New Clinker Formulations Made of Industrial Wastes

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Abstract

This work describes the formulation of new cementitious materials starting from industrial wastes, such as sludges (generated in the Al-anodizing and surface coating industrial processes, potable water filtration/cleaning operations and the cutting process of natural marble) and foundry sands. These materials are all classed as non-hazardous but are produced in high daily amounts. They were fully characterized and chemical/mineralogical predictions were made based on their location in the equilibrium diagram of the SiO_2-Al_2O_3-CaO ternary system, which are the major oxide constituents.

Powder mixtures were prepared and fired at different temperatures. For comparison, similar formulations were prepared with pre-treated and commercially available natural raw materials and processed in similar conditions. The thermal process was followed by differential scanning calorimetry (DSC) and high-temperature powder X-ray diffraction (HT-XRD) studies. The clinkers were found to contain common hydraulic phases, and corresponding cements were prepared. The setting behavior of the optimized formulations was evaluated by non-conventional techniques (e.g., impedance spectroscopy), as well as the evolution with time of the mechanical strength. The general similarity between waste-based and reagent-based formulations clearly demonstrates this recycling alternative.

Keywords: Industrial wastes, clinker and cement properties

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1. Introduction

In manufacturing 1700 Mton of Portland cement each year worldwide, an equivalent amount of CO_2 is released into the atmosphere [1]. The reason why CO_2 output is so high is because the production process not only requires the calcination of limestone yielding CO_2, but is also energy hungry, where every ton. of Portland cement requires about 4GJ of energy from fossil fuels to attain the 1000^oC temperatures required to drive the reaction which in itself produces vast quantities of CO_2. Therefore, finding an alternative product to Portland cement would, make excellent environmental sense.

A considerable degree of mitigation can be achieved by adopting principles of sustainability, not only by reducing emission of CO_2 at source, but also by reusing or recycling where possible. Significant reduction might be achieved by: (i) extending cement with supplementary materials (e.g., wastes) [2-5]; (ii) using low grade, low energy cements (e.g., belite-based) [6-8]; (iii) developing CO_2-neutral and geo-polymer type cement systems [9,10]; (iv) promoting carbonation of cementitious materials [11].

Currently the cement industry is responding to the perceived societal need for reduced CO_2 emissions by increasing the production of blended Portland cements using supplementary cementitious materials (pozzolans) that are principally derived from industrial by-products, such as blast-furnace slags and coal combustion fly ash. However, the supplies of these are limited. An alternative is to use natural pozzolans, or recycled materials such as glass, or sludges generated in stone cutting or collected in water filtration operations; other potential sources may be found in the Al-anodizing and surface coating industries or by the use of foundry sands and in particular, the exciting potential offered by carbon residues from oil refining [2-5].

Belite or sulphoaluminate–belite cements are relatively cheap and have low energy requirements. Their main constituents, C_2S and calcium sulphoaluminate ($C_4A_3\check{S}$), are known as cementitious phases for many decades. However, the potential of the last phase in non-expansive cement formulations has only recently been achieved. Required raw materials include limestone, bauxite or aluminous clay and gypsum. Calcining temperatures attain only $1300–1350^oC$ in the hot zone [6]. Belite based clinkers are more environmental-friendly than C_3S and C_3A based ones. Formation enthalpy of C_2S and $C_4A_3\check{S}$ is almost half of the one of C_3S. In addition CO_2 release is also much lower (0.58kg/mol for C_3S and 0.22 kg/mol for $C_4A_3\check{S}$) [6,12].

This work aims to study the development of clinkers and cements made from formulations based on wastes. In particular, the development of belite ($2CaO.SiO_2$) based clinkers will be detailed.

2. Experimental procedure

Four waste materials were selected and characterized, namely, (i) Al-rich anodizing sludge (A-sludge), (ii) sludge from the filtration/clarification of potable water (W-sludge), (iii) sludge generated in marble sawing processes (M-sludge), and (iv) foundry sand (F-sand). The foundry sand was milled and sieved through 75 µm. The other materials were used in the as-received condition. For comparison, and to clarify the effect of minor components, present in the waste materials, on the final product properties, similar compositions were also prepared with commercial high purity grade raw materials and used as standard samples. These alternative high purity grade raw materials were: Alcoa CT3000 alumina, Calcitec M1 calcite and Sibelco P 500 sand. The characterization included chemical composition, determined by X-ray fluorescence (XRF, Philips X'UNIQUE II), thermal behavior (DTA and TGA, Setaram) and particle size distribution (Coulter) in alcohol. The full description is given elsewhere [13].

Dried (at 110°C) components were mixed (see proportions in Table 1) in dry conditions (for 1 h, in a porcelain jar with alumina grinding balls). Figure 1 shows the location of this formulation in the ternary diagram S-A-C (named CR2 and CR2-P). The resulting loose powders were calcined at selected temperatures (10°C/min heating rate, 1 h soaking). The standard clinker (P) was prepared in a similar manner, but using the mentioned commercial reagents. Compositional changes, as a function of the firing conditions, were assessed by High-Temperature X-Ray Diffraction (Philips MRD X'Pert System, CuKα at 35 kV and 45 mA) and by Differential Scanning Calorimetry (DSC - Setaram LabSys). DSC was run up to 1500°C at heating and cooling rates of 15°C/min. and 50°C/min., respectively. During heating, samples (50 mg each) were kept for 1 hour at 1000°C to fully decompose $CaCO_3$.

Physical parameters of milled powders (about 2 h in a rings mill + porcelain jar) such as the specific surface area (SSA, by BET) and the wt% retained in a fixed sieve (75 µm) were determined.

To prepare the corresponding cements (CM) carbonate (10 wt%) and calcium sulfate (5 wt% hemi-hydrate) were added to the clinker before milling. The beginning of setting was inferred from temperature measurements on fresh pastes (w/c = 0.4). The setting process was also followed by impedance spectroscopy measurements, carried out using a Hewlett Packard 4284A impedance bridge in the frequency range of 20 to 106 Hz. Tests were performed under controlled ambient conditions (22-24°C, ~55% relative humidity) on test bars (18x9x8 mm) cast from the cement pastes into plastic moulds. More details might be found elsewhere [14].

The evolution of compressive strength with curing time was also monitored. Phases formed upon curing were determined by XRD (Rigaku Geigerflex D/max – Series, CuKα at 40 kV and 50 mA) and by DTA (Setaram LabSys).

Table 1 – Compositions (wt.%) of clinkers, based on wastes and on commercial pure reagents (named P).

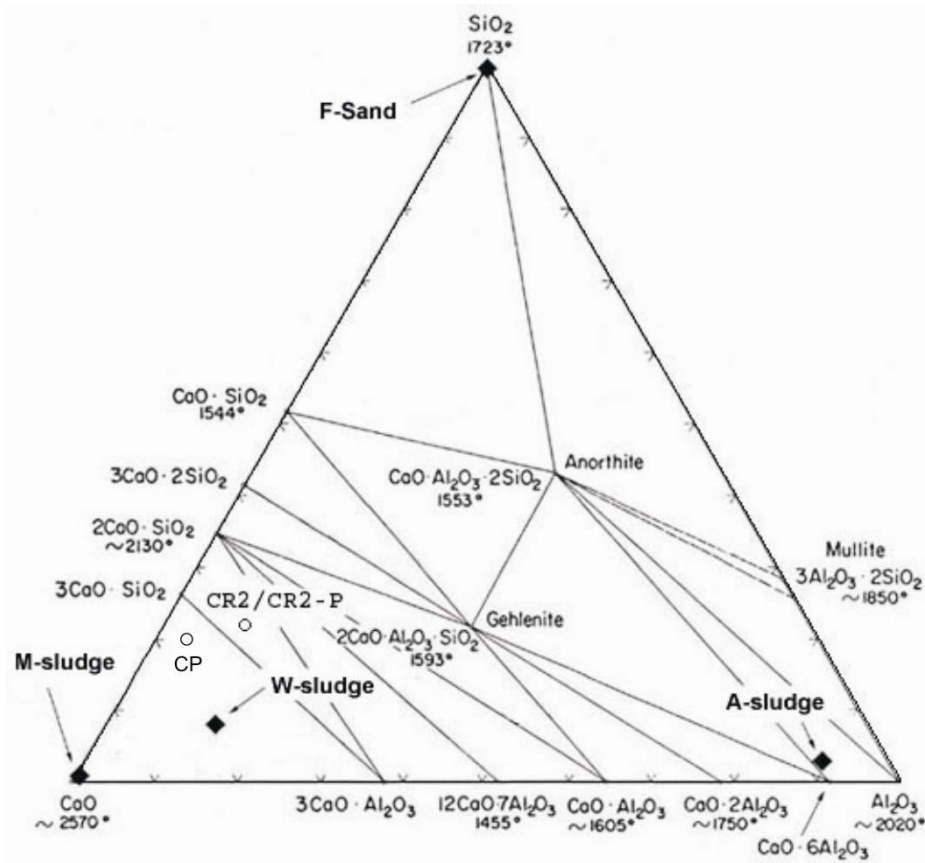| Mixtures	A-sludge	W-sludge	M-sludge	F-Sand	Alumina	Calcite	Sand
CR2	13.0	15.0	60.0	12.0	-	-	-
CR2-P	-	-	-	-	6.5	79.4	14.1

Figure 1 - Location, in the composition diagram of the SiO_2–Al_2O_3–CaO ternary system, of the wastes and the composition investigated (CR2/CR2-P). Reference OPC cement (CP) is also represented.

3. Results and Discussion

3.1. Processing and characterization of clinker

The CR2 clinker belongs to the compatibility triangle C_2S–C_3S–C_3A in the S–A–C system and those are the solid phases to be expected, if

equilibrium is established. Within this triangle, melting starts at 1470°C (i.e. slightly above the firing temperature = 1450°C). Equilibrium in the solid state is more difficult to achieve and neighboring phases richer in alumina (e.g. $C_{12}A_7$ or even C_2AS) might appear as transient phases.

Figure 2 shows the DSC curves of the clinker obtained during heating and cooling cycles. It might be assumed that the exothermic reaction at about 1300°C is the nucleation of αH-C_2S, while at ~1420°C the nucleation of αC_2S occurs. During cooling, at about 1370°C, the crystallization of C_3A can be observed, while αH-C_2S and γC_2S phases are formed at 1270 and 1210°C, respectively. All these suggestions were assessed from the comparison with curves of standard phases and from HT-XRD spectra [15].
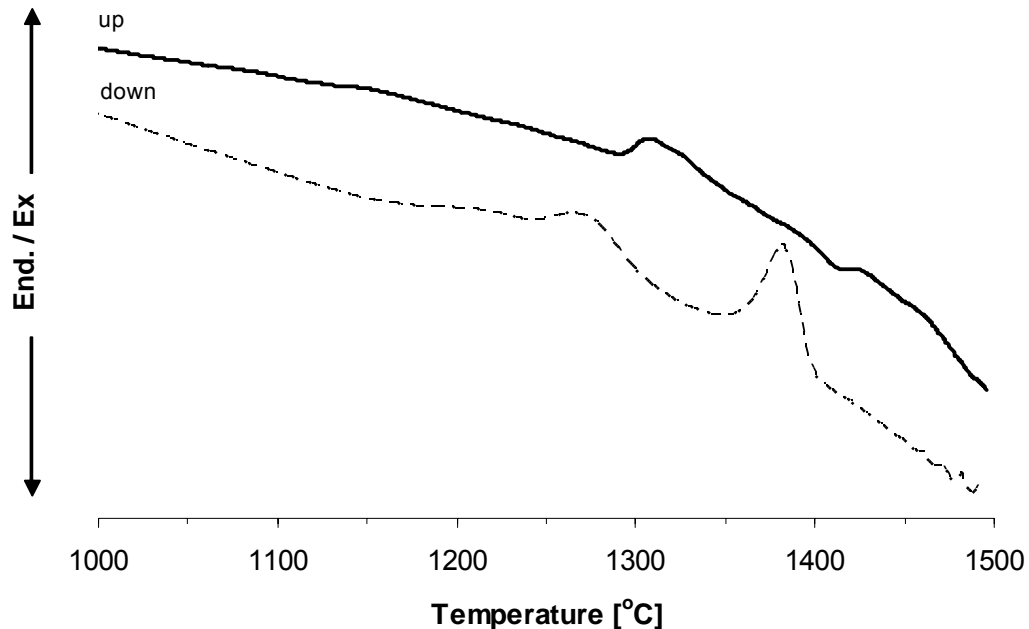

Figure 2 - DSC curves of the CR2 clinker, recorded during heating (up) and cooling (down) between 1000 and 1500°C.

Figure 3 compares the very complex powder XRD patterns of CR2 and CR2-P clinkers. CR2-P contains the expected hydraulic phases (C_2S, C_3S and C_3A), while CR2 contains, in addition to C_2S and gehlenite, $C_{12}A_7$ and calcium aluminum oxide sulfate. This mismatch is certainly due to a sluggish tendency to equilibrium in the solid state and the presence of other minor constituents in the waste materials. For example, aluminum sulfates are present in both the A- and W-sludges and, if not completely eliminated during firing, they can be responsible for the formation of other

complex sulfate phases [15]. Instead of being a problem, this occurrence was explored to prepare belite or sulphobelite based cements.
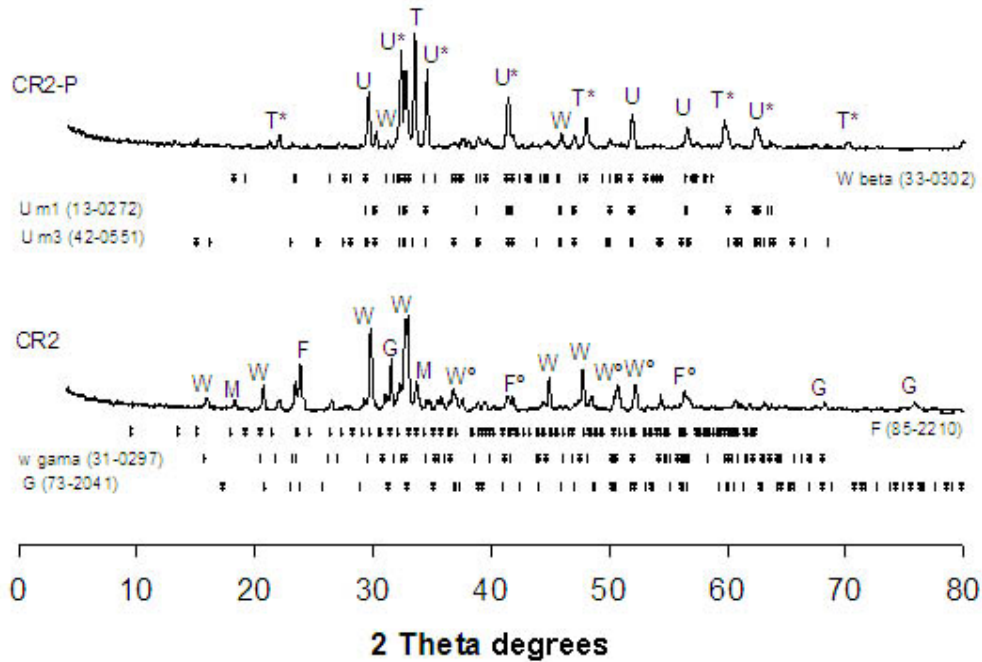

Figure 3 - XRD of CR2 and CR2-P clinkers: W (γC$_2$S or βC$_2$S in CR2-P: JCPDS 33-0302); W° (W + G); F (calcium sulphoaluminate); F° (W + F), M (mayenite, C$_{12}$A$_7$); U (alite; C$_3$S: M1 – JCPDS 13-0272 e M3 – JCPDS 42-0551), U* (U + W), T (C$_3$A: JCPDS 38-1429); T* (T + U).

3.2. Behavior of cements

Given that chemical reactions that occur during cement setting can cause significant changes in temperature, the beginning of setting might be detected from temperature measurements. However, with slower reactive formulations (like those actually processed) its definition is hard to obtain: 660 and 510 minutes for CM2 and CM2-P, respectively.

Impedance spectroscopy measurements were then applied as an attempt to overcome this difficulty. Generally speaking, the microstructure changes that occur in hydrating cements are the result of the consumption of free water and the precipitation of hydration products, giving rise to a denser matrix (suppression of pores). This results in an increase of bulk paste impedance and a decrease in solid-liquid capacitance [16].

Figure 4 shows the change of bulk impedance values with hydration time. After gypsum reaction is completed (~ 1.5 hr), no any abrupt increase is visible in CM2 sample. In that sense, the estimation of the initial setting

time from these results is rather difficult, as happened by measuring temperature changes. As mentioned before, CM2-P is more reactive than CM2 and a second rise in bulk impedance is easily observable in Figure 4 between 9 and 10 hours hydration, somewhat in agreement with the estimates derived from temperature/time measurements. In this case, the IS technique shows a better sensitivity than the temperature measurements, to detect the beginning of the setting process. The comparatively higher impedance values presented by the CM2-P paste are justified by its higher purity level, hence lower amount of soluble species in the pore solution.
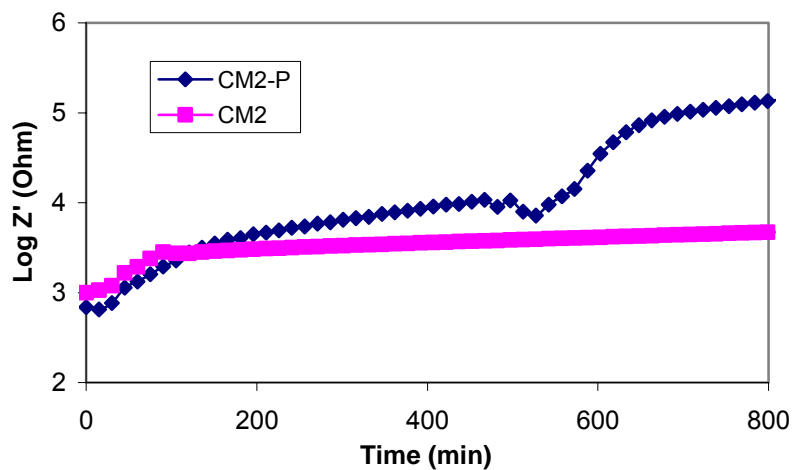

Figure 4 – Evolution of bulk impedance with hydration time of both cements.

Figure 5 shows the evolution of the compressive strength of the new cements with curing time. These values are much lower than those reported for ordinary Portland cement (also shown in Figure 5), meaning that the hardening process is much slower. However, compressive strength is more comparable. For example, samples cured for 18 months show compressive strength of about 40 MPa.

DTA of the 28 day aged samples (Figure 6) shows that decomposition reactions (between 100 and 350°C) of C-A-H and C-S-H hydrates are stronger in CM2-P, revealing their presence in higher amounts. The absence or small expression of such kind of peaks in CM2 cement is compatible with its weak hydraulic character.

Main differences between 7 and 28 day aged CM2 and CM2-P were clarified by XRD (Figure 7): (i) in CM2 the main aluminate detected is mayenite ($C_{12}A_7$), less reactive than C_3A, noticed in CM2-P; (ii) CM2 contains poorly hydraulic gehlenite and calcium sulphoaluminate phases; (iii) CM2-P contains alite (C_3S) as main silicate, known for its rapid

hardening character (as C_3A). As a consequence R, R* and Y peaks are stronger in CM2 cement.
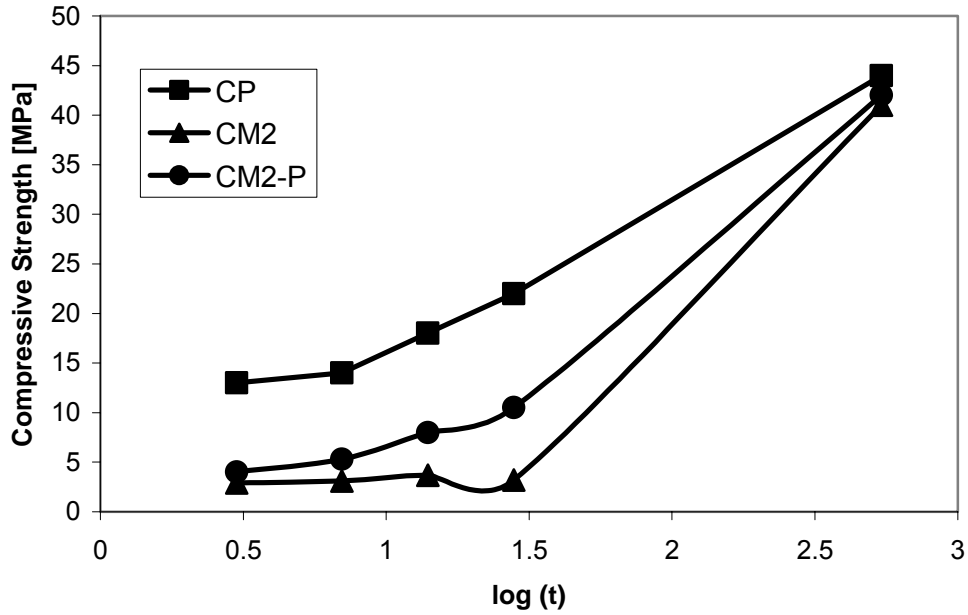

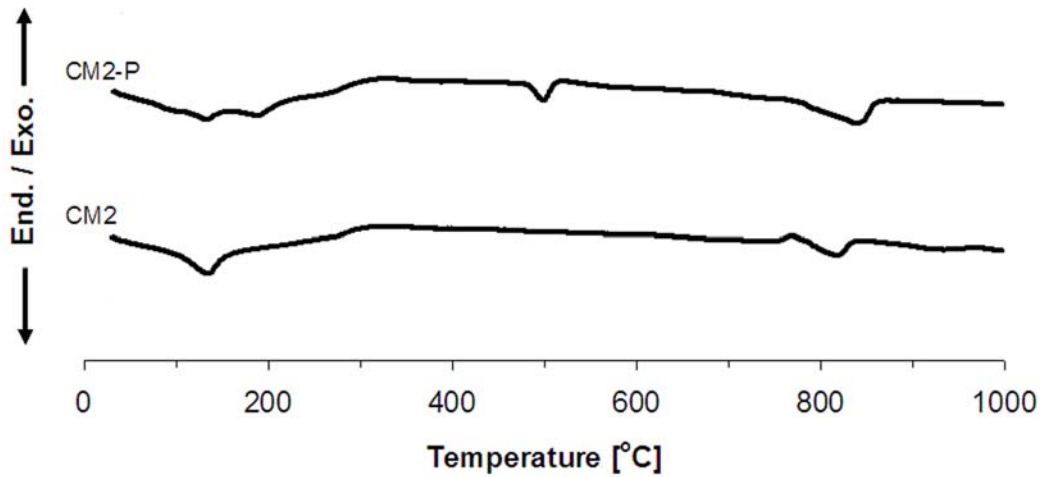Figure 5 – Evolution of the compressive strength of cements with curing time (in days).

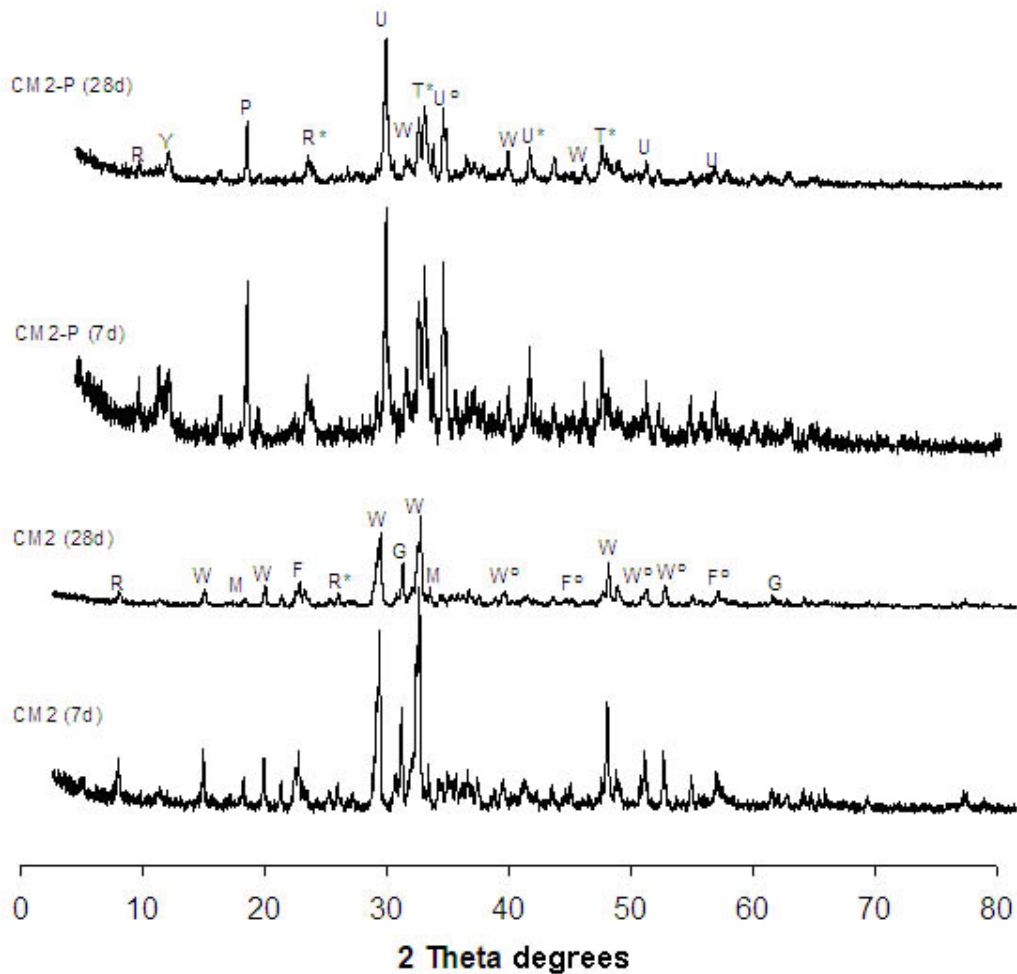Figure 6 - DTA curves of cements after 28 days of curing.

Figure 7 - XRD spectra of CM2 and CM2-P cements after 7 and 28 days curing: W (larnite, C_2S); G (gehlenite, C_2AS); Wº (W + G); Fº (W + F); F (calcium sulphoaluminate); M (mayenite, $C_{12}A_7$); R (S-C-H); R* (R + W); U (alite, C_3S); U* (U + W); Uº (U + W + P); T (tricalcium aluminate, C_3A); T* (T + U); Y (C-A-H); P (portlandite, CH).

Figure 8 shows E-SEM images of aged CM2 cement and clearly confirms the slow hydraulic/hardening character of CM2 cement. For young curing ages, the formation of hydrates is rather incipient (scarce number of typical needle-like crystals). However, after 1 year curing their presence is easily visible and is compatible with the achieved hardening process.
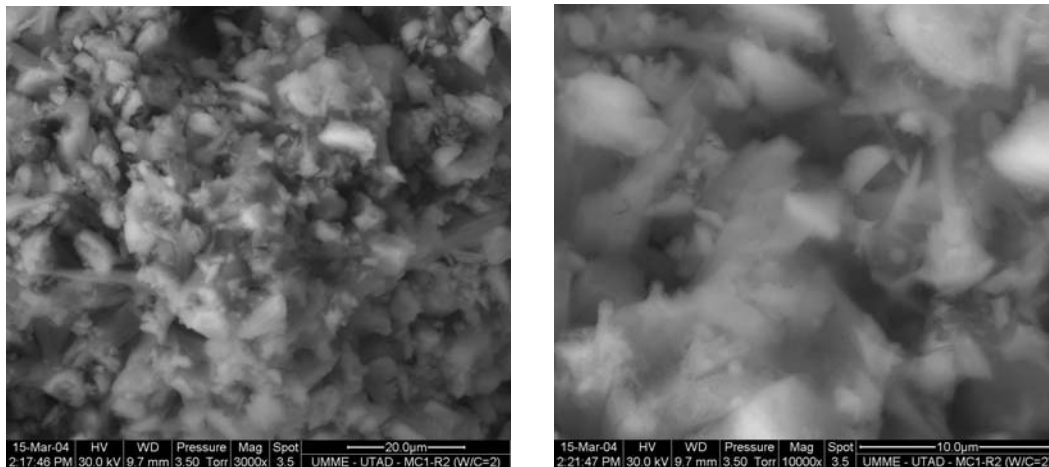
Figure 8 – Typical microstructures (E-SEM) of CM2 cement aged in room conditions for 7 days (left) and 1 year (right).

4. Conclusions

Belite-based cements can be obtained from the correct combination of industrial inorganic wastes. A good agreement was obtained between the characterization techniques used. When compared with similar compositions made from commercial high purity grade reagents, wastes-based cements show poorer mechanical properties for younger curing ages. The prevalence of gehlenite in the clinkers might account for this, but the effect of impurities could not be avoided. However, older aged cements show interesting hardening properties.

Small compositional/sintering adjustments will be tried in future trends. In particular, the use of suitable mineralizing agents should be attempted. This might be also helpful to minimize the dusting phenomena observed in CR2 clinkers due to the presence of γC_2S (as the result of the expansive crystallographic inversion, on cooling, of high temperature C_2S polymorphs).

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