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Cement Clinker Based on Industrial Waste Materials

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Abstract

The manufacturing of cement consumes energy and results carbon dioxide emissions. This work focused on producing cement clinker using coal fly ash (CFA), sewage sludge ash (SSA) and an industrial waste with a high content of calcium silicate (CS). Experiments were conducted to assume the use of a process that may consume less energy and raw materials that used in cement clinker manufacturing. The raw mixtures were prepared with lower clay and limestone contents than those used in Portland clinker manufacturing and then burned at lower temperatures, ranged from 1000 to 1200°C. Due to the content of fluxes and mineralizers of the raw mixtures, this method could decrease carbon dioxide emissions from calcination up to 60% and energy consumption up to 350 kcal/kg of clinker. The free lime content of the clinker was found out by volumetric analysis and was consistent with free lime content in Portland cement clinker. Activation energies ranged from 42.7 to 91.1 kJ/mol and the cement clinkers contents of fluorine varied from 0.82 to 3.9%. The main characterizations of the obtained clinker, which were X-ray fluorescence, X-ray diffraction and SEM, highlighted interesting composition as building material.

Keywords: Calcium silicate • Cement clinker • Coal fly ash • Industrial waste • Sewage sludge ash

Introduction

Ordinary Portland Cement (OPC) has been a priority material of construction used in many countries throughout the world. In 2017, approximatively 4,100 million metric tons of cement were produced worldwide [1]. Even though OPC is essential for construction and building purposes, its manufacturing process consumes high energy and generates carbon dioxide emissions; with the production of one ton of clinker producing 0.9 ton of CO_2 emissions [2]. The main ingredients for obtaining OPC are limestone, iron, silica and alumina. Alternative raw materials are being used in order to reduce limestone and clay consumption and also energy requirement [3]. Several studies related the use of alternatives raw materials such as coal fly ash, sewage sludge ash and some fluoride waste. Indeed, sludge and coal from wastewater treatment and power plants constitute interesting raw materials for cement industry. Coal fly ash has been tested in order to manufacture belite cement [4]. The effect of sewage sludge ash on the properties of cement composites was a purpose of study as well as its cementitious properties [5,6]. Coal bottom ash was also confirmed to reduce material and energy consumption [7]. The use of a mixture of calcium silicate and calcium fluoride, as an industrial waste material from phosphoric acid production, in the raw mixture for clinker manufacturing was successful to produce a fluoride clinker [8] as well as the production of cement at low temperature [9]. In this study, three industrial waste materials were used: a calcium silicate compound (CS), coal fly ash (CFA) and sewage sludge ash (SSA). The objectives of this study were to:

- minimize the disposal of industrial waste from phosphoric acid production, wastewater treatment and coal power plant;
- examine if it is possible to lower energy and raw materials (limestone and clay) consumption in the cement manufacturing process.

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Materials and Methods

This section highlights the raw materials, the mixtures, the burning process and the methods of cement clinker characterization.

Raw materials

Limestone and kaolin clay

The limestone (99 wt% of $CaCO_3$) was provided by Omya Canada Inc. The kaolin clay was purchased by VWR Corporation and its chemical composition is shown in Table 1.

Industrial waste materials

Table 2 summarizes the chemical compositions of the three industrial waste materials which were used. The particle sizes of the raw materials are listed in the Table 3. The CS was recovered from a process of caustification to obtain sodium hydroxide carried out in lab experiment. Actually, it is a material mainly composed of calcium silicate [10]. A class F CFA was used. The SSA was obtained from the calcination at 850°C of activated sludge provided by Corvallis Wastewater Plant (Oregon, USA).

Raw mixtures preparation

The five raw materials (limestone, kaolin, CS, CFA and SSA) were used for preparing the three raw mixtures containing three raw materials (Table 4). This preparation was definitely based on the standard values of the lime saturation factor (LSF) and the silica ratio (SR) factors as required in OPC production [11].

Burning process

After proper blending, the raw mixtures were crushed by means of a porcelain mortar and pestle and fired at the desired temperature during 30 min on an alumina crucible in a ST-1600C-445 Box furnace, with the program going to 10°C in 1 min. Four temperatures were fixed for each raw mix to study the burning process (Table 5).

Analytical methods

The obtained clinkers were analyzed to determine the burnability and the chemical composition. X-ray fluorescence studies were performed on Epsilon 3 XLE (Malvern Panalytical Manufacturing). XRD was performed, using the D8-Discover (Bruker Manufacturer). The SEM analysis was handled by the QUANTA 600 F (Fei Company). The free lime contents of the clinkers (CaOL

Table 1. Chemical composition of the kaolin.

Compound	SiO_2	Al_2O_3	TiO_2	LOI	Fe_2O_3
Content (wt %)	51.70	43.20	2.03	0.10	0.50

Table 2. Chemical composition of the industrial waste materials.

Materials (%wt)	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	SO_3	Mn_2O_3	ZnO	Cl	TiO_2	Na_2O	P_2O_5	LOI
CS	67.08	13.89	0.32	0.09	0.52	0.12	0.08	0.01	0.01	0.01	0.02	9.15	0.04	8.67
CFA	16.79	44.31	15.5	6.01	5.05	1.56	0.93	0.1	0.02	0.01	0.95	3.45	0.24	5.08
SSA	7.06	39.64	9.48	6.19	3.13	4.56	1.02	0.17	0.3	0.01	1.6	4.45	17.3	5.32

Table 3. Particle sizes of the raw materials.

Material	Limestone	Kaolin	CS	CFA	SSA
Particle size (mm)	4.43	1.50	6.82	6.61	6.93

Table 4. Raw mixtures preparation (% wt).

RM (% wt)	Limestone	Kaolin	CS	CFA	SSA	LSF	SR
RM1	25	16	59	0	0	96.8	2.34
RM2	59	0	11	30	0	93.1	2.28
RM3	59	0	11	0	30	99.4	2.83

Table 5. Temperatures of the burning process.

Temperatures (°C)			
950°C	1000°C	1050°C	1100°C
1000°C	1050°C	1100°C	1150°C
1050°C	1100°C	1150°C	1200°C

in wt%) were determined by means of the known volumetric ethylene-glycerol method. The analyzed results were compared with the chemical composition of Portland clinker as specified in ASTM C150-07 [12].

Results and Discussion

This section exhibits the experimental results of the burning process and the characteristics of the obtained cement clinker.

Burning process

The process of clinkerization at four temperatures was determined by following the free lime content. The results of the burning process are displayed in Figure 1.

The displayed results above highlighted the possibility to obtain good quality of clinker at temperatures lower than 1200°C in accordance with a free lime content ranged from 0.6 to 2%. Three samples of clinker were obtained (CL1, CL2 and CL3) based on the content of free lime consistent with the maximum value. The first type of clinker CL1, from RM1, was produced at the lowest temperature (about 1000°C). Due to the high content of CS in RM1 (59%) which acted as a mineralizer, the liquid phase formation seems to take place just after the decarbonisation ((950°C). Indeed, samples of CL1 melted at temperature higher than 1100°C. The second type of clinker CL2, from RM2 was obtained at about 1100°C. CFA, in addition to CS, increased the content of oxides which accelerated the clinkerization process at lower temperature and CL2 started melting at temperature higher than 1150°C. The third type of clinker CL3 from RM3 was produced at about 1150°C. SSA and CFA, as well known, have some similar properties and CL3 melted at temperature higher than 1200°C. The burning process depends on the conversion α.

The conversion α in terms of free lime content is simply written as:

$$\alpha = \frac{CaO_i - CaO}{CaO_i} \quad \text{(Equation 1)}$$

Where CaO_i is the initial free lime content at the initial temperature Ti and

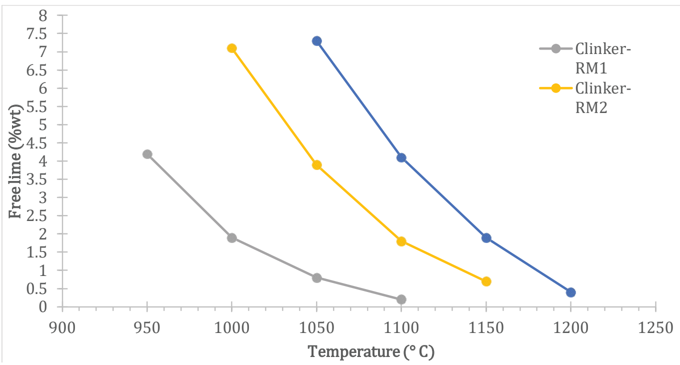

Figure 1. Burning process of raw mixes specimens during 30 min.

CaO the free lime of the obtained clinker at the temperature T.

The conversion α depends on the temperature and the following relations are used to describe the burning process of raw meals. According to Orfao [13]:

$$f(\alpha) = A\int_{T_i}^{T} e^{\frac{-Ea}{RT}}\, dT \quad \text{(Equation 2)}$$

Where:

$$f(\alpha) = \left(1 - \sqrt[3]{1-\alpha}\right)^2 \quad \text{(Equation 3)}$$

Knowing the rational approximation for the integral of the Arrhenius function, equation (2) becomes [14]:

$$f(\alpha) = \frac{AE_a}{Rx^2} e^{-x} g(x) \quad \text{(Equation 4)}$$

x being $\frac{Ea}{RT}$ and g(x) an approximative rational function

Following the fourth degree:

$$g(x)=\frac{x^3+18x^2+88x+96}{x^4+20x^3+120x^2+240x+120} \quad \text{(Equation 5)}$$

Linearizing equation (4) results equation (6):

$$\ln\left(\frac{f(\alpha)}{T^2 g(x)}\right)=\ln\left(\frac{AR}{E_a}\right)-\frac{E_a}{RT} \quad \text{(Equation 6)}$$

The activation energy can then be determined from a linear plot (Figures 2, 3 and 4) by iterative calculations starting with 100 kJ/mol based on previous study [9]. The spots of the plots below represent the activation energies of the three clinkerization reactions summarized in Table 6. These values are lower than the activation energy for OPC ranged from 200 to 500 kJ/mol [9]. Good correlations were then obtained for temperatures lower than 1200°C compared to OPC which temperature is higher than 1350°C. Indeed, the raw mixes contained already calcium silicate which is the main compound of OPC. This contain was higher in RM1 than RM2 and RM3 leading to a low activation energy.

Clinker characterization

The chemical composition (Table 7) highlights the characteristics of the obtained clinkers which were compared to the minimum (CLPm) and maximum (CLPM) values of OPC clinker.

The fluorine (F) content (wt%) estimated my microscopy is respectively 3.90, 0.82 and 1.61 for CL1, CL2 and CL3. The XRD patterns (Figures 5, 6 and 7) highlight the major phases identification. XRF analysis showed results within requirements limits aside from, Al_2O_3 and Na_2O for all the clinkers samples. In addition, the LOI of CL1 was found slightly higher than the maximum requirement. These high contents are suspected to increase the initial hydration and decrease the compressive strength. The higher Na_2O content may have an influence on the microstructure and the hydration of the obtained cements [14].

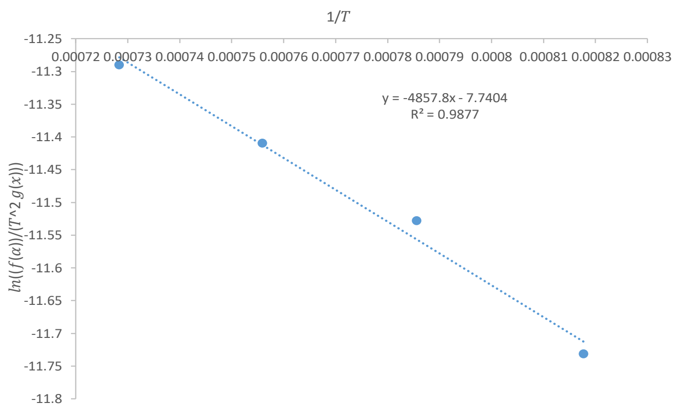

Figure 2. Equation 6's linear plot for CL1.

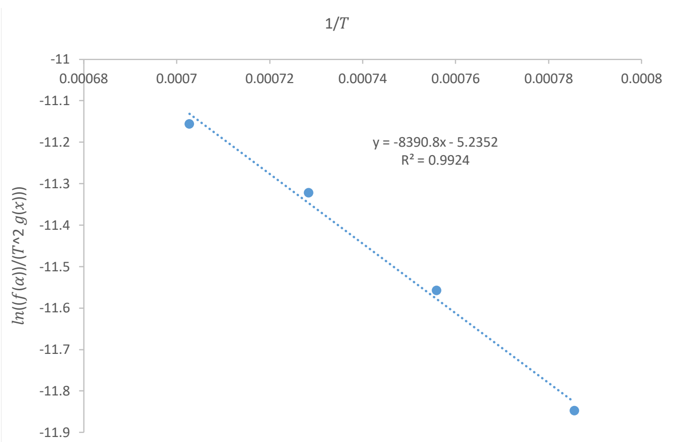

Figure 3. Equation 6's linear plot for CL2.

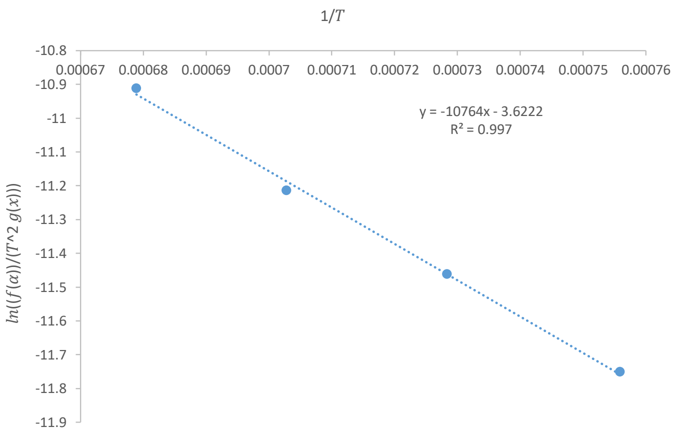

Figure 4. Equation 6's linear plot for CL3.

Table 6. Activation energy of the burning process.

Cinker	CL1	CL2	CL3
Ea (kJ/mol)	42.7	71.5	91.1

Table 7. Chemical composition clinkers (% wt).

Clinkers	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	SO_3	Mn_2O_3	ZnO	TiO_2	Cl	Na_2O	P_2O_5	LOI
CL1	61.44	20.92	7.25	0.14	1.24	0.11	0.12	0.01	0.01	0.02	0.01	4.22	0.03	1.23
CL2	62.97	21.86	7.42	1.79	0.83	0.68	1.66	0.08	0.01	0.13	0.01	1.09	0.02	0.72
CL3	61.58	21.39	7.57	4.15	1.37	1.03	0.79	0.03	0.01	0.07	0.01	1.38	0.09	0.51
CLPm	61.00	20.00	3.70	1.70	1.70	0.05	0.05	0.05	-	0.15	0.00	0.05	0.05	0.2
CLPM	68.10	24.30	7.10	5.70	4.00	1.40	1.30	1.20	-	0.40	0.10	0.70	0.60	1.10

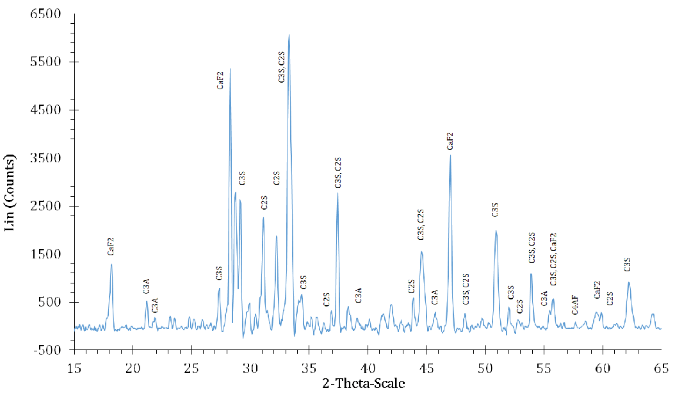

Figure 5. XRD pattern of CL1.

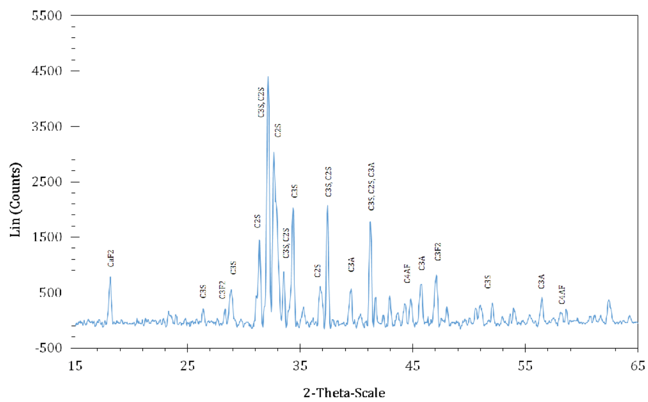

Figure 6. XRD pattern of CL2.

As well known, the difficulty in cement phases identification results in large peak overlap but also in large polymorphs co-existence. However, CaF_2, in

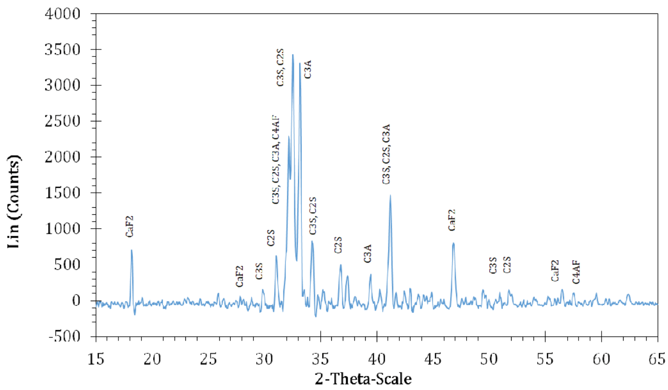

Figure 7. XDR pattern of CL3.

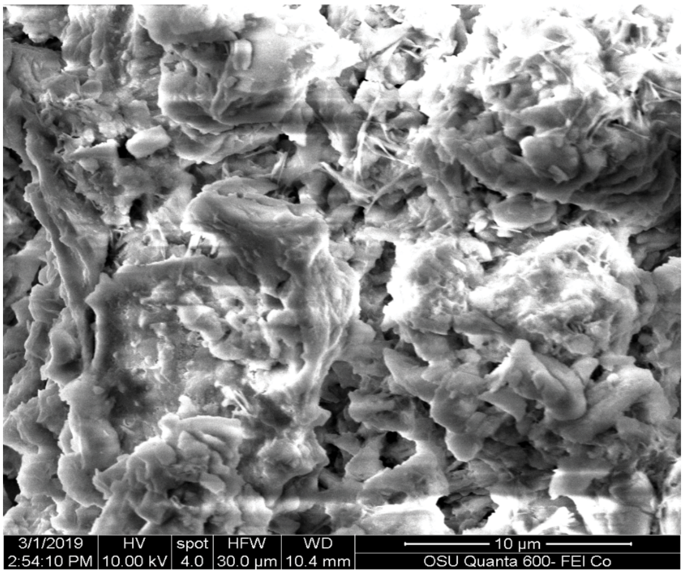

Figure 8. SEM image of CL1-1000°C.

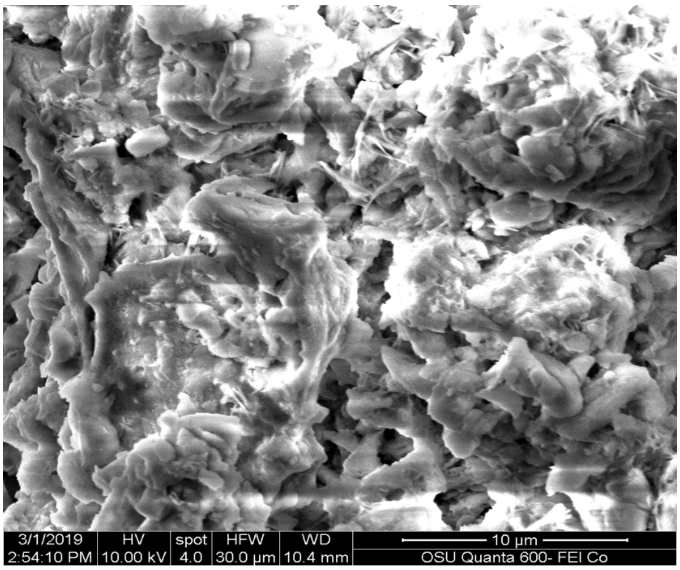

Figure 9. SEM image of CL2-1100°C.

addition to the main phases like C_3S, C_2S and C_3A was detected. C_4AF was found very low in RM1]. In addition to that, system like C_3S-CaF_2 and C_2S -CaF_2 were supposed to form. C_3S and C_2S were found in monoclinic phase. The SEM images of the obtained clinkers are shown in Figures 8, 9 and 10 in accordance with previous studies [15,16].

There are differences between the SEM images of the clinkers specimens.

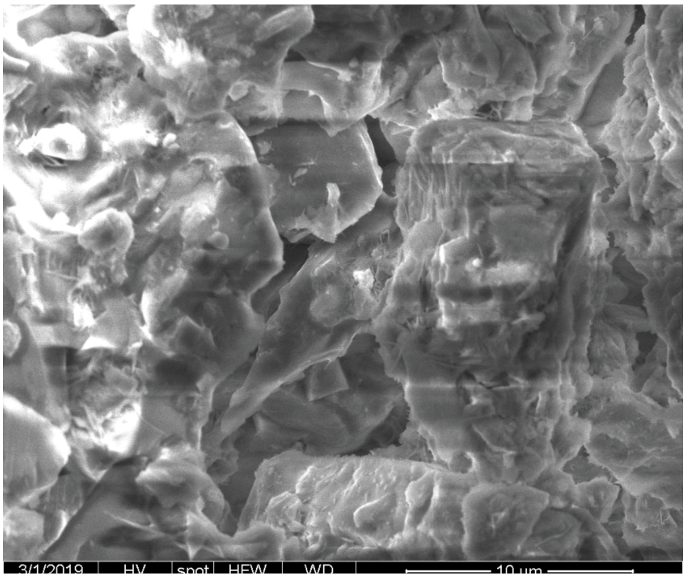

Figure 10. SEM image of CL3-1200°C.

Table 8. Mineralogical composition.

Clinkers	C_3S	C_2S	C_3A	C_4AF
CL1	42.2	28.4	19.0	0.4
CL2	37.8	34.4	16.6	5.5
CL3	31.3	37.9	13.0	12.6
CLPm	45.0	5.7	1.1	2.0
CLPM	79.7	29.8	14.9	16.5

Indeed, CL1 was obtained with the higher free lime content (1.9%), then CL2 (1.8%) and CL3 with the lowest one (0.4%). It was difficult to well define the shapes due to the presence of impurities and the poor crystallization. The mineralogical composition is shown in Table 8. Clinkers with high belite and aluminate contents were produced from the industrial waste materials on the one hand. On the other hand, the alite and ferrite contents were remarkably lower. This is due to the clinkerization process in presence of mineralizers and fluxes such as CaF_2, Na_2O, MgO, K_2O and P_2O_5 but also the high alumina and the low iron contents of the raw materials.

Conclusion

This study examined the manufacturing of cement clinker using waste materials of phosphoric acid production, wastewater treatment and coal fired power plants. Three varieties of clinker were obtained from 1000 to 1200°C with activation energies ranged from 42.7 to 91.1 and fluorine content from 0.82% to 3.9%. There was an important presence of both mineralizers (like CaF_2) and fluxes (like Na_2O, MgO, K_2O and P_2O_5) in the composition of the used industrial waste materials which contribute to decrease the melting point and the phases formation at lower temperatures. The XRF and XRD analyses highlighted interesting compositions as cement material. These alternative methods to produce cement dealt with resources conservation, energy efficiency and environmental protection. Replacing limestone or clay with these industrial waste materials can reduce the carbon footprint from calcination in cement industries up to 60% and the energy consumption up to 350 kcal/kg of clinker. Nonetheless, other physical tests such as setting time, compressive and flexural strength remain to be done in future work.

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