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KINETIC MODELLING OF CEMENT RAW MIX CONTAINING IRON PARTICLES AND CLINKER MICROSTRUCTURE

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ABSTRACT

This paper investigated the oxidation of iron particles contained in cement raw mix using stationary electric furnace.

Results showed that oxidation kinetic of metallic particles in cement raw mix was limited by diffusion and occurred mainly in the transition zone. Complete oxidation of metallic particles in the raw mix can be achieved at about 800°C. This is about 400° lower than that of abrasive slurry. The presence of CaO enhances the oxidation of metallic particles in raw mix. When used as raw mix component, abrasive slurry containing high metallic particles content can significantly influence the clinker minerals chemical composition, morphology and phases ratio. This is due to increased probability of localized high Fe_2O_3 concentration and consequently increased acidity of the liquid phase.

Introduction

The need to find new iron oxide containing by-product or deposit that can complement or even replace the presently used but scarce iron pyrite has necessitated this present research.

During oxidation of iron in air, the growth rate of the oxide coating depends on the rate of oxygen diffusion and the porosity of the oxide crystalline structure (1). In reducing or oxidizing conditions, iron in their oxides can have valencies of 0 to 3 or 3 respectively (2). During sintering of cement raw mix, iron oxides react mainly with calcium aluminoferrite (2,3,4). Calcium aluminoferrite solid solutions in reducing atmosphere are quite unstable, experiencing the reduction of Fe^{3+} to Fe^{2+} or Fe and consequently the structural deformation of the crystalline matrix (5).

Various researchers showed that alite is very unstable in a slightly reducing atmosphere (6,7). Its stability decreases with increase in Fe_2O_3 content. Slow cooling in oxidizing condition results in the transition of Fe^{2+} to Fe^{3+}, dissociation of alite to $2CaO.SiO_2$ and $2CaO.Fe_2O_3$ and consequently the disintegration of the clinker lumps due to polymorphism of $\beta\text{-}C_2S \rightarrow \gamma\text{-}C_2S$. The influence of Fe_2O_3 on clinker formation mechanism depends on its quantity in alite, belite and calcium aluminoferrite solid solutions. The stability of these compounds depend on the homogeneity of the raw mix, ratio of reacting compounds, rate of cooling, etc.

TABLE 1
Composition of Cement Raw Mix

Samples	Raw materials							
	$CaCO_3$	Al_2O_3	Abrasive	Lime Stone	Open Hearth Slag	Sand	Clay	Iron Pyrite
1			100					
2	45.0	13.9	41.1					
3				72.0			26.0	2.0
4			3.7	79.7	7.6	9.0		
5			5.0	82.0		13.0		
6			6.6	79.6	6.8	9.0		

The presence of liquid phase has been found to have a strong influence on the rate of formation of clinker mineral C_3S. The effect of the liquid phase has been investigated by christensen and Jespen (8), Mackenzie and Hadipour (9), and Jawed and associates (10).

In earlier research using IR-spectroscopy, it was observed that the shifts in and intensification of the absorption bands 648 to 656cm^{-1} (Fe - O, Al - O), 918 to 923cm^{-1} (Si - O, alite), 840 to 844cm^{-1} (Si - O, belite) with increasing burning time and quantity of abrasive slurry, were mainly due to increased Fe_2O_3 content in the clinker minerals (12). This research is aimed at investigating the oxidation of iron particles present in cement raw mix and its influence on clinker minerals.

Experiment

Abrasive slurry is a by-product of the machine building industry. It consist of 50 - 60% metallic particles, 22 - 26% liquid coolant and 18 - 22% abrasive (electrocorundum and ceramic binder). The chemical composition of abrasive slurry is, mass %: 3.02 SiO_2, 0.66 MnO, 27.0 Al_2O_3, 4.34 Fe_2O_3, 6.72 FeO, O.1 MgO, 1.82 Cr_2O_3, 0.42 TiO_2, 1.02 (Na_2O + K_2O) depending on the atmospheric condition and age. The granulometric composition is, mass %: 0 - 0.12mm 48 - 80, 0.2 - 1mm 20 to 29 and above 1mm the remainder.

The Fe content was determined as follows: to 0.5 - 1g of the averaged sample in a beaker was added 150 - 200ml $CuSO_4$ solution, diluted with water to 500ml and boiled for 25 - 30 min.

$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu;$$

the hot solution was then filtered, decanted and diluted to 100ml; 7ml H_2SO_4 and 10 granules of aluminum chips were added to the filterate and the solution observed until it becomes colourless

$$3CuSO_4 + 2Al \rightarrow Al_2(SO_4)_3 + Cu;$$

the beaker was then cooled in water and filtered ; 30ml of the filterate was immediately titrated with 0.05M $KMnO_4$ solution until a stable colouration was maintained within 30 sec.

Other chemical analyses were conducted according to (8). Experiments were conducted using samples presented in Table 1. Investigation of metallic iron oxidation process in abra-

TABLE 2
Oxidation of Metallic Particles in Abrasive Slurry During Isochrome Condition

Burning Temperature °C	Iron Content Fe, mass %	Extent of oxidation %
20	41.0	0
200	37.6	8.3
400	34.4	16.1
600	11.6	71.5
1000	9.2	77.6
1200	3.2	92.9
1400	0.2	99.5

sive slurry was performed using samples burnt at 200 to 1400°C with residence time at maximum temperature of 20 min. Samples were burnt also at 500, 600 and 1000°C for 15 to 60 min. All samples were burnt in an electric furnace using silicon heaters. The products were analysed using the differential thermal analyzer (DTA) and X-ray method. Samples 2 to 5 were thoroughly mixed, ground in vibromill, granulated at moisture content of 30% and burnt at their respective temperature and corresponding residence time. Samples 5 and 6 were additionally examined using optical microscopy.

Results and Discussion

The chemical analyses of the samples burnt at various temperature and corresponding residence time are presented in Table 2 to 7.

Table 2 showed that the oxidation of iron particles in abrasive slurry took place mainly between 500 - 600°C and was almost complete at 1200°C. Results in Table 3 showed that the process kinetic mainly depended on the burning temperature.

In Table 4 are presented results of chemical analyses of clinker produced at 1400°C at residence time of 30 min.

TABLE 3
Oxidation of Metallic Particles in Abrasive Slurry During Isothermal Condition

Burning Temperature °C	Residence time min.	Fe Content mass %	Extent of oxidation, %
500	0	33.5	0
	15	30.1	10.1
	30	29.8	11.1
	45	25.5	23.9
	60	24.1	28.1
600	0	12.7	0
	15	12.0	5.5
	30	11.9	6.3
	45	11.7	7.8
	60	11.6	8.6
1000	0	9.7	0
	15	0.4	95.6
	30	0.3	96.7
	60	0.1	98.9

TABLE 4
Chemical Composition of Cement Clinker

Sample	Oxide content, mass %			
	CaO	Fe_2O_3	Al_2O_3	SiO_2
3	64.00	7.31	5.43	22.5
4	63.00	11.00	3.60	20.40
5	62.87	12.10	1.83	23.20
6	58.60	17.40	3.80	20.20

It was observed from Table 2 that intensive oxidation of iron particles began at about 400°C, but was greatly retarded at 600°C. Calculations using the formula:

$$x = 1 - e^{-kt^n}$$

expressed in the logarithm form as

$$\log(-\log(1 - x) = K + n\log t$$

where $K = \log k + \log(\log e)$,

x - fraction of reacted iron particle,
t - isothermal residence time, min.
n - factor characterising the reaction front growth,

showed that the rate of oxidation at 500°C was significantly dependent on the residence time. At 600°C, the $\log\{-\log(1-x)\}$ versus t relation was a straigth line with gradient $n \approx 0.5$, a characteristic of diffusion controlled process. With increase in temperature, calculated n values showed that the oxidation process occurred mainly in the transition zone.

Results of chemical analyses in Table 5 and 6 of synthetic sample 2, showed that burning temperature and not time should be considered as the main limiting factor of the oxidation process. This is the characteristic of diffusion controlled process. Analyses using the above formula showed that oxidation of iron particles occurred mainly in the transition zone.

DTA of samples 1 and 2 showed that intensive oxidation of iron particles began at 450 and 500°C and ended at 905 and 760°C respectively. X-ray diagrams of sample 1, burnt at 400, 600 and 1000°C showed a continuous fall in peaks intensities characterising metallic iron (d = 0.202, 0.173nm etc.) and increase for those of Fe_2O_3 (d = 0.269, 0.254nm etc.) with increasing temperature. Remarkable changes in intensities were observed between 400 and 600°C (Fig.1).

TABLE 5
Oxidation of Metallic Particles in Synthetic Mix During Isochrone Condition

Burning Temperature °C	Fe mass %	Extent of odixation %
0	11.2	0
200	9.8	12.5
500	5.9	54.4
800	0.4	96.4
1200	0.3	97.3

TABLE 6
Oxidation of Metallic Particles in Synthetic Mix During Isothermal Condition

Burning Temperature °C	Residence time, min.	Fe mass %	Extent of oxidation, %
500	0	4.1	0
	15	3.7	8.7
	30	3.62	11.7
	45	3.48	15.1
	60	2.39	58.3
1000	0	0.96	0
	15	0.25	73.9
	30	0.20	79.2
	45	0.17	82.3
	60	0.11	88.6

Comparative analyses of X-ray diagrams of synthetic sample 2 (Fig. 2) and 1 (Fig. 1), showed that at 600°C the major iron peak d = 0.202nm was drastically reduced in sample 2. The presence of CaO and consequently the formation of calcium ferrite, could have enhanced the oxidation of the iron particles (Fig. 2). From the experimental results, it is expected that oxidation of metallic particles in the synthetic mix will be completed at about 800°C.

Chemical analyses of samples 4 and 5 showed that after 1000°C only insignificant increases in extent of oxidation were observed (Table 7).

No increase in the Fe or FeO content was observed, even at 1400°C. Therefore oxidation of Fe in the raw mix was not influenced by the reducing atmosphere in the furnace. Consequently, reduction of Fe_2O_3 to FeO or Fe observed in laboratory condition by (5), can be considered as one of the factors responsible for the dissociation of clinker minerals.

Optical photographs of sample 5 burnt at 1420°C show that the alite crystals were exceptionally long when compared with standard alite (sample 3). The presence of 3.8 mass % free CaO in the sinter 5, despite the high Fe_2O_3 content indicate that the iron oxide was localized in the raw mix (Fig. 3). At 1380°C, belite crystals were the dominant phase. For sample 6, increase in burning temperature led to the alite and belite loosing their characteris-

TABLE 7
Oxidation of Metallic Particles in Samples 4 and 5

Temperature °C	Content of Fe	mass % FeO	Extent of Fe Oxidation, %	Content of Fe	mass % FeO	Extent of of Fe Oxidation %
0	3.0	3.04	0	4.2	6.1	0
200	2.6	1.60	13.3	3.8	3.5	9.5
400	1.6	1.07	46.6	2.3	2.8	45.3
600	0.2	-	93.3	0.4	0.7	90.4
1000	0.1	-	96.6	0.2	-	95.2
1200	0.1	-	96.6	0.2	-	95.2
1400	0.1	-	98.3	0.1	-	97.6

No increase in the Fe or FeO content was observed, even at 1400°C. Therefore oxidation of Fe in the raw mix was not influenced by the reducing atmosphere in the furnace. Consequently, reduction of Fe_2O_3 to FeO or Fe observed in laboratory condition by (5), can be considered as one of the factors responsible for the dissociation of clinker minerals.

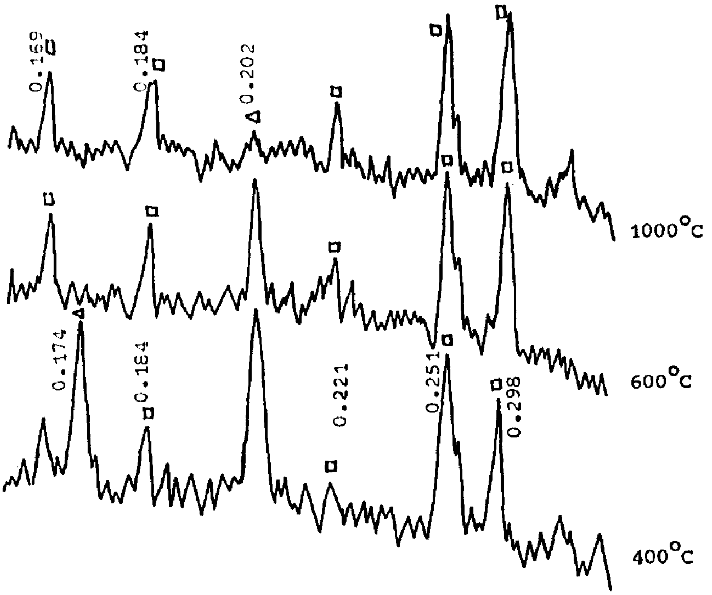

FIG. 1.
X-ray diagram of abrasive slurry burnt at 400, 600 and 1000°C. Key: Δ - Fe, ☐ - Fe_2O_3.

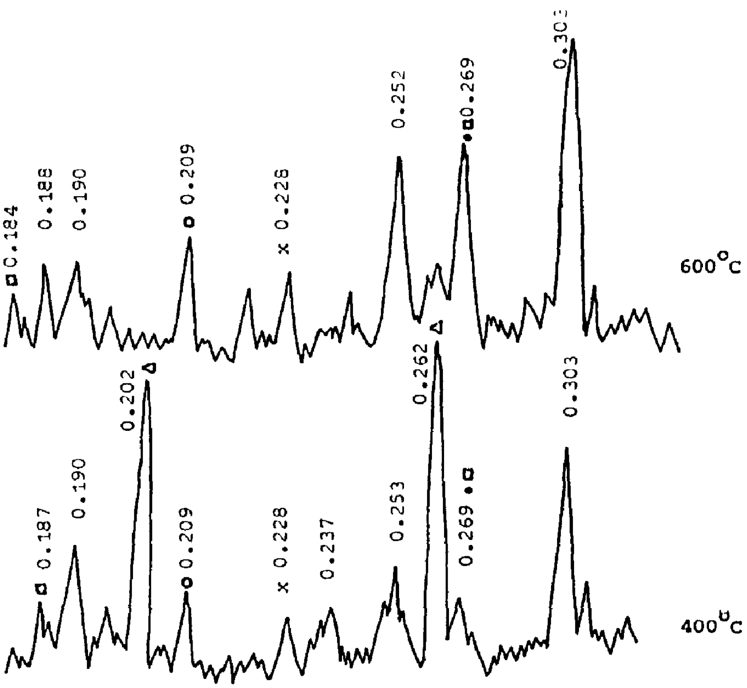

FIG. 2.
X-ray diagrams of sample 2 burnt at 400 and 600°C. Key: Δ - Fe, O - Al_2O_3, ☐ - Fe_2O_3, x - $CaCO_3$, ● - C_2F.

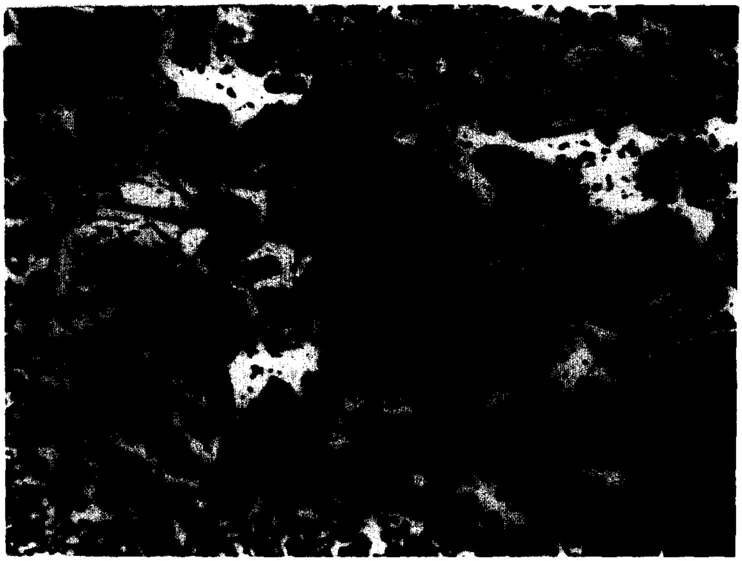

FIG. 3.
Optical photograph of sample 5 burnt at 1420°C.

tic forms (Fig. 4). Observed deviations in the crystal sizes, high distortion in the clinker minerals morphology and dissolution or disintegration of the individual minerals could be

FIG. 4.
Optical photograph of sample 6 burnt at 1420°C.

directly linked to ineffective homogenisation of the high Fe_2O_3 content and consequently the liquid phase and increased acidity of the liquid medium.

Conclusion

Oxidation kinetics of finely dispersed metallic particles in cement raw mix are limited by diffusion and occurred mainly in the transition zone. Complete oxidation of the metallic particles in cement raw mix is expected to take place at about 800°C. This is about 400°C lower than that of abrasive slurry. The presence of CaO enhances the oxidation of metallic particles. When used as a raw mix component, abrasive slurry containing high metallic particles content can significantly influence the clinker mineral chemical composition, morphology and phase ratio. This is due to the increased acidity of the liquid phase.

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