American-Eurasian Journal of Scientific Research 12 (1): 01-06, 2017
ISSN 1818-6785
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DOI: 10.5829/idosi.aejsr.2017.01.06

Use of a Fluoride Waste in the Raw Mix for Clinker Manufacturing

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Abstract: This study aims at using a mixture of calcium fluoride and calcium silicate (CFS), which is a by-product from the process of working-up aqueous fluosilicic acid solutions, in the raw mix for clinker manufacturing. The core objective is to lower the temperature of the buring process and to reduce the carbon dioxide emissions. The addition of 12.5% of this industrial waste which acts as a mineralizer reduced the temperature for clinker burning to 1373 K and the carbon dioxide emissions to about 30%. This reduction of temperature improved the clinkering process and conserved energy efficient. The obtained clinker with l.96% of free lime content could lead to an enhancement of the cement quality. Volumetric analysis of free lime content and X-ray fluorescence were used to characterize the synthesized clinker. The kinetic model of the burning processhighlighted an activation energy of 82.347 kJ/mol.

Key words: Calcium fluoride · Calcium silicate · Clinker · Fluoride waste · Raw mix.

INTRODUCTION

Fluosilicic acid (FSA) is a byproduct of phosphoric acid manufacturing. FSA is a clear liquid that, although can be used for water fluoridation, can also be manipulated into other more useful chemicals [1]. Presently, there is no waste treatment in place for the acid in Senegal. Instead, I.C.S. (*Industries chimiques du Senegal*) has been discharging it into the water body on the coast of the West African country[2]. It is important for the corporation to attempt to reduce the pollution of the Atlantic Ocean. Doing so will help to save the marine life and fishing industries in the country. The manipulation of this aqueous waste into more valuable chemicals such as the mixture of calcium fluoride and calcium silicate (CFS) [3] will create new chemical processes in industry.The research project works consisted on clinker manufacturing by using this by-product (CFS) in the raw mix. Experiments were carried out to discover a new clinkerization process. The fluoride acted as a mineralizer to decrease the temperature and the silicate as a replacement of limestone to reduce carbon dioxide emissions. Both compounds in a mixture could lead to processes which are environmentally friendly in cement manufacturing. Composition of raw materials was the main optimized parameter. In order to characterize it, the synthesized clinker was analyzed by X-ray fluorescence and volumetric dosage was used to determine the free lime content. The kinetics of the burning process was modelling to find out the activation energy in presence of CFS.

Theory: The phosphate ore mined is fluorapatite that has the chemical formula $Ca_{10}(PO_4)_6F_2$. The wet-process for the manufacture of phosphoric acid involves reacting this ore with concentrated sulfuric acid in the following reaction [4].

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$$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 + 2\ H_2O\ ?\ 10\ CaSO_4 \bullet 2\ H_2O + 6\ H_3PO_4 + 2\ HF \quad (1)$$

Phosphogypsum and hydrofluoric acid are both byproducts to the phosphoric acid process.

The hydrofluoric acid produced reacts with the less than 1% of silica contained in the phosphate rock in a side reaction[4].

$$4\ HF + SiO_2?\ SiF_4 + 2\ H_2O \quad (2)$$

The silicon tetrafluoride then reacts in a secondary side reaction through water absorption to produce fluosilicic acid[4].

$$3\ SiF_4 + 2\ H_2O\ ?\ 2\ H_2SiF_6 + SiO_2 \quad (3)$$

Elsewhere, phosphogypsum is a byproduct that can be useful in the manufacture of cement [5].

The fluosilicic acid obtained is that which must be studied. The treatment of this acid should result in a mixture of solids, calcium fluoride and calcium silicate, that can be used in the manufacturing of cement. Treating fluosilicic acid using some salts is a much more economically viable and environmentally safe alternative to discharging it into the Atlantic Ocean. This mixture of solids from the treatment would reduce the cost of heating the raw mix in cement processing and therefore reduce the cost of the process.

It is hypothesized that the expected products, calcium fluoride and calcium silicate, would then be very useful to the cement industry as a portion of the composition of manufactured cement.

Several different processes carried out during the last decades highlight advances on cement research and manufacturing [6]. These processes globally relate the nanotechnology of cement, the use of radiation energy, the clinkerization on fluidized bed and the use of mineralizers. Our research project focus on this last typical process and aims at using CFS which is a waste product containing calcium fluoride and calcium silicate in the raw mix for clinker manufacturing. Several articles relate clinker or cement manufacturing by using waste products [7]. Calcium fluorides or calcium silicates have a big influence on clinkerisation process [8]. A large number of substances offer mineralizing effect. Much research remains to be done, but it is estimated that mineralizers made by mixturing fluorspar (calcium fluoride) with another compounds appear to the most effective. The mineralizer effect of fluorspar in relation to the form of addition to an industrial raw mix [9] and the reduction of clinkerisation temperature by addition of salts containing fluorine were already studied [10]. The mixture of calcium fluoride and calcium silicate (CFS) which is generated by the manufacturing of caustic soda from sodium fluosilicate highlights an interesting composition of Portland cement constituents [11].

MATERIAL AND METHODS

Fluoride Waste Recovery and Treatment: The fluoride waste was recovered from a phosphoric acid plant in Senegal (ICS). As well known, the attack of phosphate rock by sulfuric acid lead to two main by-products (phosphogypsum and fluosilicic acid) [1]:

$$3CaF_2 + 3H_2SO_4 + 4H_2O + SiO_2 \rightarrow 3CaSO_4.2H_2O + H_2SiF_6 \quad (4)$$

The aqueous fluosilicic acid (H_2SiF_6 25wt%) was converted into sodium fluosilicate [1]:

$$H_2SiF_6 + 2NaCl \rightarrow 2HCl + Na_2SiF_6 \quad (5)$$

The sodium fluosilicate was used as a reactant with calcium hydroxide to obtain caustic soda and a precipitated mixture of calcium fluoride and calcium silicate (CFS) [2,3]:

$$Na_2SiF_6 + 4Ca(OH)_2 \rightarrow 2NaOH + 3CaF_2 + CaSiO_3 + 3H_2O \quad (6)$$

The precipitated mixture of calcium fluoride and calcium silicate (CFS) was separated from the aqueous solution of caustic soda and dried in MERMERT furnace (Fisher, Illkirch, France) at 378 K. The study on clinker manufacturing was done by using three raw materials: limestone, clay and CFS.

Raw materials: Table 1 show the different raw materials which were used for the burning process.

As it is shown in Table 1, limestone, clay and CFS (calcium fluoride and calcium silicate) were used as raw materials for this study. The limestone and the clay were extracted from a mine of SOCOCIM INUSTRIES in Senegal. The CFS was recovered from a process of caustification [2]. The raw materials were crushed by a RETSCH crusher and dried in MEMMERT furnace(Fisher, Illkirch, France) at 378 K.

Table 1: Chemical composition of raw materials (%wt)

Material	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	P_2O_5	SO_3	F^-	LOI
Limestone	50.32	4.76	1.23	0.96	0.11	0.08	0.05	0.43	0.00	0.00	39.77
Clay	28.76	27.08	5.74	2.24	4.53	0.47	0.11	0.43	0,00	0.00	30.21
CFS	37.90	7.40	0.02	0.01	0.48	0.07	6.16	0.00	0.02	48.00	0.00

Table 2: Raw mixes preparation (%wt)

Raw mix	CFS	Limestone	Clay
RM-1	2.5	56.0	41.5
RM-2	5.0	55.0	40.0
RM-3	7.5	54.0	38.5
RM-4	10.0	53.0	37.0
RM-5	12.5	52.0	35.5
RM-6	15.0	51.0	34.0
RM-7	17.5	50.0	32.5
RM-8	20.0	49.0	31.0

Table 3: Chemical composition of raw mixes (%wt)

Raw mix	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	P_2O_5	SO_3	F^-	LOI
RM-1	41.06	14.09	3.07	1.47	1.95	0.24	0.23	0.42	5E-04	1.20	34.81
RM-2	41.08	13.82	2.96	1.42	1.90	0.24	0.38	0.41	0.001	2.40	33.96
RM-3	41.09	13.55	2.88	1.38	1.84	0.23	0.53	0.40	0.002	3.60	33.11
RM-4	41.10	13.28	2.79	1.34	1.78	0.22	0.68	0.39	0.002	4.80	32.26
RM-5	41.11	13.01	2.68	1.30	1.73	0.22	0.84	0.38	0.003	6.00	31.40
RM-6	41.13	12.74	2.57	1.25	1.67	0.21	0.99	0.37	0.003	7.20	30.55
RM-7	41.14	12.48	2.48	1.21	1.62	0.21	1.14	0.35	0.004	8.40	29.70
RM-8	41.15	12.21	2.39	1.17	1.55	0.20	1.29	0.34	0.004	9.60	28.85

Burning Process: The raw materials (Table 1) were used for preparing the raw mixes (Table 2). This preparation was completely based on main oxides composition particularly calcium oxide as known by cement industries. The raw mixes (RM) were prepared according to the ratio CFS/RM. Eight samples (2.5%, 5%, 7.5%, 10%, 12.5%, 15%, 17.5% and 20% by weight) were ground to a fineness of 10% retained on 200 mesh.

The chemical composition of the raw mix (Table 3) was determined by calculations from the chemical composition of the raw materials (Table 1) and the raw mix preparation (Table 2).

After proper blending, the raw mixes were nodulised and fired on an alumina dish in a Carbolite OAF 11/1 furnace (Fisher, Illkirch, France). The temperature was setting from 1223 K to 1373 K for studying the burning process in presence of the CFS which acts as a mineralizer. In fact from literature, we known that the temperature of clinkerization can be reduce to 1423 K by using some mineralizers in the burning process [9]. For an innovative study, we suggested to limit the temperature to 1373 K. The obtained clinkers were analyzed to determine the burnability and the chemical composition. X-ray fluorescence studies were conducted using an ARL 9800 XP analyzer(Thermo ARL, Ecublens, Switzerland).The analyzed results were compared with the chemical composition of Portland clinker [12][13].

RESULTS AND DISCUSSIONS

Clinker Free Lime Content: The influence of CFS on the burning process was also studied by the determination of the free lime at 1373 K, as illustrated in Figure 1.

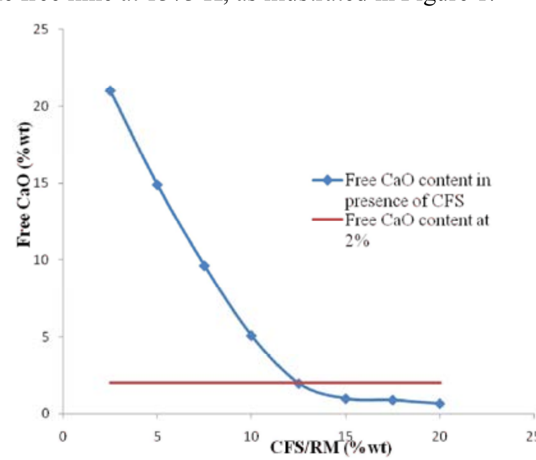

Fig. 1: Influence of CFS on the burning process at 1373 K

The free CaO content for Portland clinker manufacturing must be between 0.6% and 2.8% [13]. Nonetheless, the burnability is usually suitable when the free CaO content is about 2%. As it is shown by Figure 1, the obtained value of the free CaO was exactly 1.96% when a raw mix of a 12.5% CFS was used. The CFS which contents CaF_2 and $CaSiO_3$ completely influenced the burning process. Obviously, CaF_2 is well known as a mineralizer and $CaSiO_3$ is an essential composite medium which leads to the main oxides of clinker. In addition the use of $CaSiO_3$ in the raw mix favors the reduction of CO_2 emissions in clinker processing. Indeed, the CO_2 emissions is due to the high content of $CaCO_3$ in the raw mix (about 80%). By reducing the $CaCO_3$ content in the raw mix, the CO_2 emissions will significantly decrease.
The control of the burning process was handled by following the raise of the temperature from 1223 K to 1373 K. The results of this study are displayed in Figure 2.

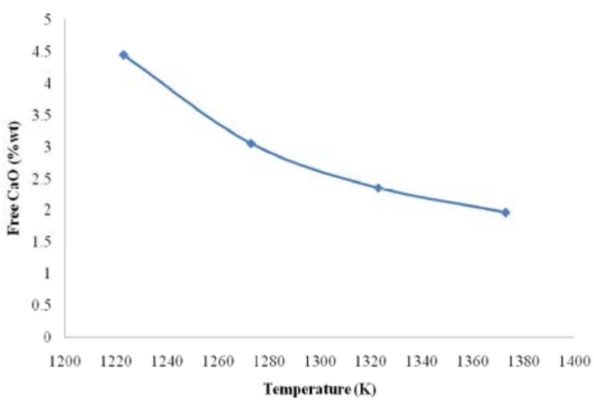

Fig. 2: Burning process with a 12.5% CFS content in the RM

These results highlight a fast decrease of the free lime content when the temperature increases due to the CFS content in the RM. Indeed, the CFS increases the velocity of the clinker formation by lowering the temperature of phases stability. This efficiency is due to the presence of F^- anion which favors the distortion and the rearrangement of the atoms to form new solids phases or create the solids melting at high temperatures.Elsewhere, the chemical compositionof CFS in melting compounds such as Na_2O let us better understanding its quality of minelizer which actives the C_3Sformation. A 2% free lime content is sufficient to obtain a good quality of clinker. At 1373 K the free lime content is less than2% (1.96%).

Modeling the Burning Process: The kinetic model can be described as an isothermal clinker formation [14, 15]. The free lime varies with temperature according to the Arrhenius law. A semi- empirical model which relays the free lime CaO_L content in the clinkeraccording to the CFS content x_{CFS} in the raw mix can be writtenas:

$$CaO_L = a\left(\frac{1}{x_{CFS}}\right)^c e^{-\frac{E_A}{RT}} \tag{7}$$

where:

a = 2.961a constant in the Arrhenius equation determined by calculations;

c = 1.837adimensionless coefficient determined by calculations;

E_A= 82.347 kJ/mol the activation energy of the burning process in presence of CFS determined by calculations

T is the temperature of clinkerization (1373K)

R is the the constant of ideal gases (8.31 $J.mol^{-1}.K^{-1}$)

The correlation between the experimental free lime content CaO_{Lexp} and the calculated free lime content from the semi-empirical model CaO_{Lmodel} is displayed in Figure 3.

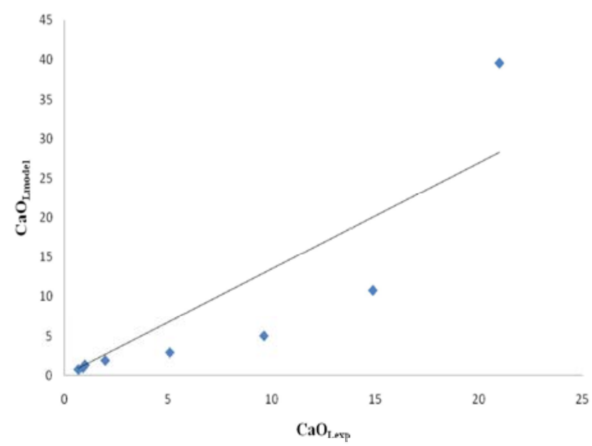

Fig. 3: Correlation between the experimental free lime content CaO_{Lexp} and the calculated free lime content from the semi-empirical model CaO_{Lmodel} at 1373 K

This correlation shows the efficiency of CFS in the activation of the burning process (E_A=82.347 kJ/mol). From litterature data for isothermal studies, the activation energy is more than 200 kJ/mol for temperatures higher than 1723 K. Nonetheless, the model is not consistent for high content of CFS at 1373 K. Therefore it is necessary to operate at temperatures higher than 1373 K ant reduce at the same time the CFS content in the raw mix.

Chemical Composition: Table 4 shows the chemical composition of clinker samples (CL).

Table 4: Chemical composition of the clinkers (%wt)

Clinker	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	P_2O_5	SO_3	F^-	LOI
CL-1	70.00	19.23	4.44	1.86	2.34	0.23	0.19	0.68	0.02	0.00	9.6
CL-2	69.00	20.08	4.41	1.80	2.53	0.17	0.33	0.65	0.02	1.7	3.42
CL-3	67.53	21.14	4.45	1.85	2.71	0.16	0.45	0.64	0.05	4.78	2.24
CL-4	65.25	22.42	4.62	1.91	3.28	0.16	0.72	0.57	0.05	5.6	0.79
CL-5	67.64	21.01	4.40	1.80	2.75	0.11	0.58	0.61	0.06	9.70	0.70
CL-6	68.84	21.48	4.45	1.78	2.99	0.08	0.76	0.57	0.04	10.7	0.08
CL-7	69.07	20.88	4.23	1.69	2.89	0.13	0.21	0.88	0.05	13.24	0.19
CL-8	69.53	19.79	3.91	1.58	2.77	0.16	0.02	1.16	0.06	17.1	0.22
CL-Pm	61.00	20.00	3.70	1.70	1.70	0.05	0.05	0.05	0.05	0.01	0.20
CL-PM	68.10	24.3	7.10	5.70	4.00	1.40	0.70	0.60	1.30	0.30	1.10

The analysis and the comparison highlight several interesting compositions for synthesized clinkers (CL). According to the free lime content the sample CL-5 seems to be more useful. In fact, for this sample, all the values of oxides content are respectful to clinker composition, only the fluor content is not beside the standard minimum and maximum values (CL-Pm and CL-PM) for Portland clinker manufacturing. It was foreseeable according to the amount of CFS in the raw mix. Otherwise the fluor could affect the mechanical properties of the obtained cement from this type of clinker.

CONCLUSION

From this study, a new type of mineralizer mainly composed of CaF_2 and $CaSiO_3$is found out. This type of mineralizer, CFS, can be useful on the burning process for Portland clinker manufacturing. Indeed CFS reduced the temperature of the burning process to 1373 K when a raw mix with a 12.5% of CFS content was used. Elsewhere the burning process lead to a clinker with a 1.96% of free CaO content.The kinetic model of the burning process highlighs an activation energy of 82.347 kJ/mol. Nevertheless, the obtained clinker had a high fluoride content.In order to limit the fluor content, the experiments will be carried out by increasing weakly the temperature of burning process and by operating with others samples of raw mix in order to obtain Portland clinker. However several studies remainto be done to make sure that the obtained cement from this clinker will be consistent with the standards of strengths.

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