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AN ECO-EFFICIENT METHOD TO VALORIZATION OF SOLID WASTES: HYDROTHERMAL TREATMENT

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Abstract

In this paper, it is presented the effect of Hydrothermal Treatment (HT) of ash from the incineration of municipal solid waste (MSWIA), classified as hazardous waste and industrial by-products such as coal combustion fly ash (FA). The most interesting results here presented they show that practically 100% of chloride ion content of some of these materials disappears after the hydrothermal treatment of the solid; they are also formed so important phases as tobermorite, C-S-H gel, belite etc, with cementing character. This treatment allows, therefore, valorise these wastes in cement-based materials and its application in the construction sector.

Keywords: Hydrothermal Treatment, Incineration Ash, Fly Ash, Ecoefficient Process

INTRODUCTION

The world climate is changing significantly due to increased emissions of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), nitrous oxides and chlorofluorocarbons. These gases catch a growing portion of the infrared terrestrial radiation being expected increases of the planetary temperature in a range understood between 1,5 and 4,5ºC. Associated to these changes, there will be great changes in the global (1) ecosystems.

The signing of the Kyoto Protocol has forced to the countries to the implementation of drastic measures to reduce emissions of such greenhouse gases. In the industrial sector, the saving measures and of emission they are specific for each process, cement and construction industry is one that has contributed to environmental impact and one of the most affected by measures taken in the Kyoto Protocol (2). For this reason, the sectors of cement and concrete are making great efforts to get that their development is truly sustainable (3). Among the measures to be taken is the use of solid waste in the development of "new eco-efficient cements". Among these cements are:

- geopolymer cements (zeolitic cements) that it implies an alkaline activation of the by-product to use.
- Ecocement: Whose raw materials are ashes from municipal solid incineration plants, with similar technology to Portland cement.
- Reactive low Energy Belite Cements (4-5): among those that highlight, fly ash belite cements (FABC).

The latter have a special interest, because it can be synthesized by means of Non Conventional Low Energy Processes (6). Inside the investigations carried out in this case, it is necessary to highlight those developed in Spain within the Institute of Construction Science Eduardo Torroja (7-12). Our investigations focused on the hydrothermal-calcination-route for making new cement based materials more environmentally friendly. In out case we are used wastes as raw materials such as fly ash from coal combustion (FA) and fly ash and bottom ash from incineration of municipal solid wastes (MSWIFA) to making reactive belite cement.

The fabrication process included a prehydrothermal treatment of the wastes, and it can describe as "eco-efficient process". The process has energy and environmental improvements, since it involves not only the preservation of natural raw materials but also a saving in energy (800 º C vs. 1400 ° C) consumption, CO_2 emissions and disposal from landfills of the wastes. All of which is a sustainable development in industrial sectors generators of these waste. In this paper, we presented the optimization of the synthesis parameter to obtain belite cement, using as raw materials (FA) and (MSWIA).

EXPERIMENTAL

As raw material we have been used two types of ash: fly ash (FA) and municipal solid waste incineration fly ash (MSWIFA). The chemical composition of the ashes is presented in Table 1.

Tabla 1. Chemical Composition of Raw Materials

	MSWIFA	FA
LOI	17.6	5.6
IR	0.1	0.3
CaO	44.9	4.65
SiO_2	11.4	48.8
Al_2O_3	11.3	26.8
Fe_2O_3	1.1	7.5
MgO	1.9	1.9
SO_3	3.9	0
Na_2O	2.1	0.7
K_2O	1.9	3.7
Cl^-	13	-
Zn^{2+}	0.36	-
Pb^{2+}	0.38	-
Cd^{2+}	.0017	-

Of note is the high content of chloride ion and heavy metal that has MSWIFA ash in its composition.

The experimental procedure includes a hydrothermal treatment (HT) (Figure 1) of the mixture: raw material (waste) and water (or alkaline solution, as appropriate). The hydrothermal treatment was carried out with a Parr model 4522 (100 mL pump with split-ring closure and a PID model 4842 temperature controller).

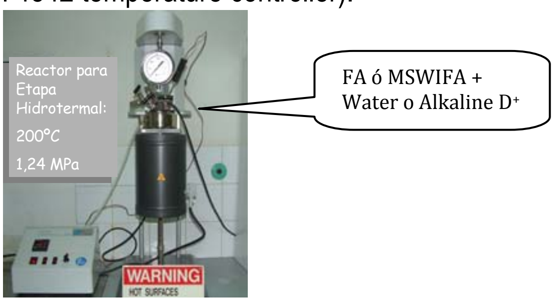

Figure 1. Hydrothermal Step: Cement Precursors Phases

The hydrothermal treatment was carried out in water and a 1 M NaOH solution for different period of time at the temperatures of 100°C, 150 °C, and 200 °C. The precursors obtained during the hydrothermal treatment were heated at temperatures of 700°C, 800 °C, 900 °C, and 1000 °C for obtaining the belite phase (C_2S).The changes of fly ash composition after the different treatments were characterized by different techniques.

Also, this process produces liquid phase that must be analyzed to assess the effectiveness of waste treatment in those with high contents of pollutants and hazardous ions for building materials (such as MSWIFA) also allow you to see the possibility of recovery of the liquid fed to the system used here. The use of calcinations temperatures below 1000 ° C, provides a "new type of cement, synthesized to very low temperature, compared with a microwave clinkering of Portland cement clinker, which reaches 1450º C.

In the case presented here, as the FA, has % by weight of CaO and SiO_2 of 4.65 and 48.8, respectively, it was given the possibility to add CaO (lime) commercial to fit the stoichiometry of C_2S. It would obtain fly ash belite cement (FABC) or municipal solid waste incinerations fly ash belite cement (MSWIFABC).

RESULTS AND DISCUSSION

1. Fly Ash Belite Cement (FABC)

The changes of starting fly ash as a consequence of the hydrothermal treatment in water have been following by X-Ray Diffration and Scanning electron Microscopy.

XRD patterns were recorded on a PhilipsPW1730 diffractometer with a graphite monochromator and Cu KR1 radiation. The main crystalline compounds of the starting fly ash are: calcite ($CaCO_3$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$), hydrated monosulfo calcium aluminate ($Ca_4Al_2(SO_4)O_6.12H_2O$), gypsum ($CaSO_4.2H_2O$), and quartz (SiO_2). When the fly ash is hydrothermally treated in demineralised water at different temperatures, 100°C, gypsum transformed in bassanite ($CaSO_4.0.5H_2O$) and appeared others precursors belite cements phase like as: katoite $Ca_3Al_2(SIO_4)(OH)_8$ (C_3ASH_4); $Ca_5Si_6H_2O_{18}.4H_2O$, C-S-H gel ($Ca_{1.5}SiO_{3.5}.xH_2O$) and α-C_2SH. The aspect of these hydrothermal changes is shown in the Fig. 2.

Subsequently, these precursors are dehydrated by controlled heating from 700 º C, 800 º C and 900 º C followed by rapid cooling the air, resulting in a mixture of varieties crystallographic α'_L-dicalcium silicate C_2S and ß-dicalcium silicate C_2S, high reactivity, such and as seen in the XRD results shown in Figure 3.

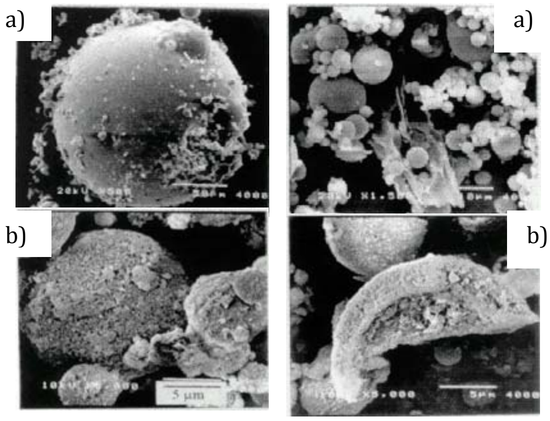

Figure 2. Morphologic of fly ash before (a) and alter hidrotermal treatment (b)

At temperatures above 800ºC, it forms mayenite $C_{12}A_7$) and gehlenite (C_2AS) phase that are undesirable due to the high reactivity of mayenite and low reactivity in the case of gehlenite.

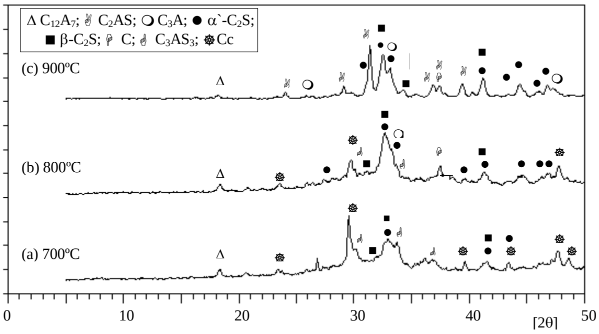

Figure 3. XRD difractograms of FABC with calcinations temperature

This kind of belite cement has at 28 days of hydration a value of compressive mechanical strength to compression of 30 MPa, comparable to ordinary Portland cement type CEM I-32.5 (9).

Furthermore, as shown in Figure 4, it is important to highlight the color of FABC, which makes it potentially useful for some applications.

Figure 4. Aspect of Mortar Samples making with FABC

2. Municipal Solid Waste Incineration Fly Ash Belite Cement (MSWIFABC)

After HT of these ashes, we proceeded to the characterization of liquid and solid phase. As it has been mentioned previously, the characterization of the liquid phase in this case has special interest for the content in metals and chloride ions of theses ashes.

2a. Liquid Phase Characterization

The evolution of liquid phase composition with time of hydrothermal treatment appeared in Table 3. The ions analysed were Cl^-, SO_4^{2-}, Zn^{2+}, Cd^{2+} and Pb^{2+} as well as pH and conductivity. Values of starting MSWFA (time 0) have been included in this Table for comparison. The units of measured concentrations in the liquid have been converted in g per kg of MSWFA by the equation m_d = cV, where c is the measured concentration of the liquid and V is the volume used (150 cm^3).

Table 3. Concentration of Elements dissolved during the Hydrothermal Treatment of MSWIFA

Time (hours)	Cl^-	SO_4^{2-}	Zn^{2+} (g/Kg MSWFA)	Cd^{2+}	Pb^{2+}	pH	σ (mS/cm)
0[1]	130	46.8	3.6	0.017	3.8	-	-
1	128	0.60	0.0086	0	0.075	12.08	27.4
2	130	0.12	0.0072	0.00013	0.123	12.07	27.0
4	130	0.60	0.0054	0.00011	0.199	12.09	27.4
6	130	0.12	0.0047	0.00021	0.045	12.15	27.3

[1] Time 0 is before the hydrothermal treatment

As shown in Table 3, a plateau of stabilisation is produced after 1 hour of treatment for chloride, pH and conductivity (σ). Chloride reached concentration values closed to that of starting MSWFA, what indicates its total dissolution. The pH stabilised at a value of about 12.1, and conductivity at 27 mS/cm. The concentration of minority Pb^{2+} increased progressively during the first 4 hours decreasing thereafter, nevertheless Zn^{2+} decreased after 1 hour. Cd^{2+} concentration is very low increasing after 6 hours of treatment.

2b. Solid Phase Characterization

The main crystalline compounds of the untreated MSWFA (Fig. 2(a)) are the follows: NaCl (alite), KCl (sylvite), $CaCl_2.Ca(OH)_2.H_2O$, $CaSO_4$ (anhidrite), $Ca(OH)_2$ (portlandite), $CaCO_3$ (calcite), $Ca_2Al_2SiO_7$ (gehlenite), Fe_2O_3, SiO_2 (α-quartz), Al and probably C and Mg_2C.

After 1 hour of hydrothermal treatment, all the X-ray reflections of chloride-compounds disappeared, what suggest that they have been dissolved as the analyses of liquid showed (see Table 3), where the concentration of chloride represents the 100% of total amount of chloride of starting MSWIFA. Al reflection at

38.4 of 2θ angular zone disappeared, what indicates its dissolution which is favoured by the high pH (12.1) of the liquid.

The $Ca_{1.5}SiO_{3.5}.xH_2O$ (called CSH gel) appeared although its reflections are overlapped with those of calcite, but it was confirmed from IR analyses by the strong absorption band at 950 cm^{-1}, see Figure 5.

As was mentioned in the introduction, chloride and metallic aluminium of MSWFA represent the main problems from the point of view of its potential valorisation towards construction materials. The hydrothermal treatment of this wastes, avoids the presence of chloride and metallic aluminium, in addition new hydraulic phases are formed: C_3ASH_4 and $Ca_{1.5}SiO_{3.5}.xH_2O$. These phases have the property of incorporating a wide range of species providing, therefore, stabilisation mechanisms for minority toxic elements of MSWFA.

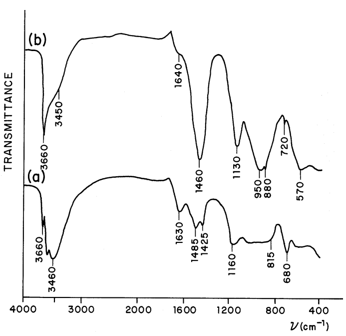

Figure 5. FTIR Analyses of the MSWIFA: a) before and b) after 1hour of HT.

As for the evolution of the precursor's phases with calcinations temperature, it is observed that from 700ºC, it obtained dicalcium silicate phases: α yβ, that are the main components of the belite cements. These kinds of cement have important advantages and applications like construction materials.

CONCLUSIONS

From the point of view of the construction materials, the hydrothermal treatment is an useful method to valorise these solid wastes.

1. Hydraulic phase are formed, precursors of new belite cements, which have the capacity of immobilising toxic ionic species like Cd, Pb and Zn.
2. In general, the manufacturing process, has important advantages:
    a. Environmental, such as the use of wastes as raw material and the reduction of CO_2.
    b. Energy, because it achieves a significant reduction in energy of the process (800 º C vs. 1450 ° C) and a milling process elimination.
3. It remains deeply into some aspects, related raw materials heterogeneity given their origin; high water demand and a lack of specific legislation to use these wastes

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