; Insulating plates; Fireproof products; Waste recycling

1. Introduction

The protection of the environment should be promoted by the recovery (reuse or recycling) of waste materials. In many cases, recycled materials must compete with low cost products. However, when the properties of the waste make its use possible in specific, high added value applications, these products can successfully compete with products made from primary materials, and reduce the environmental costs of waste disposal.

Fly ash (FA) from the combustion of coal in power plants and the residues of the first attack on ilmenite in the production of titanium dioxide using the sulfate process (RTi), have physical and chemical properties which make them suitable, in principle, for recycling as insulating material. These two waste products may be used as the basic constituents of materials cast in plates of differing thicknesses, with insulation and fireproofing properties, which can be then used in various building items such as fire-resistant compartmentalization panels or fire-screen doors.

FA is a powdery material made up basically of very fine vitreous particles, either spherical or rounded, whose chemical composition, morphology and mineralogy, which includes different silicates (mullite, quartz, anorthite, etc.) lend excellent high temperature performance to products manufactured with them, thanks to the low expansion, high stability and low thermal conductivity of some of the above mineral phases.

The quantity of coal ash annually produced worldwide in large power stations probably exceeds 550 Mt [1]. On the average about 50% of these residues are utilized (with large variation from country to country) as additives in cement and concrete production or in civil construction. Depending on perspective these by-products (coal combustion by-products; CCBs) are either a valuable resource or a troublesome waste material incurring significant disposal costs.

The uses for ash are determined by the different physical and chemical characteristics of the ash. These uses can be subdivided into two broad groups [2–5]:

(1) Those in which the FA can be used directly. This group can be further divided into three subgroups: (a) those that make use of ash as a pozzolanic material, (b) those that use it as an inert material with beneficial bulk properties and reasonable handling characteristics, and (c) those that use certain chemical properties of the ash.
(2) Those in which the FA requires processing either physically or chemically to produce an end product which can be used. The "processed" uses can be subdivided into (a) those in which pozzolanic or related properties are again used to combine the FA with other materials, forming a structural product such as bricks or concrete blocks and (b) those in which a valuable component of

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the FA is selectively removed (e.g. the recovery of aluminum or magnetite).

RTi residues can also be a source of by-products with added value. These residues are obtained from the digestion of ilmenite with concentrated sulfuric acid at 150–220 °C, when the titanium separates in the form of titanyl sulfate which, after hydrolysis, precipitation, and calcination, is transformed into TiO_2. The RTi are generally neutralized or stabilized and solidified before finally being placed in landfills. Since, with very few exceptions, inorganic titanium compounds are considered to have very low toxicity, the trend at present is to reuse these residues in two ways, either being recycled in the process or being reused as an additive in the ceramics industry.

The idea of using RTi together with FA in applications where these components are subject to high temperatures is based on the fact that RTi have mineral phases with certain properties analogous to those of the silica contained in FA. Silicon oxides and titanium oxides form immiscible crystalline phases at a wide range of temperatures, but however require high temperatures for the crystallization of the vitreous phases of SiO_2–TiO_2. Under certain conditions of temperature and composition, the silica or calcium silicate crystals may become distorted as a result of the replacement of Si^{4+} ions by Ti^{4+} ions, producing different types of titanates in the CaO–SiO_2–TiO_2 system [6]. Therefore, the mixture of FA and residues with TiO_2 mineral phases may generate different thermally stable titanates at high temperatures.

In order to make the material more porous and to reduce its density, a small amount of exfoliated vermiculite has been added to the FA–RTi mixture. Vermiculite also improves the properties of the developed products, due to the delayed heat transmission caused by the loss of the water which it retains (moisture and adhered water), during exposure to high temperatures.

Therefore, the aim of this article is to demonstrate the recycling possibilities for products composed mainly of FA–RTi (>90 wt.%), that is, of waste materials, with a view to their possible use in the manufacture of insulating and fireproof plates which can be used in fire-resistant items such as fireproof doors and firewalls. The characteristics of other products similar to the one presented in this paper, denominated PO-2, have recently been described [7]. The present results form part of the general possibilities for reuse and recycling of FA, which are described in other papers [2–5].

2. Experimental

2.1. Raw materials

For the manufacture of plates of the PO-2 product the following residues and materials were used:

- FA from the combustion of powdered coal obtained from electrostatic precipitator ESP units, produced in the Los Barrios Power Plant (Cádiz, Spain), from the combustion of Colombian coal (ASTM Class F).
- Residues from the first attack on ilmenite in the manufacture of TiO_2 in the Tioxide España plant (Huelva, Spain). This is unaltered ilmenite with a high moisture content and a sulfuric acid content of less than 5%. The solid residues from the digestion of ilmenite are in the form of inert solids: the insoluble mineral which has not reacted with the sulfuric acid and the undissolved digestion cake which is washed with water to eliminate part of the acid.
- Commercial vermiculite containing 56% of particles with a diameter of less than 2.83 mm. The exfoliated vermiculite is a mineral from the group of hydrated ferromagnesian aluminium silicates.

2.2. Manufacture of the plates

The plates were made using simple, low cost manufacturing methods, with no prior treatment of the residues. The plate manufacturing process was as follows:

- the components of the mixture comprised mainly of FA (>50%, w/w), titanium waste (>35%, w/w) and vermiculite (<10%, w/w) were weighed according to the formulation;
- then the components were placed in a planetary mixer with enough water so that the mixture was homogenous;
- finally, the mass was poured into 28 cm × 18 cm molds with different thicknesses. The plates were taken out of the molds after being allowed to set for 24 h at ambient temperature.

2.3. Insulating capacity

The standard fire-resistance test described in Spanish regulation UNE-23.093 [8], similar to other widely used international standards, is the result of the observation and analysis of several actual fires. To simulate the conditions of exposure to fire, the regulation requires that one of the sides of the protective material be exposed to heat according to a standard temperature curve defined by the equation: $T = 20 + 345 \log_{10}(8t + 1)$, where T is the oven temperature for the tests in °C and t the time in minutes from the beginning of the test.

To study the insulating capacity of the plates, a special oven was designed so that the molded plates could be subjected to the standard fire-resistance test mentioned above, after a curing period of more than 1 month. The furnace door can be replaced with a special door in which the plates to be tested were inserted. This furnace allowed us to record the surface temperature of the exposed face of the plate by means of a type S thermocouple inside the oven (see Fig. 1), which was used to regulate the power of the oven by means of a proportional controller, so that the standard temperature curve was produced.

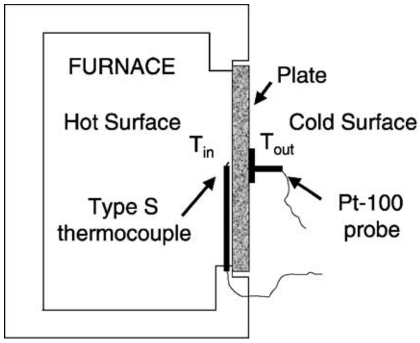

Fig. 1. Insulating capacity test.

On the unexposed face, the temperature is registered by means of a Pt-100 probe with a stainless steel contact surface (see Fig. 1). At the same time, the oven has an output of 0–10 V, proportional to the power used, which allowed us to measure this parameter.

2.4. Characterization of materials

2.4.1. Thermal behavior

Thermal analytical techniques such as DSC–DTA (TA Instruments 2920) were used to determine the thermal behavior of the materials. The study was carried out using a 20 °C/min heating ramp rate and air atmosphere.

2.4.2. Compressive strength and bending strength

The compressive (ASTM D-1633-84 and UNE 80-101-84) and bending (ASTM D-1635-87) strengths of the samples were also evaluated. These mechanical tests were carried out for at least 1 month after the manufacture of the test pieces.

2.4.3. Porosity and density

The pore-size distribution of the samples was determined by Hg injection porosimetric analysis using a Micromeritics 9320 Poresizer Unit and the apparent density of the solid was also determined.

2.4.4. SEM and XRD

For the X-ray diffraction study, a Siemens D5000 apparatus was employed using Ca Kα radiation with a nickel filter. SEM analysis was carried out using a JEOL JSM-5400 system with a Linx analyzer and beryllium window.

2.5. Environmental study

An environmental study was also carried out by means of leachability study (TCLP [9] and DIN 38414-S4 [10] leaching tests) of the PO-2 product. Major and trace element contents in leachates were determined by ICP-AES and ICP-MS. The leachates were subjected to two ecotoxicological biotests: *Photobacterium phosphoreum* luminescence test and *Daphnia magna* inhibition test, which are the two biotests used for the characterization of hazardous waste in Spain.

3. Results and discussion

3.1. Chemical analysis

Table 1 shows the chemical analysis of the constituents of product PO-2.

As can be seen in the Table 1, these are class F FAs with a slightly high calcium content (8–9%, w/w as CaO). The titanium waste shows a very high moisture content for a material which contains over 50% of titanium dioxide. The vermiculite analyzed has a high magnesium and silica content.

3.2. Thermal properties

Fig. 2 shows the results of the DTA study carried out on the different constituents of the material and the developed product. The figure shows more or less additive thermal behavior of the constituents in the DTA of the PO-2 product. This appears to indicate that there have been no significant reactions between the constituents of the material. The figure also highlights the following characteristics:

- The strong exothermal peak between 500 and 800 °C of the FA due to the oxidation of the unburnt coal present.
- The endothermic depression (as far as 180 °C) of the titanium waste due, among other things, to the high moisture content and the endothermal peak around 625 °C, due possibly to the decomposition of different sulfates and titanium hydrolyzates retained in the waste and which have

Table 1
Average composition (wt.%) of the individual constituents of the PO-2 product

Loss on ignition	CaO	MgO	Fe_2O_3	Al_2O_3	SiO_2	MnO_2	TiO_2	K_2O	Na_2O	SO_3
Fly ash (%)										
3.5	8.38	1.86	2.39	34.40	45.30	0.05	1.40	0.57	0.40	0.46
Moisture	Fe_2O_3	CaO	MgO	Al_2O_3	SiO_2	TiO_2				
Titanium waste (%)										
37.10	19.10	0.28	0.13	1.70	11.06	50.63				
Vermiculite (%)										
4.58	7.87	0.60	25.26	10.19	47.87	1.22				

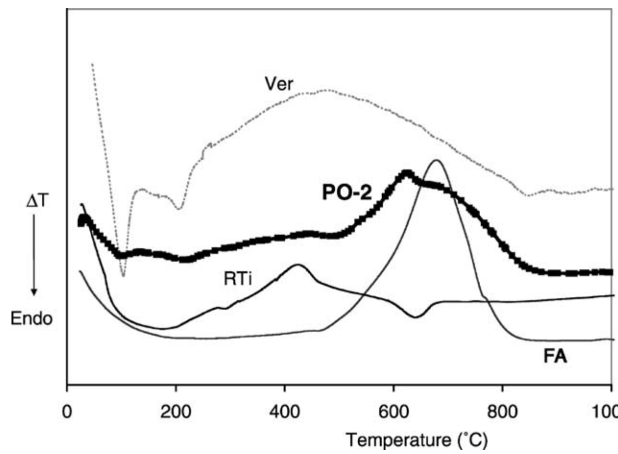

Fig. 2. DTA of individual components and PO-2 product.

not been extracted in the process of digestion of ilmenite with sulfuric acid.
- The endothermal peaks at 100 and 200 °C in the vermiculite thermogram, the first due to the evaporation of water from the pores and the second caused by the loss of moisture adhered between the mica flakes of the mineral.
- The high thermal stability of the constituents at temperatures over 800 °C.

3.3. Insulation properties

The criteria for the insulation behavior of the plates is based on a general concept of insulation described in standard UNE-23093, in which the insulation properties are quantified by time in whole minutes, measured in the course of test in which the sample maintains its function as a separator without reaching high temperatures on its unexposed side. In this paper, the insulation capacity was calculated by measuring the time necessary for the unexposed side to reach a temperature of 180 °C (t_{180}), when the exposed side is subjected to the standard fire-resistance temperature.

Fig. 3 shows the results obtained in this thermal test for plates of 20 and 33 mm thick. This figure shows the importance of thickness in the insulation capacity of the material, with t_{180} values of over 60 min for thicknesses of 33 mm. This figure can compete with that of commercial products and is interesting for possible applications of this type of material as internal insulation elements in fire doors or fireproof compartmentalization panels.

It can also be observed that, especially in the thicker samples, there is an evaporation plateau for the unexposed side, due to the moisture in the material as a whole and the inherent water contributed by the vermiculite. The fact that the curve gradients before and after this plateau are different is possibly because, the continuous evaporation and condensation of steam flowing from the exposed to the unexposed side increase the thermal conductivity of the material. Because of this, the gradient in both cases is higher before the

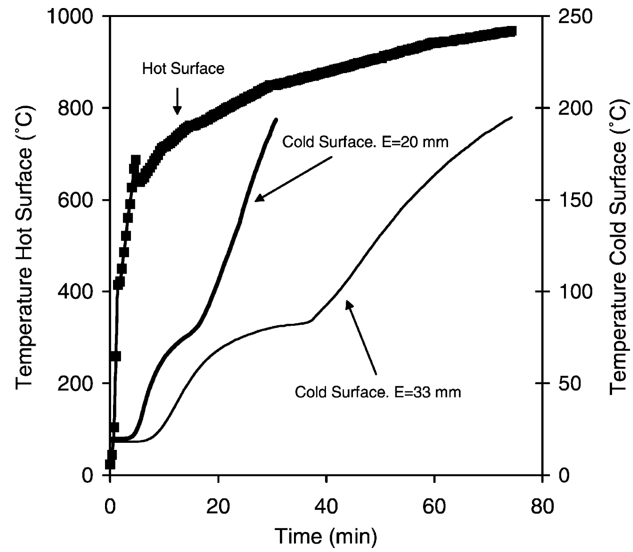

Fig. 3. Thermal test of the PO-2 product.

evaporation plateau than after it, when the product is dry. The duration of the plateau clearly depends on the thickness of the material, as is logical. Finally, it should be pointed out that no smoke was emitted from the plates at any time during the test.

3.4. Mechanical and structural properties

After the thermal test, the plates maintained their structural integrity, and in no case were cracks or crumbling observed. There was practically no loss of dimensional stability.

The mechanical stability of the product is probably due to the pozzolanic reaction of the FA and to the neutralization of the sulfuric acid in the unaltered ilmenite with the calcium oxide of the FA giving anhydrite ($CaSO_4$), which gives the material sufficient mechanical stability at high and low temperatures.

Table 2 shows the average mechanical resistance values of the product in 5 cm × 3.3 cm × 17 cm ($W \times T \times L$) specimens, cut from the plates before (0) and after (1) the test.

The most striking thing in the above table is the reduction in the mechanical resistance of the product when it is subjected to the thermal test, probably due to internal stresses created between the exposed and the unexposed sides. In order to clarify this point, an SEM study was carried out, with the results described in Fig. 4, which shows representative micrographs of the exposed and the unexposed sides

Table 2
Mechanical parameters of the PO-2 product (MPa)[a]

	$\sigma_C(0)$	$\sigma_C(1)$	$\sigma_F(0)$	$\sigma_F(1)$
PO-2	0.31	0.12	0.08	0.05

[a] σ_C: compressive strength; σ_F: bending strength.

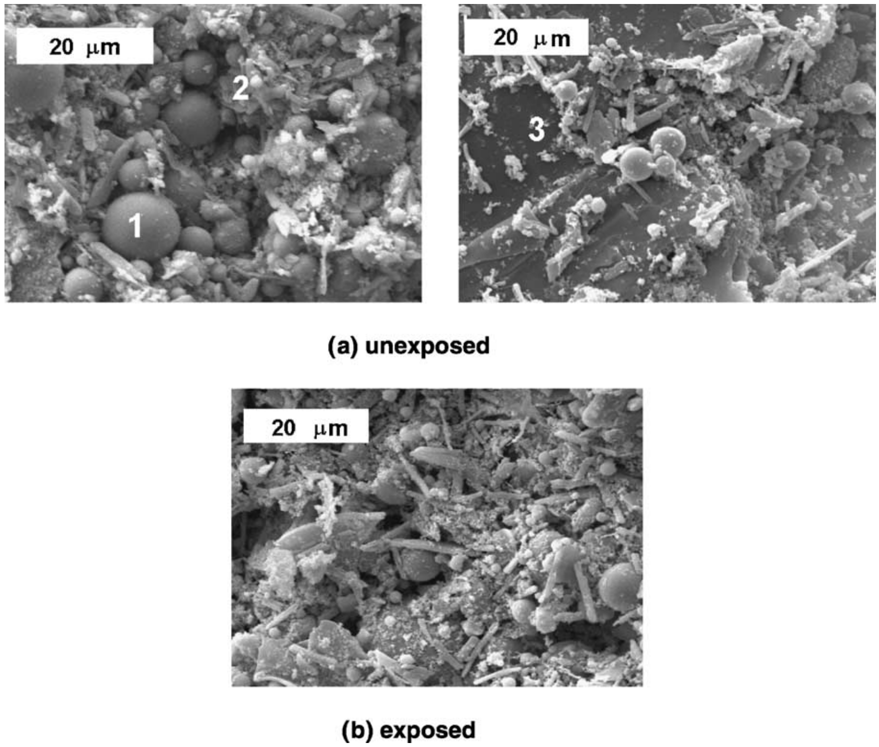

Fig. 4. SEM study of exposed and unexposed sides of the PO-2 plates (1, FA; 2, RTi; 3, Ver).

of the material after the test, complemented with an X-ray diffraction study.

The photos show the similar structure of the material, both on the exposed and the unexposed sides, and the constituent materials (FA, RTi, and Ver) of the product can be clearly distinguished, with slight alterations on the exposed side. No significant morphological changes are observed. All of this appears to coincide with the observed stability of the product after exposure to high temperatures, demonstrated by the absence of visible cracks or crumbling in the plates after heating not withstanding the high temperature gradient between both sides of the plate during the test.

The X-ray diffraction analyses of the exposed and unexposed sides after the test show the following main mineral phases in the exposed side: mullite, quartz, rutile, muscovite, ilmenite, and anhydrite, while the unexposed side has the same mineral phases, but with vermiculite instead of muscovite. In any case, the change in volume due to the partial change of vermiculite to muscovite on the exposed side was not enough to cause noticeable structural changes.

The porosimetric study of the product demonstrates its high porosity, with average pore diameters between 0.5 and 10 μm and an average density of 740 kg/m^3.

3.5. Environmental study

Since this product is obtained from different waste materials, an environmental study was carried out to characterize more completely the PO-2 product and be able to evaluate better, its possible uses. The study involved subjecting the product to two of the most commonly used leaching tests in the waste management field, TCLP and DIN 38414-S4 tests, a chemical analysis of the extracts and an ecotoxicological assessment of the leachates obtained.

Table 3 shows the figures for the concentrations of different metals analyzed in the DIN and TCLP leachates. In general it can be seen that the concentrations of the metals showed are low and are in all cases at parts per billion level (ultratraces). It can also be observed that concentrations in the TCLP leachates are in general higher than in the DIN leachates, which reflects the more aggressive nature of the leaching fluid (an acetic solution) of the TCLP test.

Very few countries have standards in force, regarding the reuse of residues. In relation to this, the Netherlands may be emphasized within the EU. The recycling or reuse of secondary materials in the Netherlands within the building industry is commonplace; more than 10% of all granular

Table 3
DIN and TCLP leachability of the PO-2 product (μg/l) (N.D.: under detection limit)

	Ti	V	Cr	Co	Ni	Cu	Zn	As	Se	Mo	Cd	Sn	Sb	Ba	Hg	Pb
DIN	199	35	44	2	29	17	46	21	N.D.	88	1	13	8	41	N.D.	2
TCLP	170	11	77	83	264	284	430	46	N.D.	3	4	20	24	328	N.D.	7

Table 4
Metals limits for DIN leachates according to Wastes Catalogue of Catalonia and DIN leachability of the PO-2 product (μg/l) (N.D.: under detection limit)

	Cd	Cr	Ni	Cu	Zn	As	Hg	Pb
A	100	100	500	2000	2000	100	20	500
B	200	100	1000	5000	5000	500	50	1000
PO-2	1	44	29	17	46	21	N.D.	2

Table 5
Concentration limit values for heavy metals according to LAGA and DIN leachability of the PO-2 product (μg/l) (N.D.: under detection limit)

	Cr	Ni	Cu	Zn	As	Hg	Cd	Pb
Z0-LAGA	15	4	50	100	10	0.2	2	20
Z1-LAGA	30	50	50	100	10–40	0.2–1	2	40
Z2-LAGA	300–350	50	50	100	40–100	2	10	40
PO-2	44	29	17	46	21	N.D.	1	2

Table 6
Ecotoxicity tests and pH values of the PO-2 leachates

Leaching method	Luminiscence, EC_{50}	*D. magna*, EC_{50}	pH
DIN	>250000	–	9.72
TCLP	4400	4400	4.51

materials used within the building industry are recycled materials.

The Dutch building materials decree (BMS) [11] contains rules relating to the use of stony building materials and earth in construction and other works. The aim of the BMS is to prevent pollution of the soil and surface water. The decree prescribes a standardized column leaching test for granular building materials (NEN 7343) and a tank leaching test (NEN 7345) for bound or shaped materials. For this reason, although BMS is one of the most advanced regulations related to the reuse of residues, as the Dutch standard refers to different leaching tests, it does not make much sense to compare the DIN and TCLP results with the limits stated in the BMS.

In Spanish legislation there is no legal requirement for the reuse of waste materials in this type of products. Only the Autonomous Government of Catalonia has established regional regulations for waste management, including limited recycling for some wastes. Among other concepts, the law defines three types of residues. To classify the residue as being either inert, non-special or toxic, a certain methodology is used as per Decree 34/1996 of 9 January 1996 [12]. The classification process requires determining the standard DIN 38414-S4 leachate. According to the Wastes Catalogue of Catalonia, in order to classify wastes, the concentration of certain heavy metals in the leachate must be determined. Table 4 gives the limits of the three categories with regard to those metals. A waste is classified as inert if the values are below those of column A, non-special if the values are between those of column A and B and toxic if the values exceed those of column B. Taking into account the metal concentrations in the DIN leachate, the PO-2 product can be considered as an inert waste, as it has chemical parameters below the limits established by the standards. Practically, the same limits stated in column A apply to the assessment of different slags (metallurgical and MSWI slags) in the construction sector, also according to Catalan regulations, which are currently the only Spanish regulations concerning the use of residues as by-products [13].

Specifications of the CEN (European Committee for Standardization) concerning the use of FA as construction material are contained in EN 450 for concrete and EN 197-1 for cement. Although the European standards do not contain limits on the heavy metals concentration and leaching, there are countries in which these limits exist [14]. In Germany, for example, the use of mineral waste in this context is regulated by the requirements of LAGA [15]. The specifications of LAGA distinguish among three types of wastes to be used in open-air construction works:

- waste that can be used without any safety precautions (Z0 waste);
- waste that can be used only in specific sites (Z1 waste);
- waste that can be used only if specific measures are taken (Z2 waste).

The classification of waste is made after the waste origin, the waste composition and its leachability. The German legislation classifies waste after an estimation of the metals mobility, based on the leaching of metals (the same eight metals mentioned in the Catalan regulation described above) using distilled water (DIN 38414 test). The comparison among DIN leachate concentrations shown in Table 5 indicates that the PO-2 product may be classified as Z2 with respect to its metals leachability (FA from coal firing is always classified as Z2 waste), as it surpasses the Cr limit for Z1 wastes. Nevertheless, we have to take into account that only materials used in outside construction are covered by LAGA (the same is true for the Dutch BMS). However, the product described in this paper is to be used in the interior of buildings or even in the inside of a fire-screen door and thus, the demands on such construction materials should be lower than those required by this German regulation.

After obtaining the leachates, these were subjected to two ecotoxicological biotests: *P. phosphoreum* luminiscence test and *D. magna* inhibition test. None of the samples analyzed had values less than the legal limits (Luminiscence limit EC50: 3000 mg/l and *D. magna* limit EC50: 750 mg/l for TCLP waste leachates) established in Spanish regulations for hazardous wastes [16] (see Table 6).

4. Conclusions

This study reveals the possibilities for the joint recycling of two industrial wastes, FAs from the combustion of coal and a residue from the production of TiO_2 pigments. As described in this paper, these by-products can be processed to produce insulating plates with fireproof properties comparable to those of commercial products on the market, in an application which, in addition to the evident improvement in environmental management of FAs and RTi, gives a higher added value than that of other recycling options already studied for these by-products.

Acknowledgements

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References

[1] W. Vom Berg, CCP Utilization in Europe-outstanding option and continuous challenge, in: Proceedings of the ECOBA Anniversary Conference on CCP utilization in Europe, The European Association for Use of By-products of Coal-Fired Power Stations, Essen, Germany, June 15, 2000.
[2] L.L. Sloss, Trends in the use of coal ash, CCC/22, IEA Coal Research, London, 1999.
[3] L.L. Sloss, I.M. Smith, D.M.B. Adams, Pulverised coal ash-requirements for utilisation, IEACR/88, IEA Coal Research, London, 1996.
[4] L.B. Clarke, Legislation for the management of coal-use residues, IEACR/68, IEA Coal Research, London, 1994.
[5] L.B. Clarke, Applications for coal-use residues, IEACR/50, IEA Coal Research, London, 1992.
[6] N.K. Katyal, S.C. Ahluwalia, R. Parkash, Effect of TiO_2 on the hydration of tricalcium silicate, Cem. Concr. Res. 29 (1999) 1851–1855.
[7] L.F. Vilches, C. Fernández-Pereira, J. Olivares del Valle, M. Rodríguez-Piñero, J. Vale, Development of new fire-proof products made from coal fly ash: the CEFYR project, J. Chem. Technol. Biotechnol. 77 (2002) 361–366.
[8] UNE Spanish Standard 23093-1, Fire resistance tests. Part I. General requirements, 1998.
[9] US EPA, 1986, Test methods for evaluating solid waste, Toxicity characteristic leaching procedure (TCLP), Method 1131 SW-846, 3rd. Washington, DC, November 1986, 40 CFR 261 Appendix II, Fed. Reg. 55: 11863, March 29, 1990.
[10] DIN 38414 S4, German standard procedure for water, wastewater and sediment testing, Group S (sludge and sediment), Determination of Leachability (S4), Institüt für Normung, Berlin, 1984.
[11] The Building Materials Decree (Bouwstoffenbesluit) (nr. 12689/165), The Netherlands Ministry of Housing, Spatial Planning and the Environment (VROM), 1995.
[12] Waste Catalogue of Catalonia, Decree 34/1996, January 9, 1996, Generalitat de Catalunya DO, 1996, p. 2166.
[13] Order of Valorisation of Slags, Generalitat de Catalunya DO, February 1996, p. 2181.
[14] R. Cenni, B. Janisch, H. Spliethoff, K.R.G. Hein, Legislative and environmental issues on the use of ash from coal and municipal sewage sludge co-firing as construction material, Waste Manage. 21 (2001) 17–31.
[15] Länderarbeitgemeinschaft Abfall (LAGA)- Mitteilungen, Anforderung an die stoffliche Verwertung von mineralischen Reststoffen/ Abfällen, Stand: September 5, 1995, 20, Erich Schmidt Verlag, Berlin, 1996.
[16] Spanish Order of October 13th, Methods of characterization of hazardous wastes, BOE no. 270 10 de Noviembre de 1989.