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Evaluation of spray-dried sludge from drinking water treatment plants as a prime material for clinker manufacture

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ABSTRACT

This study evaluates the suitability of a water treatment plant spray-dried (atomized) sludge as a prime material for clinker manufacture. A study of the thermal behaviour of the atomized sludge was followed by a comparison of the burnability of two raw mixes, one (control) made with industrial prime materials (limestone, clay, sand) and the other with the same components except that the clay was replaced by sludge. The materials were ground to the same fineness in both mixes. The composition of the two raw mixes was: silica modulus ($M_s = SiO_2/(Al_2O_3 + Fe_2O_3) = 2.30$), the lime saturation factor ($LSF = CaO/(2.8SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3) = 0.98$) and flux modulus ($M_f = Al_2O_3/Fe_2O_3 = 1.50$). The free lime in the two raw mixes was measured after clinkerization at 1400, 1450 and 1500 °C for 30 min. The clinkers obtained at 1450 °C were characterized with XRF, XRD, FTIR, OM and SEM/EDX.

Atomized sludge can be used as a prime material in cement manufacture, as a substitute for clay (and also partially for limestone). Its organic fraction of the spray-dried sludge was observed to burn at around 300 °C, releasing 678 J/g sludge. This combustion temperature is high enough to guarantee the absence of spontaneous combustion and explosions in the raw meal mill.

The control clinker contained less free CaO than sludge clinker at all three temperatures. When mix with atomized sludge was studied with the Miller procedure, the reactivity of the sludge, as a component of the raw mix, was found to be high. Both clinkers contained high proportions of alite (>70%) and their microstructure was similar in terms of alite and belite crystal size and composition, while the distribution of the liquid phase was somewhat more uniform in the control.

1. Introduction

The sludge removed from drinking and waste water treatment plants generates growing amounts of waste, which have to be managed. Sludges contain a large amount of water and to be re-used in the cement industry they have to be dried.

To manage the waste generated at a drinking water treatment plant (at Aguas de Barcelona's San Joan Despí), a new experimental treatment process by atomization has been used, which reduces sludge volume 600-fold and converts it to a readily handled powdery material that might be reusable in the cement or concrete industry [1]. The process involves the following stages: Sludge gathering and storage, pumping to thickening area, thickening, storage of thickened sludge, pumping to dehydration area, dehydration, atomization and final storage. Coagulant and polyelectrolyte dosing top off the process [1].

In a prior paper [2] the authors reported on the physical, chemical and microstructural characterization of a drinking water treatment plant (DWTP) sludge subjected to the new spray-drying process, and evaluated its possible use as an addition in industrial cement. Atomized sludge (M2) is a powdery, conveniently handled material. Its specific weight is 2.2 g/cm^3, its particles are rounded with a mean size of 23.84 μm, 90% with a diameter smaller than 50 μm. Chemically, its four majority oxides are of silicon, aluminium, calcium and iron, while its crystalline phases include muscovite, clinochlore, calcite, quartz and dolomite. The moisture content is under 5% by weight and the organic matter, primarily fatty acids, accounts for 12–14%. All these properties make it initially apt to form part of a raw mix with no need for prior burning.

Studies [3–10] have been conducted to attempt to recycle water treatment sludge by using it in cement, mortar or concrete

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manufacture. Most of these papers refer to the recycling of sewage sludge and only a few include DWTP sludge.

Of the latter, Kikuchi [11] produced pilot scale (50 t/day) clinker from a blend of incinerated solid municipal waste ash, drinking water plant waste ash and limestone. Based on the setting and compressive strength of the cement made with that clinker, the author concluded that it was apt for use. Moreover, he observed that no secondary contamination occurred during the pilot test. He further concluded that 50% of prime material for cement production could be obtained from the ash generated by incinerating solid municipal waste.

Lin et al. [12,13] produced clinkers using ashes from different types of sludge (including sewage sludge and drinking water treatment plant sludge), limestone and steel mill slag, as raw materials; the moduli used were: silica modulus (1.9–3.2), iron modulus (1.7–2.5) and the lime saturation factor (0.8–0.95). According to their findings, sludge and steel mill slag can be used to replace up to 20% of the mineral components in cement prime materials.

A conclusion drawn from the reviewed literature is that due to the high water content in sludge, which rules out its grinding in raw meal mills or direct blending with such mixes, incinerated sludge ash has consistently been used in these studies as a prime material to make raw mixes or as a possible active addition. Incineration calls for facilities and additional energy that, however, render the process scantly viable.

As noted earlier, atomized sludge is readily handled and contains only 5% moisture, although it conserves part of the organic matter. Moreover, it is not treated at a sufficiently high temperature to destroy the crystalline structure of the inorganic constituents, or reduce them to ashes. This study aimed to determine the suitability of a water treatment plant spray-dried (atomized) sludge as a prime material for clinker manufacture. The burnability of a raw mix in which atomized (not incinerated) sludge was used to replace clay (and partially limestone) was determined. The composition and microstructure of the clinkers obtained with this and an equivalent industrial raw mix were also compared.

2. Experimental program

2.1. Sludge thermal behaviour

Thermal behaviour of the atomized sludge was studied with differential thermal and thermogravimetric analysis (ATD/DSC/TG), heating specimens at a rate of 4 °C/min. to a maximum temperature of 1050 °C in air. A TA Instruments SATQ600 apparatus was used.

Sludge M2 was subjected to isothermal heating at 400, 500, 600 and 700 °C for 30 min to identify the processes giving rise to the signals on the thermogram. The product obtained was characterized with XRD and a LECO furnace was used to determine the total carbon and sulfur content.

2.2. Burnability of raw mix containing atomized sludge

To evaluate the use of sludge as a prime material in Portland cements, burnability was compared in two raw mixes: one (the control) made with industrial prime materials (limestone, clay, sand) and the other (mix M2) with the same prime materials except for the clay, which was replaced with sludge. The Fe_2O_3 used in both cases was a laboratory grade reagent. The two mixes were designed with the same silica ($M_s = 2.30$) and flux ($M_f = 1.50$) module and the same lime saturation factor (LSF = 0.98). The limestone used to make the raw mixes was ground to under 125 μm and the sand and clay to under 45 μm. Ungrounded sludge was used, with its original particle size distribution [2].

The chemical analysis of the limestone, clay, sand, atomized sludge and iron oxide is given in Table 1. X-ray fluorescence (XRF) techniques were applied analyze the majority elements of all the prime materials, using a Philips PW1404 X-ray spectrometer fitted with a Sc–Mo tube, Super-Q software and four analyzer crystals: PX-1, GE, LIF200, LIF220. The working conditions were 40 kV and 70 mA. Minority element concentration was determined in a Thermo Jarrel ASH PW 2400 ICP-AES plasma spectrophotometer. Loss on ignition at 1000 °C was likewise determined, using a muffle furnace.

Once the prime materials had been proportioned, (the control contained 82.32% limestone, 16.14% clay, 0.6% sand and 0.94% Fe_2O_3; the M2, contained 80.13% limestone, 12.81% atomized sludge, 5.8% sand and 1.23% Fe_2O_3) mixed and blended, cylindrical wafers measuring 2 cm in diameter and weighing approximately four grams were made and subjected to three isothermal treatments at 1400, 1450 and 1500 °C for 30 min. After the treatments, the samples were removed from the kiln and air-cooled at ambient temperature. The clinkers obtained were ground and their free lime content was determined as specified in Spanish standard UNE 80-243-86.

Mix thermal behaviour was studied up to 1500 °C with DTA/TG/DSC. The heating rate was 10 °C/min, the maximum temperature 1500 °C and the atmosphere was air (100 ml/min.).

2.3. Mineralogical and microstructural study of the clinkers obtained

A Bruker D8 Advance X-ray diffractometer, consisting of a high voltage, 3-kW generator and a (1.54-Å Cu Kα) copper anode X-ray tube normally operating at 40 kV and 50 mA was used for the mineralogical characterization of the clinkers. This instrument was

Table 1
XRF (% by weight) and ICP (ppm) chemical analysis of the prime materials: (1) clay; (2) limestone; (3) sand; (4) sludge M2; (5) Fe_2O_3.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO	P_2O_5	Li*	
XRF (%)													
1	52.00	15.10	6.02	4.01	4.95	2.60	0.58	4.55	0.73	0.10	0.15	9.2	
2	5.60	1.30	0.58	51.10	0.58	0.00	<0.01	0.23	0.07	0.01	0.10	40.5	
3	89.40	3.90	0.61	2.06	0.03	0.00	0.07	1.79	0.04	<0.01	0.03	2.1	
4	29.63	17.57	5.18	11.85	2.15	0.34	6.09	2.85	0.56	0.15	0.94	22.7	
5	0.00	0.00	96.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.5	
	ZnO	ZrO_2	PbO	BaO	B_2O_3	Cr_2O_3	V_2O_5	Co_3O_4	NiO	CuO	As_2O_3	Sb_2O_3	CdO
IPC (ppm)													
1	<20	<20	<20	725	480	75	195	<20	<20	<20	<20	<20	<20
2	<20	<20	<20	<20	<20	<20	57	<20	<20	<20	<20	<20	<20
3	<20	<20	<20	<20	<20	468	<20	<20	<20	<20	<20	<20	<20
4	186.7	65.8	<10.8	435.4	483	62.8	339.2	12.2	64.9	61.3	72.2	1.9	<2.3

* Li: loss on ignition at 1000 °C.

coupled to a Lynxeye detector with a 3-mm anti-scatter slit and a (0.5%) Ni K-beta filter, with no monochromator. The crystalline phases of the clinkers were quantitatively analyzed with Rietveld refinement of the XRD patterns recorded on a Philips X'Pert MPD PRO diffractometer using Cu Kα_1 radiation (λ = 1.5406 Å) [Ge(111) primary monochromator]. The slit settings were ½° (fixed divergence), 1° (fixed incident anti-scatter), and ½° (fixed diffracted anti-scatter). The diffractometer was fitted with an X'Celerator RTMS (Real Time Multiple Strip) detector set to scanning mode and maximum active length. The data were collected from 5° to 70° (2θ) for ~2 h, rotating the samples at 15 rpm to enhance particle statistics. The X-ray tube settings were 45 kV and 35 mA.

Ten FTIR scans were performed on KBr pellets at frequencies of from 4000 to 400 cm^{-1} and a spectral resolution of 4 cm^{-1} with a Thermo Scientific Nicolet 600 FTIR spectrometer. Portions of clinker were packed in resin, cut, polished and etched with 0.1% HNO$_3$ solution, for examination under a reflected light Nikon Eclipse ME600 optical microscope. Sludge morphology and structure were studied under a JEOL model JSM-5400 scanning electron microscope fitted with an OXFORD EDX apparatus and ISIS LINK software.

3. Results

3.1. Sludge M2 thermal behaviour

Figs. 1 and 2 show the DSC/TG [2] and DTG curves for atomized sludge M2. While sample mass declined steadily at all temperatures, the substantial changes in the rate of weight loss exhibited by the DTG curve denoted the existence of successive and overlapping processes. Total mass loss came to 24.35%. The DSC curve for the sludge had two endothermal signals with minima at 115 and 760 °C, respectively attributed to the loss of moisture and hydration water in organic matter, and the thermal decomposition of carbonates and water loss in mica [14]. The respective enthalpies were −56 and −192 J/g.

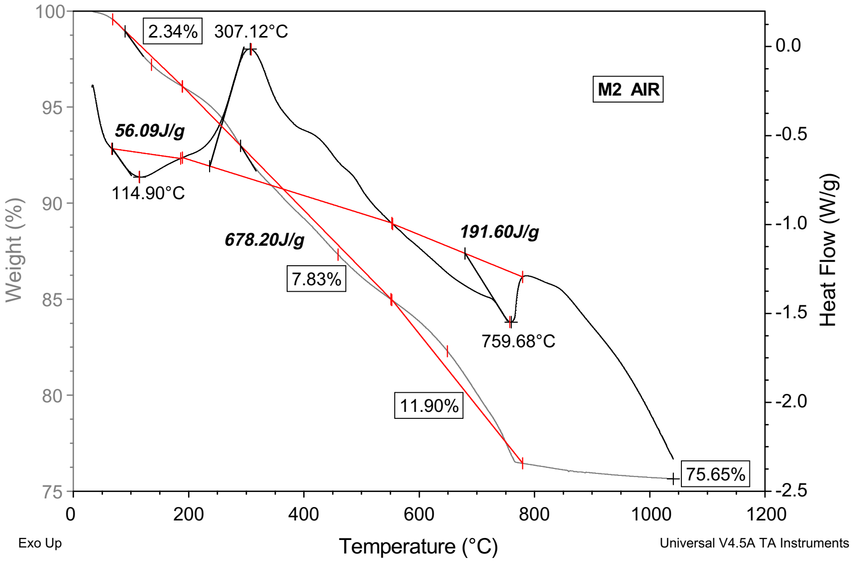

Fig. 1. DSC/TG for spray-dried sludge M2 in air.

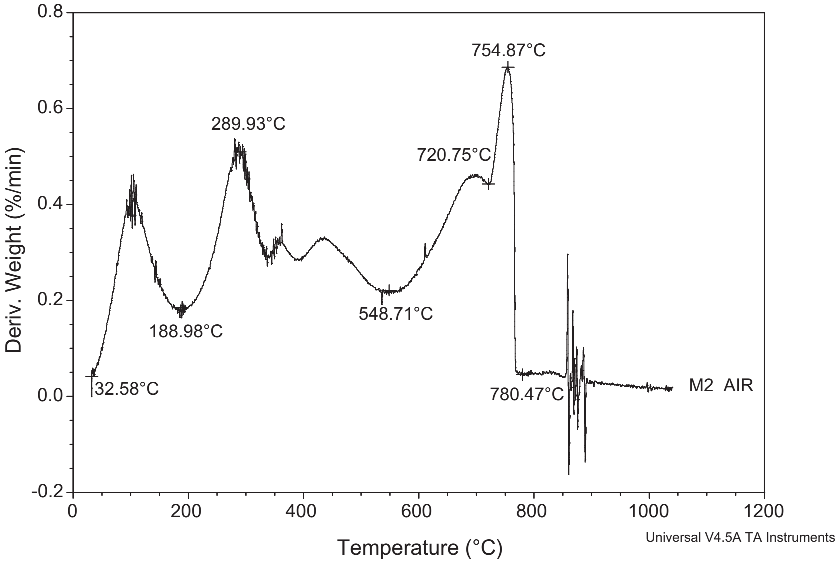

Fig. 2. DTG for spray-dried sludge M2 in air.

The strong exothermal signal with a peak at 307 °C also observed was due to the combustion of the organic matter in the material; the mass loss associated with this peak amounted to 7.83% and the enthalpy came to 678 J/g.

Moreover, the endothermal signal with a minimum at 760 °C on the DSC curve for the atomized sludge was highly asymmetric and encompassed overlapping processes that entailed mass loss (11.90%) beginning at around 550 °C (see DTG curve), with a substantial rise in the rate of loss at 721 °C.

The sludge was subjected to isothermal treatments (2 g for 30 min at 400, 500, 600 and 700 °C) and mineralogically characterized to ascertain the nature of the changes that took place at each temperature observed on the DSC/TG and DTG curves.

Fig. 3 shows the XRD patterns of the treated samples and Table 2 gives their total carbon and sulfur contents.

No difference was observed between the diffractograms for the original sludge and the sample heated at 400 °C. The chlorite (clinochlore) peak ($2\theta = 12.5°$) disappeared in the XRD pattern for the 500 °C sample. The signals for calcite ($CaCO_3$) declined in the sample heated at 600 °C, and the reflections for mica and feldspar disappeared in the 700 °C material, while the quartz peak and especially the calcite signal declined. The new reflections observed were attributed to a product of the reaction between the silicoaluminates (nepheline: $NaAlSiO_4$) ($2\theta = 21.18$; $2\theta = 27.15$; $2\theta = 29.61$ $2\theta = 30.84$; $2\theta = 38.27$) and CaO ($2\theta = 37.33$; $2\theta = 53.92$).

3.2. Technological aptness of sludge M2 as a raw mix component for Portland cement

Two raw mixes with the same composition were proportioned as follows: $M_S = 2.30$, $M_f = 1.50$ and LSF = 0.98. One, the control, contained 82.32% limestone, 16.14% clay, 0.6% sand and 0.94% Fe_2O_3. The other, M2, contained 80.13% limestone, 12.81% atomized sludge, 5.8% sand and 1.23% Fe_2O_3. In mix M2 the sludge replaced the clay entirely. Since the proportion of sand was greater, the reactivity of this mix may have been lower.

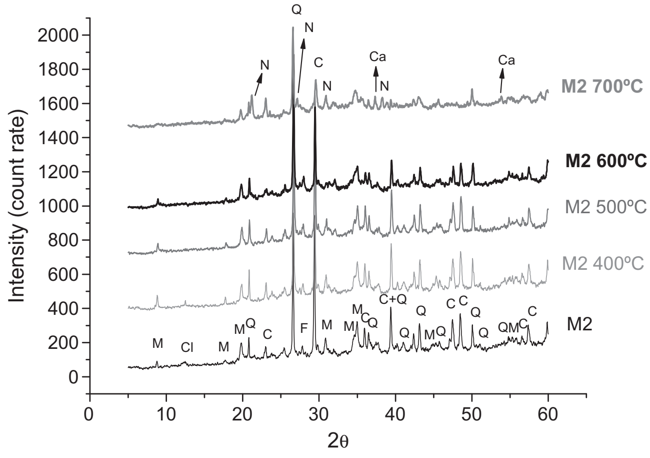

Fig. 3. Diffractograms for sludge M2 treated for 30 min at 400, 500, 600 and 700 °C Q = quartz; C = calcite; M = mica; F = feldspar; Cl = chlorite;N = nepheline; Ca = CaO.

Table 2
C and S contents of these samples.

Sample	Original sldg.	400 °C sldg.	500 °C sldg.	600 °C sldg.	700 °C sldg.
% C	5.10	3.14	2.19	1.34	0.61
% S	0.07	0.11	0.12	0.13	0.14
S[SO_3]	0.18	0.27	0.29	0.32	0.20

Figs. 4 and 5 shows the DSC/TG curves for the control and atomized (M2) mixes during heating. The exothermal signal observed at 298 °C for sludge-containing mix M2 was due to combustion of the organic matter. The endothermal signal between 580 and 880 in both the control and M2 was due to decarbonation [15].

The exothermal signals between 1210 and 1290 °C may be attributed to solid state reactions and the progressive formation of C_2S (belite), $C_{12}A_7$, C_4AF (FF) and C_3A [16]. The raw mix containing atomized sludge (M2) exhibited an intense exothermal signal (1220 °C), present but less intense on the control curve, which had two other strong exothermal signals, at 1268 °C and 1288 °C.

The endothermal signals associated with the formation of the molten mass in the clinker [15,16] appeared at over 1300 °C in the control mix (1304 °C), and at a lower temperature in the mix containing atomized sludge (M2) (1282 °C). The small differences between Thermal behaviour of both control and M2 raw mixes would indicate the aptness of sludge M2 as prime material for clinker manufacture.

3.3. Burnability of control and atomized sludge (M2) mixes

Table 3 gives the free CaO values for the control and M2 mixes, burned at 1400, 1450 and 1500 °C for 30 min. The free lime values in the M2 clinkers were higher than found for the control clinkers

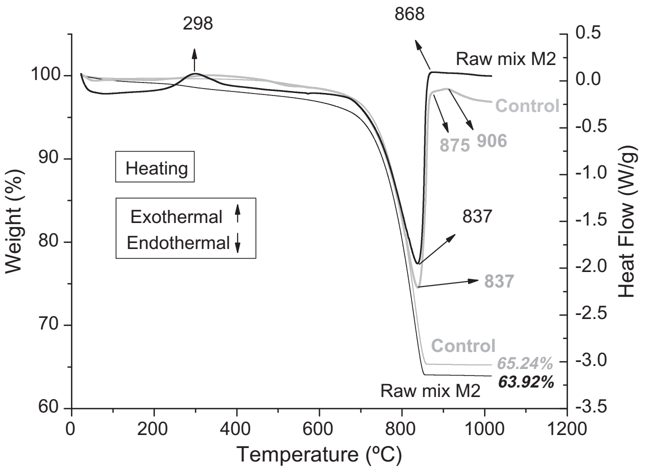

Fig. 4. DSC/TG for control and spray-dried (M2) raw mixes during heating (to 1000 °C).

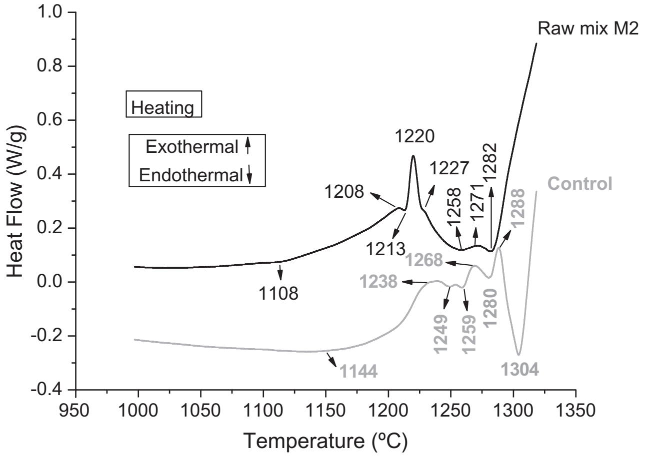

Fig. 5. DSC/TG for control and spray-dried (M2) raw mixes during heating (950–1350 °C).

Table 3
Free CaO values in clinkers (% by weight).

1400 °C		1450 °C		1500 °C	
Control (%)	M2(%)	Control	M2	Control (%)	M2 (%)
2.38	3.20	0.46	1.99	0.66	1.92

at all three temperatures studied. Table 4 shows the results of the chemical analysis of clinkers obtained at 1450 °C.

The two clinkers had similar chemical compositions, with a higher Na_2O content in clinker M2 due to the presence of the sludge, although the value observed was within the normal range [12,17]. The variation in the MgO content in clinker M2 can be explained by the replacement of clay with sludge M2.

An increase was likewise observed in the percentage of P_2O_5 in clinker M2, with a value slightly higher than normal (0.2%) [17]. Further to the literature, cements produced with clinkers having 2.5% P_2O_5 exhibit lower strength due to the decomposition of the C_3S, which yields P_2O_5-rich α-C_2S [17]. Raising the P_2O_5 content raises the free CaO content and lowers the C_3S/C_2S ratio [12,17]. When the P_2O_5 content in the clinker exceeds 0.5%, C_3A formation declines, and with it cements strength.

3.4. Mineralogical characterization of the clinkers obtained at 1450 °C

The FTIR spectra (Fig. 6) showed OH stretching vibration bands at 3436 cm^{-1} and H–O–H bending vibration bands at around 1631 cm^{-1} present in water The most intense band at around 925 cm^{-1}, the silicate Si–O stretching vibration zone, had two shoulders, the first at 876 cm^{-1} and the second at 841 cm^{-1}, characteristic of alite and belite, respectively. Another signal appeared at 720 cm^{-1}, denoting the Al–O vibrations in ferrite and tricalcium aluminate. The band at 522 cm^{-1} can be attributed to the two calcium silicates and the signal at 454 cm^{-1} to the Al–O vibrations in C_3A. A small signal in the C–O group vibration zone in the carbonates was wide on the control clinker spectrum, but exhibited two peaks, at 1446 and 1412 cm^{-1}, on the M2 spectrum, denoting slight weathering of the sample.

Figs. 7 and 8 show the diffractograms for the two clinkers and a detail of the $2\theta = 28–38°$ region. Four majority phases were identified: the chief differences between the two clinkers were the presence of free lime in the sludge clinker, not detectable in the control, and the proportions of tricalcium aluminate and ferrites.

The quantitative analysis via Rietveld refinement of the phases in the atomized sludge (M2) and control clinker samples, normalized to 100% crystalline phases (i.e., excluding the amorphous material content), is given in Table 5.

According to the XRD results, both clinkers contained very high and similar percentages of alite and a relatively low proportion of belite. Nonetheless, the composition of their respective interstitial phases varied substantially, with a very high aluminate and low ferrite content in clinker M2, and proportions closer to the Bogue formula calculations in the case of the control (Table 5).

The fact that clinker M2 contained more crystallized C_3A might be related to the rate at which the sample was cooled, for C_3A is known to crystallize more effectively at slower rates. As a result, the ferrite obtained contains less Al in its structure. When cooling

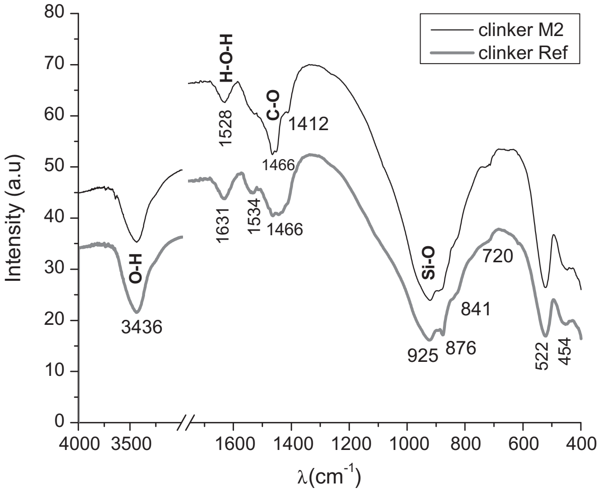

Fig. 6. FTIR spectra for the raw mixes made with M2 and clinkerized at 1450 °C for 30 min.

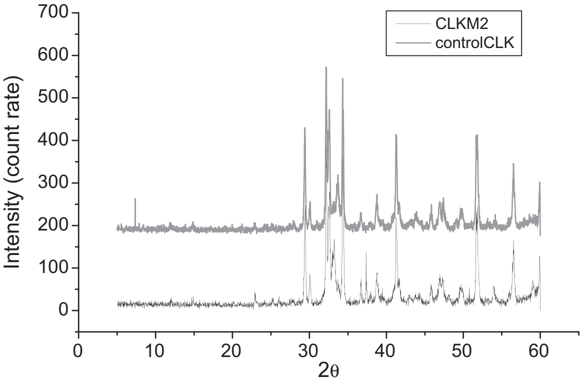

Fig. 7. XRD patterns for M2 and the control clinkerized at 1450 °C for 30 min.

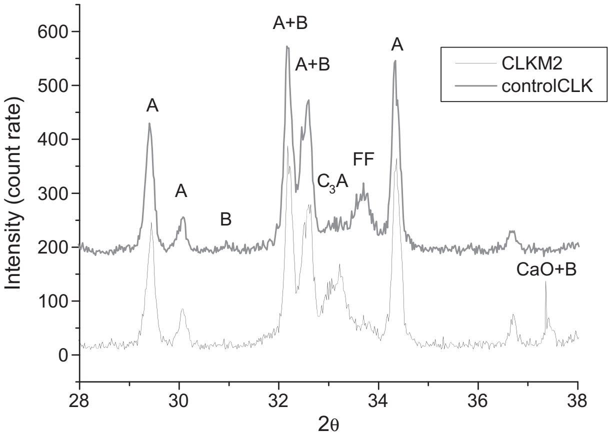

Fig. 8. Detail of the diffractogram in Fig. 7. A = Ca_3SiO_5 (alite); B = Ca_2SiO_4 (belite); $C_3A = Ca_3Al_2O_6$; FF = $Ca_4Al_2Fe_2O_{10}$ (ferritic phase); CaO.

Table 4
Chemical analysis of the control and M2 clinkers, expressed in oxides (% by weight). Loss on ignition: control clinker: 0.32%; clinker M2: 0.43%.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO	P_2O_5	SrO
Ct. cl.	20.80	5.60	3.82	66.00	2.05	0.07	0.18	0.45	0.28	0.04	0.11	0.05
Cl.M2	20.90	5.30	3.66	66.90	1.26	0.07	0.34	0.33	0.20	0.04	0.27	0.05

Table 5
Quantitative analysis of the phases in clinkers obtained at 1450 °C.

Phase (%)	Clinker M2		Control clinker	
	(XRD, Rietveld)	(XRF, Bogue)	(XRD, Rietveld)	(XRF, Bogue)
C_3S (Ca_3SiO_5)	72.1(1)	64.50	73.4(1)	65.57
C_2S (Ca_2SiO_4)	4.6(4)	11.35	7.3(4)	10.25
C_3A ($Ca_3Al_2O_6$)	18.0(2)	7.90	5.4(2)	8.42
C_4AF ($Ca_4Al_2Fe_2O_{10}$)	3.8(1)	11.13	13.9(1)	11.61
SiO_2	0.7(1)			
CaO	0.8(1)	1.99		0.46

is faster, however, the C_3A obtained is microcrystalline, the ferrite has a higher Al content and part of the aluminium remains in the vitreous interstitial matter where it cannot be detected by XRD.

3.5. Reflected light optical microscopy

Clinker M2 exhibited numerous alite crystals ranging from 10 to 40 μm (Fig. 9) surrounded by the interstitial phase, in turn characterized by the presence of large tricalcium aluminate crystals.

Note the presence of belite clusters (Fig. 10) surrounded by a barrier of intergrown alite crystals which are larger than in other areas of the sample. The belite clusters are associated with the solid state reaction of large quartz particles with lime, surrounded by smaller proportions of molten mass than the rest of the clinker. At temperatures of 1340 °C the belite crystals dissolved around the edges, reacted with the CaO dissolved in the molten mass and began to precipitate, while the growth of alite crystals ultimately formed a physical barrier around the unreacted belite crystals. This hindered the diffusion of silicate ions outward from and calcium ions inward to the cluster, thereby impeding the advance of the alite formation reaction in this area [18–20].

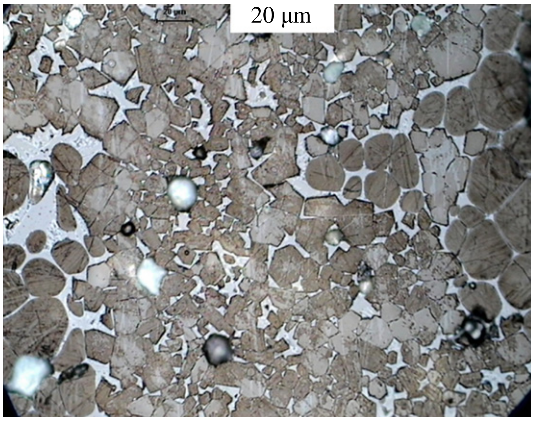

Fig. 9. Clinker M2. Idiomorphic alite crystals between large belite crystals.

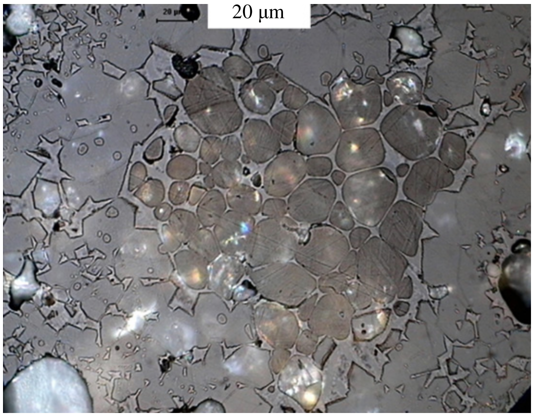

Fig. 10. Clinker M2. Belite cluster surrounded by interstitial phase.

The non-uniform distribution of the interstitial phase observed in other areas (Fig. 11) was associated with the melting of thick, flux-bearing particles, in this case thick sludge M2 particles.

The control sample exhibited uniform phase distribution (Figs. 12 and 13) and had a smaller proportion of belite. The main difference, however, was found in the interstitial phase, which had a higher ferrite content in the control clinker and a higher C_3A content in clinker M2. Belite clusters were also observed, as above.

3.6. Elemental phase analysis

The phases constituting Portland clinker form as a result of the solid state reaction involving elemental oxides and of crystallization out of a molten mass, with the uptake of a series of elements in their structure not included in their stoichiometric composition. The solubility of the majority and minority elements in the clinker phases depends not only on the chemical composition of the raw mix, but also on the heating and cooling rates, maximum temperature attained and so on.

The elemental composition of these phases was studied with BSE/EDX, using the polished samples examined under a reflected light microscope.

Table 6 gives the results for alite and belite, expressed in the form of oxides, as well as for the aluminates and ferrites in the interstitial phase.

These results showed that Mg was more soluble in alite, while belite solubilized Na, K, Al and Fe more effectively. Large amounts of Si but barely any S were solubilized in the aluminates and ferrites, which were analyzed jointly because the spatial resolution of the microscope was insufficient for separate analysis.

4. Discussion

The DSC/TG study of the atomized sludge yielded findings of technological interest. According to these results, the organic fraction of the atomized sludge burned at around 300 °C, releasing 678 J/g sludge, a combustion temperature high enough to guarantee the absence of spontaneous combustion and explosions in the raw meal mill. Organic matter combustion continued under the experimental conditions to a temperature of 500 °C. Although between 400 and 500 °C the XRD analyses showed no other change in the sample than the disappearance of the clinochlore reflections, around 1% of carbon was lost in that range. This effect must be attributed to organic matter and not to carbonates, given the fairly low temperatures involved. The carbon content in the sample treated at 500 °C (2.19%) was found in the inorganic fraction carbonates, an observation consistent with the mineralogical composition of the atomized sludge [2] (16.7% calcite and .3.1% dolomite). Thermal decomposition of the carbonates began at temperatures of over 500 °C and became especially intense at 700 °C, along with decomposition with the constituent mica, feldspar and so on. Moreover, solid state reactions involving nepheline took place at this temperature.

Atomized sludge M2 replaced the clay in raw mix M2. Since the chief compositional difference between clay and sludge is SiO_2, the mix containing the latter had to be prepared with a higher content of quartz sand, whose burnability is low. Another important difference is the much higher proportions of CaO and Na_2O in the sludge than in the clay, which in turn contains much more MgO. Replacing the clay with atomized sludge also raised the relative amounts of

Fig. 11. Interstitial phase-rich area of clinker M2.

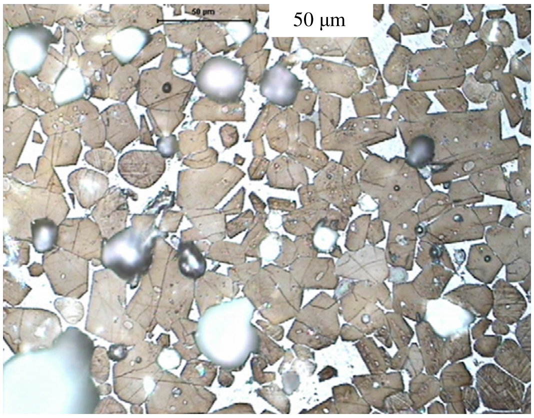

Fig. 12. Control clinker. Well crystallized alite surrounded by interstitial phase.

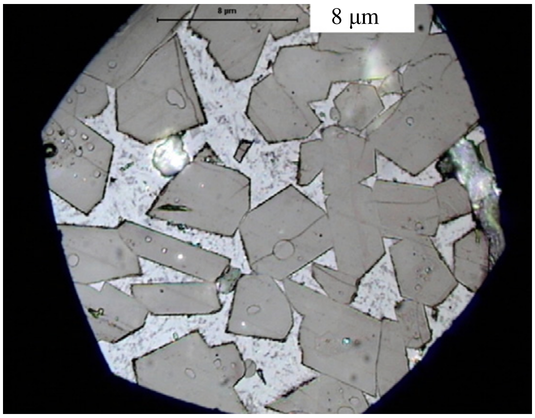

Fig. 13. Control clinker by uniformly distributed phase.

certain minority oxides, namely Zn, Zr, V, Ni, Cu and As, and lowered the BaO content.

The thermal behaviour of the two raw mixes was similar up to 1200 °C, with no differences in decarbonation temperatures. The exothermal solid state reaction signal was higher in raw mix M2, whose eutectic temperature was around 15° lower than in the control. The intense exothermal signal on the 1220 °C DSC curve for mix M2 may have been due to the mass formation of C_2S, inasmuch as quartz and lime react in a narrow temperature range. That reaction would have taken place at lower temperatures in the control due to its lower quartz content. Moreover, quartz is known to be less reactive with lime than the SiO_2 in clay [21]. That may be an indication of the lower reactivity of raw mix M2 than the control at solidus temperatures. Furthermore, the presence of MgO in the control mix and of Na and K in mix M2 would explain the temperature at which the first molten mass was formed (1304 °C and 1282 °C respectively), several degrees lower than the eutectic temperature in the $CaO–SiO_2–Al_2O_3–Fe_2O_3$ system [22].

Table 6
EDX chemical analysis of clinker M2 and the control.

Oxide	ALITE		BELITE		FF + Al	
	Ct. cl.	Cl.M2	Ct. cl.	Cl.M2	Ct. cl.	Cl.M2
Na_2O	0.07(9)	0.6(2)	0.21(7)	1.5(1)	0.03(6)	2.9(4)
MgO	1.1(1)	0.8(1)	0.4(2)	0.34(7)	3.0(5)	1.2(4)
Al_2O_3	0.2(6)	0.6(1)	0.8(5)	1.1(5)	21(4)	22(3)
SiO_2	26.8(3)	27(1)	33.3(8)	33.3(6)	9(4)	8(3)
SO_3	0.12(8)	0.13(5)	0.15(8)	0.21(5)	0.11(7)	0.09(1)
K_2O	0.56(8)	0.4(1)	1.5(1)	0.73(4)	2(1)	0.8(1)
CaO	70.4(5)	70(2)	62.4(3)	61.3(5)	51(4)	50(2)
Fe_2O_3	0.8(1)	1.0(9)	1.4(4)	1.6(4)	14(2)	14(2)

Raw mix burnability is related to the rate at which CaO combines during the thermal process and is evaluated in terms of chemical, physical and mineralogical parameters. The empirical equations developed by Miller [23], (1 and 2) were used to evaluate the contribution of the M2 residue to the total free CaO in the clinkers obtained at 1400 and 1500 °C. These equations, which incorporate chemical parameters and raw mix particle size, are as follows:

$$\mathrm{CaO}_{1400^\circ\mathrm{C}} = 0.31(\mathrm{LSF}\text{-}100) + 2.18(M_s\text{-}1,8) + 0.33\mathrm{C}_{125} + 0.73\mathrm{Q}_{45} + 0.34\mathrm{Aq} \qquad (1)$$

$$\mathrm{CaO}_{1500^\circ\mathrm{C}} = 0.21(\mathrm{LSF}\text{-}100) + 1.59(M_s\text{-}1,9) + 0.22\mathrm{C}_{125} + 0.40\mathrm{Q}_{45} + 0.08\mathrm{Aq} \qquad (2)$$

where LSF is the lime saturation factor; M_s, the silica modulus; C125, the% of limestone with a particle size >125 μm; Q45, the% of sand >45 μm; Aq, – the% of clay material >63 μm.

The free lime in the clinkers obtained at the above two temperatures can be calculated from the Miller prediction models, i.e., by applying Eqs. (1) and (2) to the raw mixes. The free lime in the control mix was determined by raw mix compositional parameters LSF and M_s, inasmuch as the particle size terms were nil (the limestone grain size was <125 μm and the sand and clay particles were <45 μm). For the raw mix containing atomized sludge, both

Table 7
Calculated and experimental free lime values and new modulus values computed from the chemical composition of the clinkers.

	Clinker modulus			1400 °C		1500 °C	
	LSF	M_s	M_f	Experimental (%)	Calculated Eq. (1)	Experimental (%)	Calculated Eq. (2)
Control clinker	98.02	2.20	1.46	2.38	0.26	0.66	0.06
Clinker M2	99.62	2.33	1.44	3.20	1.99	1.92	0.83

compositional and sludge particle size terms were used in the calculations, for 2.8% of the sludge particles were over 63 μm [23].

The analysis of the clinkers obtained when the raw mix was burned at 1450 °C (Table 4) revealed slight compositional differences between the two. Their LSF and M_s values found from the aforementioned chemical analyses are given in Table 7, along with the free lime values found experimentally and calculated with Eqs. (1) and (2).

The free lime values obtained experimentally were higher than predicted by the model in both clinkers at both temperatures used in the study; i.e., prime material reactivity was somewhat lower than the statistical mean.

The experimental free lime values were consistently higher in the sludge-containing clinker than in the control. In the clinker M2 obtained at 1400 °C, but not in the material obtained at 1500 °C, this difference is explained by the contribution of the Aq term in the polynomial (0.95% of CaO due to sludge M2 particle size). The reason lies in the higher quartz sand content (which is harder to burn than clay or sludge) in the atomized sludge mix, or its higher alkali content, whose origin is to be found in the sludge.

The coefficients affecting term Aq in Eqs. (1) and (2), calculated by entering the respective values in the equations, i.e., free lime, LSF, M_s and the percentage of atomized sludge particles larger than 63 μm, are given in Table 8. The Aq coefficient for raw mix M2 burned at 1400 °C was 50% lower than Miller's statistical mean. This is an indication of the good burnability of sludge as a component of the raw mix; nonetheless, the coefficient was 25% higher than the statistical mean when the mix was burned at 1500 °C.

The mineralogical differences between the two clinkers revealed by XRD analysis, primarily relating to the composition of the interstitial phase, are consistent with different cooling rates. De la Torre et al. [24] showed that a clinker cooled slowly may a have much higher aluminate and lower belite content than when it is subjected to more effective quenching, even though the Bogue mineralogical composition would be the same in both cases. Clinker M2 was cooled more slowly and as a result more C_3A and less ferritic phase crystallized out of the molten mass, which presumably had a smaller proportion of Al than the control clinker, which was cooled at a higher rate. The microscopic study of the clinkers obtained at 1450 °C confirmed the higher C_3A content and the larger particle size of this crystal in the clinker M2 than in the control clinker interstitial phase.

The clinkers obtained contained a high proportion of silicates, whose exact value differed, however, depending on whether it was estimated by the Bogue or Rietveld methods. The alite content found with XRD was similar and around 8% higher than calculated with the Bogue formulas, whereas the belite values found with the Bogue method were higher. The explanation may be that the Bogue approach assumes that calcium only exists in non-tetrahedral crystallographic silica and that only silicon is taken up in the tetrahedral sites (whereas the microanalysis in Table 6 shows Mg and Al uptake as well).

Finally, according to the microscopic study, the morphology of the silicates in the two clinkers was similar, although the phase distribution was less uniform in clinker M2 than in the control.

Table 8
Aq coefficient values for raw mix M2 calculated from clinker chemical composition, free lime and fineness data.

Sample	Aq coefficient	Aq coefficient (Miller equation)
Mix M2, 1400 °C	0.168	0.34
Mix M2, 1500 °C	0.103	0.08

5. Conclusions

In this study the suitability of a DWTP atomized sludge as a prime material for clinker manufacture has been evaluated. The main conclusions are:

1. The organic fraction of the atomized sludge burns at around 300 °C, releasing 678 J/g sludge. Under the present experimental conditions, the organic matter continued to burn up to a temperature of 500 °C. These combustion temperatures are high enough to guarantee the absence of spontaneous combustion and explosions in the raw meal mill.
2. The burnability of atomized sludge-containing raw mix is somewhat lower than in the control mix. This can be attributed to the higher quartz content in the former, inasmuch as sludge reactivity was found to be high.
3. The clinker obtained after burning raw mix with 12% atomized sludge at 1450 °C for 30 min contained over 75% silicates and 22% interstitial phase. The microstructural analysis showed no differences in silicate crystal size or composition between this clinker and the control.
4. Atomized sludge studied can be used as a raw mix prime material in cement manufacture, as substitute for clay and partial substitute of limestone.

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