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Recycling of Moroccan coal gangue in the elaboration of a Portland clinker

D. Belkheiri[a,b], A. Diouri[a], M. Taibi[b*], O. Sassi [b], J. Aride[b]

[a] *Université Mohammed V, Laboratoire de chimie du solide appliquée, Faculté des sciences, Rabat, Maroc (Morocco).*
[b] *Université Mohammed V, Laboratoire de Physico-Chimie des Matériaux Inorganiques et Organiques, Ecole Normale Supérieure, Rabat, Maroc (Morocco).*

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[*]*Corresponding Author. E-mail: taibiens@yahoo.fr; Tel: +212668460628*

Abstract

We investigated the possibility of recycling and recovery of Moroccan coal gangue (coal mine of Jerada). The analysis of the waste showed that it is formed essentially of silica and clays. We were interested to elaborate a Portland clinker from mixtures composed of limestone and coal gangue. A preliminary study was focused on the optimization of the composition of the mixture. We have taken as a reference the clinker synthesized with the raw materials of a cement plant. The products obtained were analyzed by X-ray diffraction and infrared spectroscopy. They contained essentially the main mineralogical phases of Portland clinker. A study of the hydration of these clinkers was carried out using a micro-calorimetry technique and the hydrated products were characterized by X-ray diffraction. The results showed that the clinker elaborated using the coal waste have the same properties of the reference one. So we can provide an opportunity for recycling and recovery of coal gangue in the Portland clinker development. In addition, it was possible to obtain an energy saving resulting from the combustion of coal residues contained in the gangue.

Keywords: coal gangue, recovery, clinker, hydration.

Introduction

The total world production of coal, including past and future production, is estimated at about 680 Gt [1]. Unfortunately coal production is accompanied by large amounts of solid waste estimated between 15 and 20% [2]. Around the world, the accumulation of coal waste poses environmental and economic problems [3,4]. It contaminates the soil, water and air. Many scientific studies were interested in recycling coal waste. For example, some studies have focused on the recycling of coal waste and ash [5, 6, 7] in the field of civil engineering materials like bricks [4], ceramics [8,9], concrete block pavements [10]and in cements. Shuang studied [2] the partial replacement of the cement by the heated coal gangue, in quantities between 10 and 40% by weight. Moreover, recycling in cement production can provide useful impurities [11]. For example impurities such as phosphorus can stabilize highly reactive varieties of dicalcium silicate [12-15] and other impurities such as manganese and chromium contribute to allotropic form of tricalcium silicate with larger hydraulic reactivity [16]. Other studies have focused on the pozzolanic properties of coal gangue activated when annealing at high temperature (700 to 1000 °C) [17-21]. Another study was interested in pozzolanic behaviour of compound activated red mud-coal gangue mixture [22].

In the mine of Jerada, at the northeast of Morocco, coal production started in 1930 and stopped in 2003. It was accompanied by the large quantities of solid waste formed essentially by the gangue with other coal waste. A large amount of 20 Mt (million tons) is stored as a slagheap. The coal of Jerada is an anthracite type with pyrite content of about 5% and its waste abandoned in the wild, creates environmental problems by affecting the quality of air, soil and groundwater. The oxidation of the pyrite in air with the presence of water produces sulfates. Bendra et al. [23] showed the presence, in groundwater, of large amounts of sulfates, chlorides and nitrates (exceeding World Health Organization Guidelines). Darmane et al. [24] were interested in recycling a part of this gangue and turn it into paints and enamel based on ferric oxide. In our earlier study [25], we conducted mineralogical and chemical characterizations, which showed that this gangue is constituted by a large mineral part formed of silica and clay (2:1) and an organic part formed by coal residues. This coal gangue is formed mainly by oxides of silicon, aluminum, iron, which are typically encountered in the construction materials and in cements. In this work we studied the possibility of recycling this gangue by mixing it with the materials used in the Portland cement manufacturing. In fact, such waste provides clay which is a raw material that constitutes 20% in cement manufacturing. Also the exothermic combustion of residual coal, in this gangue, allows a certain input of energy. We studied different mixtures composed of coal gangue and materials used in the manufacture of cement (limestone, raw). After various heat treatments, at temperatures up to 1450°C, the products were analyzed by X-ray diffraction and infrared spectroscopy. We studied and compared the results of the clinker's hydration using calorimetry, X-ray diffraction and scanning electron microscopy.

2. Materials and methods

2.1. Raw materials and mixtures

It is proposed to develop clinkers from mixtures of limestone and coal gangue.

- Limestone from a cement plant denoted L (lime).
- The gangue (sterile) of the coal mine of Jerada denoted G.

The mixtures limestone-gangue, with a certain percentage % of gangue, are denoted LG%.

We used a raw cement plant to serve as a reference, and it is denoted R. We also used an industrial clinker as (other) reference and it is denoted C. The X-ray fluorescence analysis of these materials gave the results shown in Table 1.

Table 1: Composition of used materials

Oxide\Material	Lime(L)	Gangue(G)	Raw(R)
CaO	50.17	0.81	42.79
SiO_2	4.85	52.4	12.27
Al_2O_3	1.38	21.9	3.65
Fe_2O_3	0.61	4.55	1.74
SO_3	0.14	3.54	0.34
K_2O	0 .48	2.24	0.88
Na_2O	-	1.53	-
MgO	1 .5	1.26	1.97
P_2O_5	-	0.135	-
MnO_2	-	0.104	-
L.O.I*	40.64	10.6	36.25

(*L.O.I: loss of ignition)

From both limestone and gangue materials, we made mixtures of around of 20% of gangue. Their compositions are given in Table 2.

Table2: Chemical composition of studied mixtures

%gangue \ %oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3
10	72.53	15.39	5.50	1.61
15	66.96	18.74	6.98	1.88
17	64.81	20.04	7.55	1.98
18	63.91	20.60	7.79	2.03
18.5	63.22	21.01	7.97	2.06
19.5	62.16	21.63	8.25	2.11
20	61.65	21.95	8.84	2.14
31	50.78	28.51	11.24	2.67

Cement notation (used below): C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3 and H= H_2O.

2.2. Methods

Our goal is to achieve an optimal mixture of limestone-gangue materials, which gives after heat treatment a clinker approaching the one of the reference (of cement manufacture). In a first step, in order to produce such mixtures, the following three criteria are respected:

- Choosing the right proportions of major oxides (C, S, A, F) to obtain clinker with targeted phases compositions.
- Using correct values for the factors of mix proportioning [11, 26]: lime saturation factor (LSF between 96 and 100), silica ratio (SR between 2.8 and 3.2) and the alumina ratio (AF between 1.4 and 1.8). These values concern the relative relationships of the various quantities in main oxides. They influence the clinker phase ratios C_3S/C_2S, C_3A/C_4AF, burnability and temperature of annealing.
- Getting good Bogue estimates for the compositions of the main phases in clinkers: C_3S, C_2S, C_3A and C_4AF.

This stage includes a calculation of the variation of criteria retained according to the percentage (% weight) of gangue as variable. Some results are given in table 2.

Then we approached the experimental part through the heat treatments at 1400°C of mixtures which contain between 10% and 31% of gangue. Finally, we chose optimized mixtures which were treated at T= 1450°C. The limestone-gangue mixtures containing G% of coal gangue treated at a temperature T are noted LG%T. The used materials were grinded to a particle size of 160 μm. Each mixture placed in a platinum crucible is then raised, with a furnace, to the desired temperature T. We conducted heat treatments at different temperatures for different durations: T= 500°C (24h), T=1000°C (12h), T=1200°C (4h),T=1300 °C (1h), T=1400°C (40min) and T=1450°C (40 min). The different heat treatments were followed by a quenching and then the products were crushed. The powder of the obtained products were analyzed by X-ray diffraction ($\lambda_{\alpha 1}$ = 1.5406 **Å**) using the Siemens D5000 diffractometer. FTIR infrared spectroscopy was performed using a Perkin Elmer apparatus on KBr pellets. The curves of hydration were obtained using a micro-calorimeter type Tian Calvet. The microstructure was studied using a Scanning-Electron-Microscope (SEM).

3. Results and discussion

The composition of the coal gangue varies with the geology of the site. For example, one could compare the compositions (of studied samples) in Morocco to those of other countries like Spain [17], Portugal [3] and China [4]. The clay contained in Moroccan gangue is essentially 2:1; whereas for the others it, also, contains the kaolinite 1:1. The composition of silica and alumina is comparable to other gangues; but it is lower for the oxides of iron and calcium. In our previous study [25] it was found that the small granulometry of this gangue, is rich in iron oxide. The low content of iron oxide in the analyzed samples (taken from the surface) can be attributed to wind dispersal during the decades of existence of the heap**.** The comparison of this coal gangue to the usual clays shows that it is richer in silica and alumina, but poorer in calcium and iron oxides.

3.1. Optimization of the mixture limestone-gangue

For each mixture, we studied the changes in the three criteria values when changing the percentage of gangue in the mixture limestone-gangue. We found that the mixtures where the oxide composition is close to that of the reference had percentages comprised between 15 and 18% of gangue. This gangue could be likened to the clay used in cement plants to about 20%.

The correct value for the lime saturation factor (LSF between 96 and 98) can be obtained with the mixtures formed with 17-18% of gangue. It is noted that the silica ratio (SR) is lower than the reference's one. The alumina ratio (AF) is higher due to the low iron oxide content in the coal gangue (clay). The LG mixtures with less than 16% of gangue are expected to have too much free lime.

The increase in the percentage of coal gangue causes a decrease in the percentage of C_3S and an increase in the percentage of C_2S. Mixtures having similar compositions in C_3S and C_2S to those of the reference contain between 17 and 18% of gangue. It is noted that the estimated value of the percentage of C_3A is greater than the one of the reference and increases with the percentage of gangue, while the % of C_4AF still below the value obtained for the reference. It is interesting to note that the method of Bogue is approximate because it doesn't have thermal equilibrium during the quenching and it ignores solid solutions formation.

According to the previous general study, we can choose mixtures with some characteristics similar to those of the reference and we can't have agreement on all parameters. For example three special mixtures are presented in Table 3 with the percentages of gangue that can achieve them: $C_3S_{mix} \sim C_3S_R$:17.41 %, $C_2S_{mix} \sim C_2S_R$: 17.12 %, LSF ~ 100 : 16.68%.

Table 3: Examples of special mixtures limestone-gangue

Features \ %CG	17.41%	17.12%	16.68%
%C	64.38	64.68	65.15
%S	20.31	20.12	19.84
%A	7.668	7.586	7.462
%F	2.006	1.991	1.968
LSF	96.52	97.90	100
SR	2.099	2.101	2.104
AF	3.82	3.81	3.97
%C_3S	50.07	53.38	58.31
%C_2S	20.48	17.42	12.82
%C_3A	16.93	16.73	16.44
%C_4AF	6.104	6.059	5.989

In conclusion, for the studied mixtures (limestone-gangue), we can choose our optimum between 17% and 19.5%. These values are consistent with those found in the literature for oxides (C: 60-69%, S: 18-24%, A: 4-8%, F: 1-8%) and for the clinker's phases (C_3S**:**55-60%, C_2S:15-20%, C_3A:5-10%, C_4AF:5-8%).

3.2. Heat treatments

In our previous thermal characterization of the coal gangue [25], it was observed an exothermic effect between 300 and 600°C attributed to the coal residues; then a TG analysis showed a mass loss between 700 to 900°C attributed to the thermal decomposition of clay (illite, muscovite) and this corroborates with other studies [27, 28].

After heat treatment at 500°C, the color of the limestone-gangue mixture became similar to that of the reference mixture; this was due to the disappearance (combustion) of coal residues. After thermal treatment at T = 1000°C, the X -ray diffraction analysis showed, in the two mixtures, the presence of lime obtained by calcining limestone; also for the LG % mixture, activation of the coal gangue takes place at temperatures between 700-1000°C, which promotes the formation of the cement compounds. Indeed Li et al. [19] reported that the activity of the coal gangue is improved by calcination (700°C-1000°C) and this activity increases with the addition of CaO. During heat treatment between 1200 and 1450°C, we observed occurrence of interesting clinker phases.

3.3. X-ray diffraction analysis

In a preliminary study we chose to work with a wide range of gangue percentage between 10% and 31% treated at T=1400°C. The obtained products were analyzed by X-ray diffraction (figure 1).

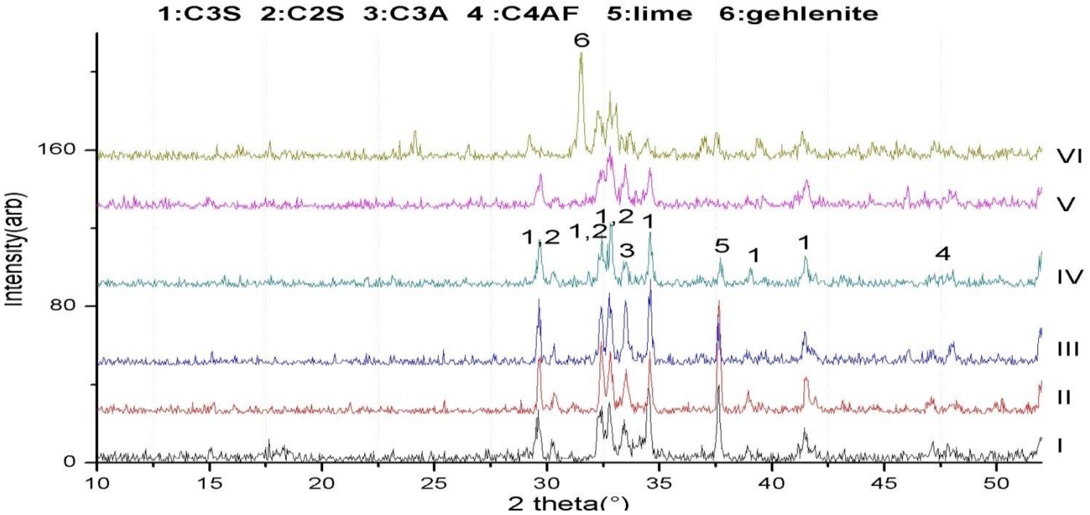

Figure 1: X-ray diffractograms of mixtures treated at 1400 °C
LG10(I), LG15(II), LG18(III) , REF(IV), LG20(V) and LG31(VI).

The first mixture LG10 and the last one LG31 had very low contents in C_3S, C_2S, C_3A and C_4AF. These ‘’clinkers’’ are the most different from the reference one. After heat treatment, the mixture LG10, with 90% of limestone, contains mainly free lime which can causes the expansion in concrete[29]. The contents of silica and alumina increase with the percent of gangue in the mixture, so we noted that the mixture with 31% of gangue contains mainly gehlenite C_2AS, which is poorly hydraulic [30]. In the literature Yang et al. [8] obtained glass ceramics containing mainly gehlenite from a mixture formed by 70 wt.% of coal gangue and 30 wt.% of calcium oxide; whereas our mixture LG31 contained 45 % of coal gangue and 55 % of calcium oxide.

As expected, for mixtures containing between 15% and 20% of gangue, it is significant to obtain the usual phases of clinker: C_3S, C_2S, C_3A and C_4AF in different contents. The LG18T1400 and LG20T1400 mixtures are the closest ones to the reference. These mixtures contain the main phases of clinker: C_3S and C_2S.

Based on the study carried out at T = 1400°C, we choose to work with limestone-gangue mixtures with percentages of gangue: 17, 18.5 and 19.5%. These blends and the ones of the reference (R) were treated at T = 1450°C. Figure 2 shows the X-ray diffractograms of previous mixtures and also the diffractogram of the industrial clinker.

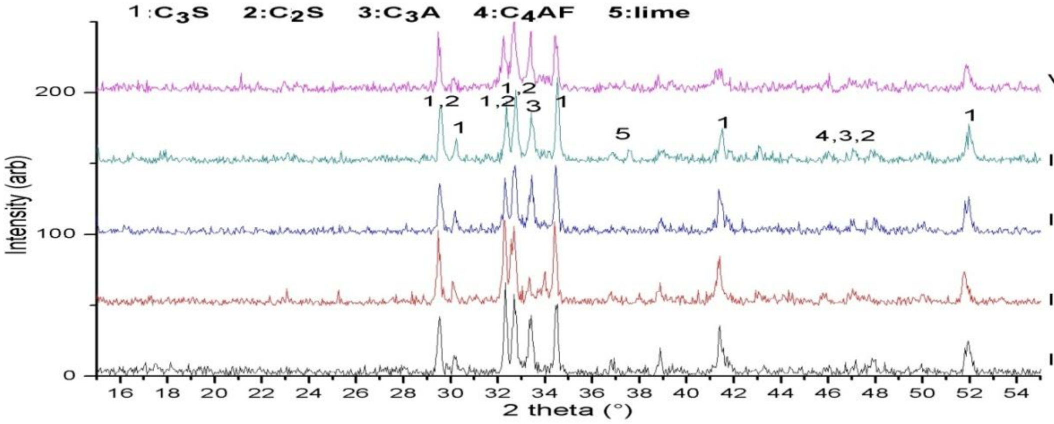

Figure 2: X -ray diffractograms of mixtures heated at 1450°C

The comparison of the X-ray diffractograms shows that there are similarities between the clinkers obtained from the studied mixtures. We note that they contain mainly the clinker‘s principal phases of: C_3S, C_2S, calcium aluminate and calcium aluminoferrite**.** It was found that industrial clinker gives the main four phases of clinker but the other clinkers gives some intermediate phases and this can be interpreted by our experimental procedure which is different from the industrial process. The clinker of reference gives low C_3S and C_2S quantities; it contains free lime, intermediate phases and therefore the clinkering reactions are incomplete. The elaborated clinker with 18.5% of gangue gives better results than the one with 19.5% of coal gangue and its diffraction pattern is quite close to those found in the literature [31, 32].

3.4. Analysis by infrared spectroscopy

The clinkers corresponding to mixtures LG18.5, LG19.5 and for the reference (R) were characterized by infrared spectroscopy. Their curves of infrared transmission are shown in Figure 3. We can note that infra red spectra are similar to those of usual clinkers [33-35] and it is possible to do some assignments as reported in Table 4. It was noted a broad band near 3400 cm^{-1} which can be attributed to traces of water and a small peak characteristic of Portlandite for the reference’s clinker at 3644 cm^{-1}. Other bands were also observed with wave numbers at (cm^{-1}): 620, 1715, 2923, 3443, etc…In conclusion a very close similarities was observed between the studied limestone-gangue mixtures and the reference.

3.5. Hydration

The clinkers (obtained at 1450°C) LG17, LG18.5, LG19.5, R (reference) and C (industrial clinker) powders were reduced to a particle size of 0.25 mm. A mass of 1g of clinker was hydrated at room temperature with water-clinker ratio W/C = 0.5. In contact with water, silicates are dissolved as ions, which interact and form hydrated calcium silicate (C-S-H) and Portlandite CH. We followed, over time, the resulting heat of hydration. The obtained thermograms are shown in Figure 4.

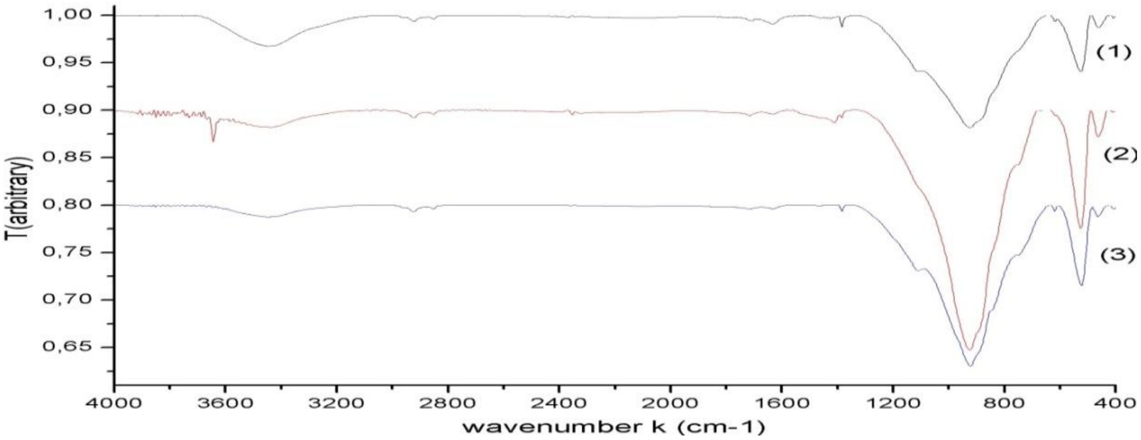

Figure 3: Infrared spectra of the clinkers: LG19.5 (1), R (2) and LG18.5 (3).

Table 4: Assignment of observed bands in infrared spectra of the clinkers LG18.5, LG19.5 and R

Wavenumber (cm^{-1})	Clinker	Possible assignment
922	LG19.5	Si-O stretching
924	LG18.5	Si-O stretching
925	R	Si-O stretching
523	LG19.5	out-of- plane bending
525	LG18.5	out-of- plane bending
526	R	out-of- plane bending
461	LG18.5	in-plane bending
463	R	in-plane bending
464	LG19.5	in-plane bending
3644	R	OH in Portlandite

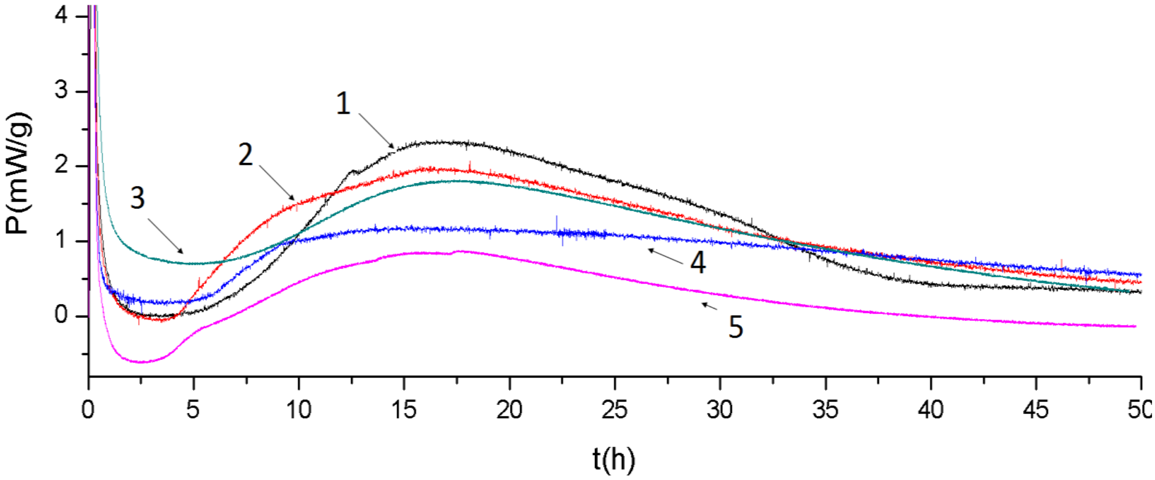

Figure 4: Thermograms of hydration of the clinkers C(1), LG18.5(2), R (3), LG19.5(4) and LG17(5)

The five stages of hydration were observed with two exothermic peaks**.** The first one rapid and very exothermic corresponds to the hydration of C_3A (flash set : formation of C-A-H**)** ; in Portland cement, gypsum is added to to retard C_3A hydration. The hydration of C_3S, C_2S gave CSH (calcium silicate hydrate) and Portlandite CH. The industrial clinker gave the greatest heat generation. The behaviour of the calorimetric curves is similar between the clinker of the mixture LG18.5 and the industrial one. The mixture corresponding to (LG18.5) provided a good clinker compared to LG19.5 and LG17.

The hydrated compounds were studied by X-ray diffraction at different ages to follow the evolution of the main crystalline phases. The main hydration products are the Portlandite and hydrated compounds (C_xS_yH) with a variable stoichiometry**.**

The X-ray diffraction analysis after 7days of hydration showed for the clinker LG18.5, the presence of remaining C_3S, C_2S and formation of hydration compounds: C_2SH (hillebrandite), C_2SH_3, C_3SAH_4 (katoite) and Portlandite. The hydration of C_3S and C_2S produced Portlandite CH and CSH where the ratio of C/S increased with time (5/6 in day 1 to 2 in day7) and also it was noted hydration of C_3A which produced C_3AH_6.

3.6. Scanning Electron Microscopy

Figure 5 shows the microstructure appearance of the optimal clinker LG18.5 (Figure 5a) and its hydration products after 28 days (Figure 5b). We note the presence of C_2S which is rounded, C_3S with more angular shape and the brightest regions corresponds to C_4AF and C_3A. The SEM characterization of the hydrated clinker LG18.5 is also illustrated and we note the appearance of fibrous matrix of hydrate (CSH) and Portlandite crystals (CH).

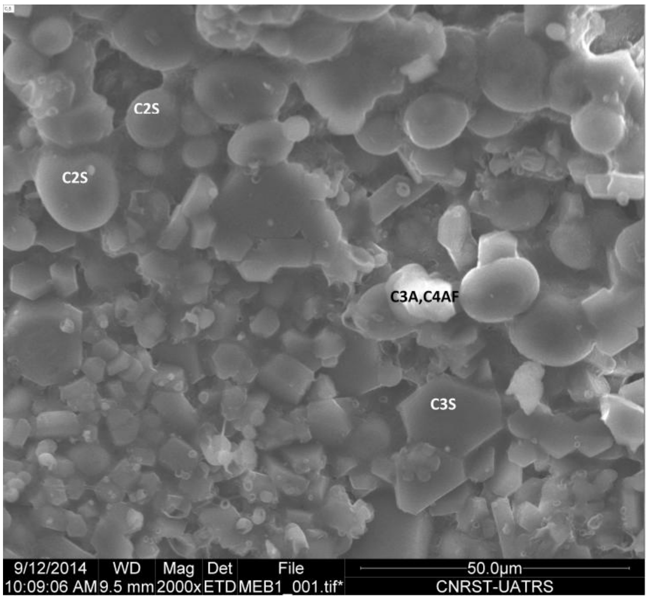

Figure 5a: Scanning Electron Microscopy (2000X) of the clinker LG18.5.

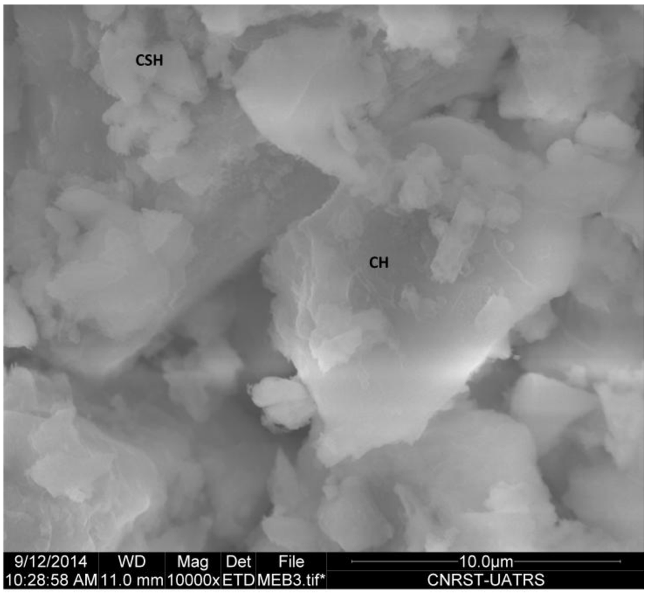

Figure 5b: Scanning Electron Microscopy (2000X) of the hydrated clinker LG18.5 (28 days).

Conclusion

The analyzed samples, of Moroccan coal gangue, contain mainly a mineral part formed by silica and clays. The possibility of using this coal gangue to develop a clinker was investigated. It could play the role of clay when properly mixed with limestone. We have determined the optimal proportions of limestone-gangue mixture that would lead to the formation of clinker similar to Portland one produced from the industrial raw used in cement plant. The investigation was based on the percentage of major oxides, the mix proportioning factors (LSF, SR, AF) and the estimated values of clinker phases. The characterization and hydration behaviour of clinker elaborated from limestone and coal gangue of Jerada (Morocco) was taken out.

The obtained products at T=1450°C, were analyzed by XRD. The analysis showed the presence of the main clinker phases: alite, belite, aluminate and aluminoferrite. The optimized mixture formed by 18.5% of gangue was close to the one given by the reference mixture. The hydration of clinker LG18.5 is compared to the reference using calorimetric measurement, X-ray diffraction. The hydration steps of elaborated clinker shows similarities in the behavior to the reference one. Limestone-gangue mixture that comes closest to the reference one considered in our study contains 18.5% of coal gangue. The oxide composition for this mixture: C = 63.2, S = 21.0, A = 7.97, F = 2.06, which are close to the values used in the manufacture of cement.

It is therefore possible to recycle and valorize coal gangue in the development of Portland clinker. Also when mixing coal gangue with other materials such as limestone and raw, we obtained other clinkers and other compounds such as gehlenite and Akermanite.

In conclusion, this recycling has economic and environmental benefits. Recycling of coal waste will reduce its impact on the air, the land and especially on the water, which is most affected by acid drainage sulfate resulting from the oxidation of pyrite. In addition, it is possible to obtain an energy benefit from burning coal remains contained in this gangue**.**

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