Comparison of clinker characteristics including the heavy metal concentration with and without the use of alternative fuels

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Abstract: For economic and environmental reasons, many of the cement industries are increasingly utilizing industrial waste products and alternate fuels during clinkerisation. Considering the ingress of heavy metals during such incorporations it is important to assess their impact on clinker quality. Present paper attempts to assess the impact of wastes containing metal oxides like Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ba and Pb on industrial clinker characteristics by examining clinkers from around 17 clinkerisation units, with and without use of such materials. The parameters which are emphasized during comparison include the composition of silicate phases, speciation and distribution of heavy metals especially incorporated in silicate phases and matrix, their influence on texture and microstructure and Bond work index of clinker evaluated using SEM - EDX and optical microscopy. CaO/SiO_2 molar ratio in examined clinkers is found to be varying in the range of 2.78 – 3.11 in alite and 2.07 -2.41 in belite phase. Belite is observed to be getting enriched preferentially in terms of low-volatile heavy metals like Cu, Zn, Ba and Pb. High volatile metals like Na, K and S, on other hand, are found to be getting concentrated around alite crystals. Metals like Sc, Ti, V, Cr, Mn, Ni, Co, and Pb are found to be homogeneously distributed in silicates as well as in matrix. However, the inclusion of these metals in the clinker is found to be having a negligible influence on the phase proportions and microstructure of the examined industrial clinkers.
Keywords: Clinker, metal concentration, alternative fuel.

Introduction

Some of the more traditional fuels used in the cement industry are fossil fuel, petroleum coke, natural gas, furnace oil, and other type of coals. However, due to the potentially environmentally friendly aspect, in combination with the possibility of a substantial decrease in cost, the cement industry is increasingly turning to alternative fuels. Some typical alternative fuels used are agriculture waste, tyre chips, municipal solid waste, saw dust, paint sludge, textile waste, etc. which may replace some of the traditional fuels (Bhatty, 2004) mentioned above. These fuels enriched in heavy metals, are the non-combustible product that may change the clinkering reaction and modify the chemical composition, structure and texture of the silicate and interstitial phases and may impact the hydration and setting behavior of cement, the durability of concrete (Amin et al., 2006) and also grindability of clinker. So it is very important to examine the heavy metal concentration in the clinker phases and their effect. This paper deals with the study of the chemical composition of individual clinker phases, their grain characteristics, inter-relation, and distribution of grains and heavy metals in the clinker.

Experimental Materials

The clinkers used in this work have been collected from 17 different production units located in India designated as C1 to C17. In C1 to C7 clinkers, around 0.5 to 2.0% of alternative fuels were used by replacing coal and in C8 to C17, a combination of coal and petroleum coke was used. The clinkers were characterized by OM, ESEM/ EDX, XRD, and XRF to know the quantity of heavy metals, phase percentage, and development of microstructure.

Preparation of samples

All the clinkers were crushed to 5mm to make representative samples after coning and quartering. The samples have been subjected to vacuum impregnation to fill up the pores. The impregnated mould was ground initially with diamond abrasive paper to get a fairly smooth surface. Further fine grinding was done with 240,360,600 and 800 carbimet papers. The etching was performed with HF vapor for the sample taken for structural study. The grain size distribution and phase quantification were done using image analysis software in line with ASTM C-1356M. The same polished clinker samples have been directly observed in ESEM without any deformation using a back-scatter detector with variable pressure by keeping a working distance of 8.5mm, EHT 20 kv, and probe current 250 pA. As per Harrison's technique (Harssion, 2008) X-ray spectra were collected from individual crystals in the samples by positioning the electron beam over the crystal to be analyzed and stopping the scan so that x- rays were collected from a limited volume of each crystal generated by the interaction of the stationary beam with the surface region. Quantitative analysis were carried out by comparison of the energy dispersive spectrum obtained from the crystals with a set of standard spectra collected under the identical condition from reference materials of known composition. Around 30 spot analysis of each crystal were conducted and an average composition of crystals is reported. This approach provided an indication of the spread of composition within each crystal type.

Phase composition, Microstructure and Clinker Quality

Chemical composition of silicate phases in their process of formation

The four principal phases identified as constituents of clinkers are C 3S, C2S, C3A, and C4Af. But these don’t exist in pure form in industrial clinkers. Industrial clinkers are always contaminated by minor and heavy metals like K, Cr, Ti, Mn, Pb, Cu, and Zn, etc. in solid solution. The most widely accepted composition of the four major clinker minerals, are alite, belite, ferrite and aluminate. The chemical composition of alite and belite are - alite: Ca106 Mg2 (Na1/4 Fe1/2) O36 (Al2 Si34 O144) belite: Ca87 Mg Al Fe (Na1/2 K1/2) (Al3 Si4 O180) Jeffery gave the formula of alite as 54CaO.MgO.Al2O3.16SiO2, where as Yamaguchi and Takagi (Yamaguchi et al., 1969) suggested Ca104Mg2A1(Na1/4K1/4Fe1/2)O36 (Al2Si35O144). Midgley observed that the alite formula can be represented based on the clinkers studied by him as Ca105.54 Fe1.43Al1.92 Na0.80 K0.18 Mn0.02 Ti0.11 Si34.84 O180. Although Midgley detected the presence of a few other trace elements, he observed that Mg, Al and Fe are present as important additions in Alite. Kristmann found that in coexisting alites and belites S, Na, K, Fe are incorporated mainly in belite and Mg in alite. Aluminium can be incorporated both in alites and belites. Similarly, in belite Yamaguchi and Takagi gave the formula as Ca85 Mg Al2 Fe (Na1/2 K1/2) (Al2Si43O180). According to Midgley, the average molar composition of belite can be represented by Na2O0.008, K2O0.008 MgO0.010, TiO2 20.002, Al2O3+Fe2O3 0.026. Taylor suggested a typical chemical composition of alite and belite in Portland cement clinker (wt %) as given in Table 1.

Table 1. Chemical composition of alite and belite suggested by Taylor (Wt%).

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Mn_2O_3	Fe_2O_3
Alite	0.1	1.1	1	25.2	0.1	0.1	0.1	71.6	0	0	0.7
Belite		0.5	2.1	31.5	0.1	0.2	0.9	63.5	0.2	0	0.9

The phase composition of alite and belite of C1 to C17 clinkers are recorded in Table 2. It is observed that there is wide variation in chemical composition of silicate phases compared to Taylors value, this may be due to change in fuel and raw material quality and process upgradation.

Table 2. Chemical Composition of alite and belite in C1 to C17 Clinker (Wt%).

Clk	phase	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	TiO_2	C/S	Imp %
C1	Alite	68.6	24	2.34	2.49	0.9	0.06	0.23	0.6	0.41	3.0	7.04
	Belite	62	29.8	2.09	2.27	0.34	0.08	0.5	1.3	0.27	2.2	6.89
C2	Alite	68.7	23.8	2.11	2.39	0.89	0.12	0.13	0.7	0.33	3.0	6.63
	Belite	62	29.5	1.92	2.09	0.44	0.23	0.3	1.5	0.45	2.2	7.03
C3	Alite	68.9	23.8	1.74	2.07	0.79	0.07	0.15	0.5	0.17	3.1	5.48
	Belite	61.5	29.7	2.18	2.16	0.44	0.19	0.6	1.8	0.33	2.2	7.66
C4	Alite	68.8	23.8	2.19	1.87	0.63	0.04	0.1	0.8	0.41	3.9	6.06
	Belite	62.1	27.5	2.66	2.3	0.45	0.15	0.4	1.9	0.57	2.4	8.48
C5	Alite	68.4	23.5	2.37	2.25	0.6	0.02	0.3	1.1	0.48	3.1	7.18
	Belite	62.7	27.1	2.68	2.1	0.46	0.14	0.5	2.3	0.66	2.4	8.84
C6	Alite	68.4	23.7	3.13	2.43	0.9	0.02	0.1	0.1	0.37	3.9	7.15
	Belite	62.2	30.1	2.54	2.23	0.51	0.08	0.4	0.3	0.59	2.2	6.78
C7	Alite	66.9	23.8	2.74	2.32	0.82	0.15	0.4	1.1	0.19	3.1	7.71
	Belite	61.5	30.6	2.14	2.11	0.38	0.14	0.4	1	0.2	2.1	6.4
C8	Alite	67.7	25.5	2.73	1.52	0.62	0.06	0	0.3	0.38	2.8	5.67

	Belite	61.3	30.4	2.35	2.41	0.56	0.28	0.3	0.6	0.37	2.1	6.92
C9	Alite	68	25.9	2.26	1.73	0.86	0.04	0.1	0.1	0.34	2.8	5.48
	Belite	61.3	31.8	2.28	2.04	0.54	0.08	0.5	0.2	0.41	2.0	6.06
C10	Alite	69	24.8	2.16	1.82	0.69	0.02	0.1	0.4	0.23	2.9	5.38
	Belite	62.4	29	2.48	2	0.56	0.16	0.3	1	0.19	2.3	6.8
C11	Alite	68.5	24.9	2.3	1.93	0.74	0.08	0.1	0.4	0.28	2.9	5.87
	Belite	61.8	30.1	2.34	2.01	0.49	0.21	0.4	1	0.48	2.2	6.88
C12	Alite	68.2	25.5	2.12	1.26	0.85	0.04	0.3	0.6	0.27	2.8	5.49
	Belite	61.6	29.7	2.04	2.05	1.17	0.05	0.3	1.1	0.23	2.2	6.94
C13	Alite	67.6	26	2.06	1.66	0.65	0.02	0.2	0.5	0.2	2.7	5.32
	Belite	61.1	30.9	2.23	1.71	1.17	0.04	0.4	1.7	0.25	2.1	7.5
C14	Alite	67.7	25.6	2.22	1.89	0.81	0.08	0.1	0.4	0.37	2.8	5.88
	Belite	61	31.1	2.22	2.15	0.69	0.05	0.4	1	0.42	2.1	6.94
C15	Alite	67.4	25.7	2.16	1.95	0.8	0.09	0.1	0.4	0.3	2.8	5.84
	Belite	61.5	30.5	2.15	2.1	0.5	0.25	0.3	0.9	0.47	2.1	6.76
C16	Alite	67.1	25.7	2.2	1.74	0.82	0.12	0.1	0.8	0.36	2.8	6.19
	Belite	61.8	30	2.25	2.05	0.69	0.3	0.3	1	0.34	2.2	6.92
C17	Alite	67.4	25.4	1.99	1.79	0.92	0.14	0.2	0.1	0.28	2.8	5.44
	Belite	61	31.5	1.51	1.72	1.74	0.24	0.6	0.3	0.29	2.0	6.38

The impurity levels found in alite is 5.48 - 7.71% and belite 6.4 - 8.4% in C1 to C7 clinker, while in C8 to C17 clinker impurity in alite is 5.32 - 6.19% and in belite 6.06 -7.50 %. The distribution of impurities in C1 to C7 clinker is not uniform in both silicate phases and higher in quantity. Taylor mentioned minimum impurity level in alite is 3.2% and 5.1 % in belite. But the examined value in both set of clinker is slightly higher than the Taylors value; this may be is due to greater content of Fe2O3, Al2O3 and heavy metals present in the clinker. Stoichiometrically C/S molar ratio in alite is 3.0 and in belite are 2.0. But the examined molar ratio of C1 to C7 clinker varies from 3.01 to 3.11, which makes its crystal lattice more susceptible to impurities. In C8 to C17 clinker, the molar ratio value varies from 2.80 - 2.98%. Belite crystals are more uniform in composition than alite crystals. In all examined clinkers. C/S ratio in belite is higher than the stochiometric value (2.0) and amounts to 2.07 to 2.48. The increase in impurity level and C/S molar ratio in the clinker is due to different chemical composition of fuel, their dispersity and burning conditions in the clinkerisation process. One of the most interesting findings observed in all clinker is that the chemical composition has directly affected the shape of belite crystals. If the belite crystal is round in shape, C/S is around 2.0 to 2.03 while if it is sub-round in shape, the ratio is more than the stochiometric value (2.0).

Heavy Metal concentration in Silicate phases and their effect

Bhatty (2004) reported that Sc, Cr, V, Mn, Ni, CO, Cu, Zn, Ba, and Pb are volatile in nature mainly coming from alternative fuels, coal and raw materials. These are generally incorporated into the clinker when introduced into the kiln system. Such compounds may modify the temperature of the first liquid phase formation and /or the amount of melt, change the rate of reactions occurring in the solid state within the liquid phase or at the liquid-solid interface, alter the viscosity and surface tension of the melt and affect both crystal growth and morphology.

In our investigation, the oxides of heavy metal detected in silicate phase are Sc, Cr, V, Mn, Ni, Co, Cu, Zn, Ba and Pb, of course, not all are necessarily present in every crystal. Metals like Cr, V, Mn, Ni, Co are homogeneously distributed in silicate and matrix phases. The concentration of heavy metals in alite is 0.25 to 1.61 and the quantity of heavy metals is more in C1 to C7 clinker. Metal oxides like Cu, Zn, Ba and Pb are not detected in alite phases. The presence of heavy metals in C8 to C17 clinker is in trace amounts, so it has not affected the chemistry and microstructure of clinker. Similarly, heavy metal concentration in belite is around 0.41 to 1.64, while oxides like Cu, Zn, Pb, Ba and Pb are mainly entrapped in to the belite phases. The bond index of C1 to C7 clinker is increased as compared to C8 to C17 clinker. Keeping this view in mind, a regression analysis was done against heavy metals in alite and belite versus bond index of clinker. A strong correlation has been observed between concentrations of ZnO in belite vs. Bond index of clinker (Fig. 1). It is found that the bond index of clinker increased with an increase in ZnO%. The heavy metal oxide concentration in silicate phases are recorded in Table 3.

Table 3. Heavy metal concentration in alite and belite crystals (Wt%).

Clk	phase	Sc	Cr_2O_3	V_2O_5	MnO	NiO	CO	CuO	ZnO	BaO	PbO	BI
C1	Alite	0	0.05	0.02	0.13	0	0	0	0	0	0	13.9
	Belite	0	0.03	0.05	0.09	0.1	0.1	0.03	0.14	0.61	0.16	
C2	Alite	0	0.06	0.15	0.12	0.1	0.1	0	0	0	0	15
	Belite	0	0.1	0.09	0.12	0.1	0.1	0.15	0.26	0.38	0.18	
C3	Alite	1.1	0.11	0.12	0.09	0.1	0.1	0	0	0	0	14.2
	Belite	0.1	0.09	0.08	0.05	0	0.1	0.05	0.18	0.16	0.04	
C4	Alite	0.8	0.07	0.04	0.05	0.1	0.1	0	0	0	0	12.2
	Belite	0.6	0.06	0.06	0.09	0.1	0.1	0.04	0.09	0.4	0.18	
C5	Alite	0.5	0.06	0.05	0.04	0	0	0	0	0	0	12.8
	Belite	0.2	0.05	0	0.08	0.1	0.1	0.11	0.11	0.16	0.13	
C6	Alite	0.2	0.12	0.04	0.08	0.1	0	0	0	0	0	10.3
	Belite	0.3	0.1	0.05	0.05	0.1	0.1	0.06	0.05	0.06	0.04	
C7	Alite	0.7	0	0.04	0.11	0.1	0	0	0	0	0	14.3
	Belite	0.4	0.06	0.12	0.06	0.2	0	0.11	0.21	0.02	0.11	
C8	Alite	0.7	0.05	0.01	0.07	0.1	0	0	0.02	0	0	12.4
	Belite	0.6	0.04	0.05	0.08	0.1	0	0.04	0.07	0	0.12	
C9	Alite	0.2	0.08	0.04	0.08	0	0	0.03	0	0	0	10.5
	Belite	0.1	0.06	0.1	0.09	0.1	0	0.05	0.04	0	0.08	
C10	Alite	0.3	0.03	0.05	0.05	0.1	0	0.01	0	0.02	0	11.9
	Belite	0.2	0.05	0.03	0.03	0.1	0.1	0	0	0.64	0.04	
C11	Alite	0.2	0.03	0.02	0.05	0.1	0.1	0	0	0.11	0	11.3
	Belite	0.1	0.06	0.06	0.03	0.1	0.1	0	0.03	0.59	0	
C12	Alite	0.5	0.06	0.04	0.02	0.1	0.1	0	0	0.01	0	12.6
	Belite	0.5	0.09	0.03	0.02	0	0	0.04	0	0.1	0	
C13	Alite	0.7	0.06	0.05	0.06	0.1	0	0.01	0	0	0	12.8
	Belite	0	0.08	0.07	0.06	0.1	0	0.04	0	0.06	0	
C14	Alite	0.4		0.03	0.04	0.1	0.1	0.01	0.01	0	0	11.7
	Belite	0.4		0.03	0.05	0.1	0	0.06	0.02	0.08	0.1	
C15	Alite	0.4		0.03	0.03	0	0.1	0.03	0	0	0	11.3
	Belite	0.4		0.02	0.01	0	0	0.05	0.06	0.44	0.08	
C16	Alite	0.7		0.02	0.04	0.1	0	0	0	0	0	11.1
	Belite	0.4		0.06	0.05	0	0.1	0.04	0.02	0.31	0.08	
C17	Alite	0.8		0.04	0.03	0.1	0	0	0	0	0	ND
	Belite	0.8		0.03	0.05	0	0	0.05	0.07	0.01	0.02	

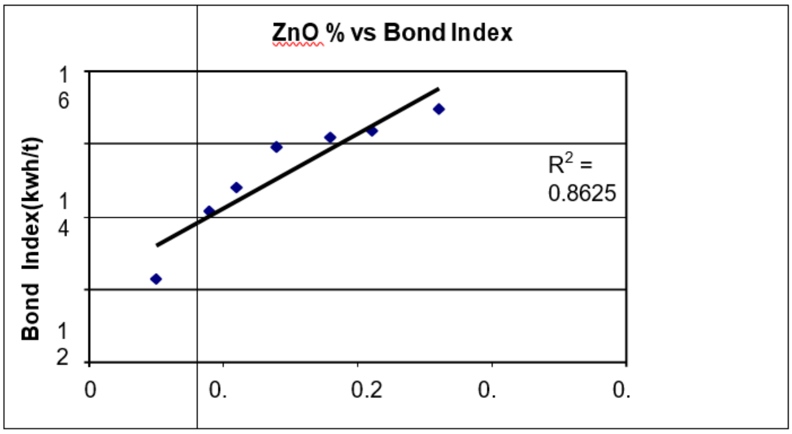


Fig. 1. Correlation between ZnO% vs Bond Index.

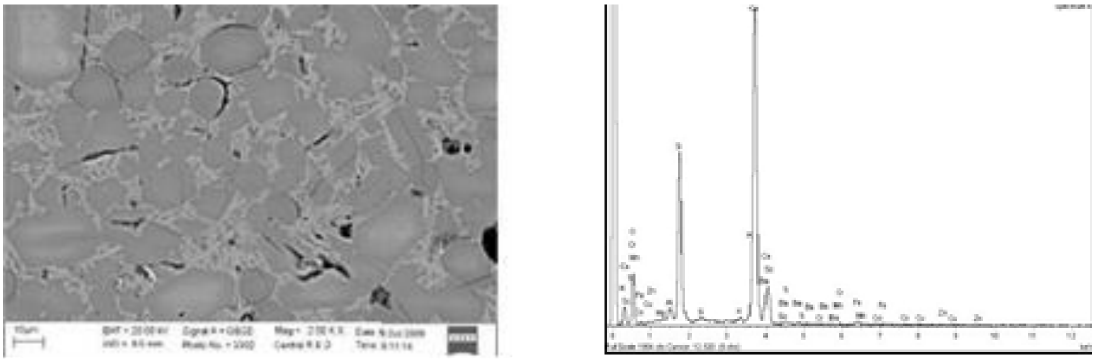


Fig. 2. Microanalysis of Alite Crystal.

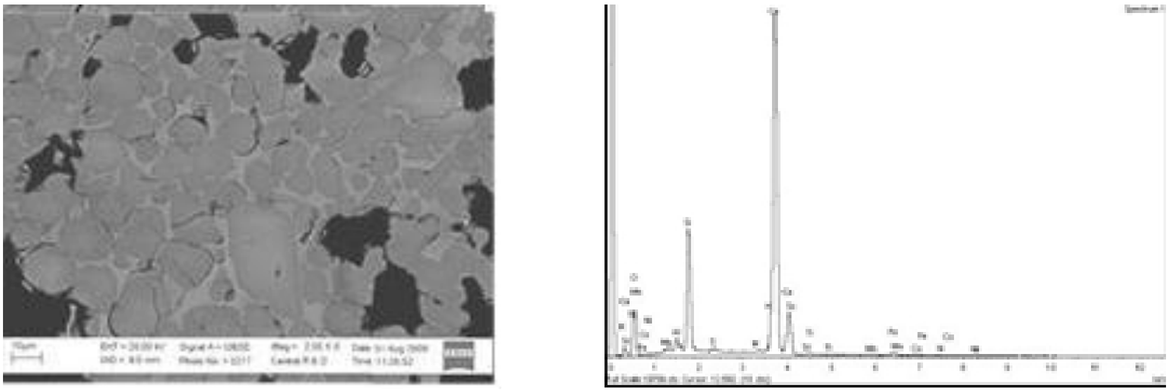


Fig. 3. Microanalysis of Belite Crystals.

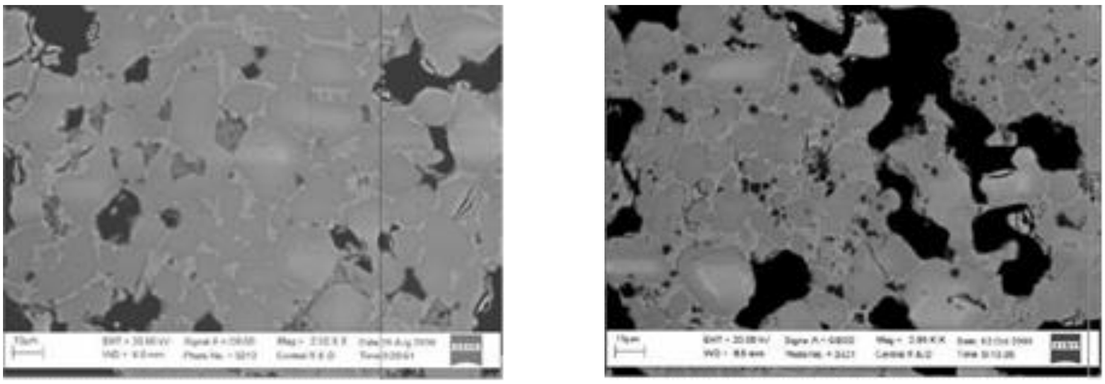


Fig. 4. Microanalysis of Alite Crystals which show formation of alkali bearing phases in and around Alite crystals.

X-Ray mapping

The distribution of elements over a particular area of the sample can be viewed using element maps. Elemental mapping utilizes the x-ray signal from a specified energy range in order to show elemental distribution. Qualitative mapping gives information on the x-ray intensity distribution over the selected region of the sample. The grayscale value for a given pixel in any digital map corresponds simply to the number of x-rays which enter the x-ray detector within the energy range and, therefore, gives an idea of the distribution of the elements. For the present series of x-ray maps on oxford - INCA software, a scan rate of 400 seconds was found acceptable for all the elements. Figure 5 (A) shows the mixture of all elements in a particular area, and Figure 5 (B-F) indicates the inclusion of elements in crystal lattice. From the x-ray mapping of Mn, Co, Ni, Cu, Zn, Pb and Ba it was found that the metals like Mn, Co, and Ni are homogeneously distributed throughout the structure of silicate phases in all clinkers and Cu, Zn, Ba and Pb is mainly trapped into belite crystal lattice. From Scattered plot analysis it is observed that the Na and K is mainly associated with S and forms alkali-bearing phases at the boundary of the alite crystals, which may be hindering the crystal growth of alite phases.

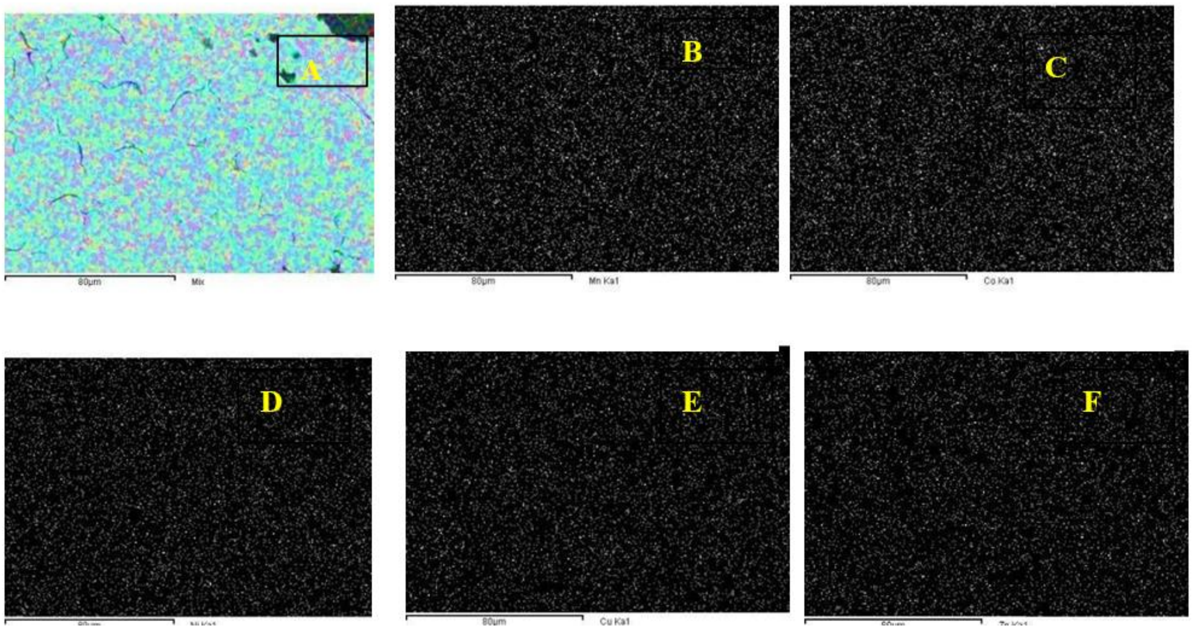


Fig. 5. X-ray maps of some elements in clinker. (A) Mixed, (B) Mn, (C) Co (D) Ni, (E) Cu, (F) Zn.

Microstructure, Texture and size distribution of clinker phases

The textural analysis reveals that the clinker porosity in C1 to C7 clinker is lower as compared to C8 to C17 clinker. All clinkers contain underdeveloped with almost equigranular alite and inequigranular belite crystal with distinct morphology (Fig. 6). The color of alite crystals is brown and belite crystals are having multi-color when etched under HF vapor. Almost in all nodules, smaller discrete primitive form of alite and belite crystals in different morphological form were found embedded in adequate liquid phase (Fig. 7). In C1 to C7, clinker inclusion of belite inside alite (Fig. 8) is frequently observed while in C8 to C17 clinker, a considerable decrease in the number of close packed belite clusters (Fig. 9) indicates higher fineness and improved state of homogeneity of raw mix as compared to C1 to C7 clinker and also support the idea of consistency in quality variation which may lead to smooth operation. Most of the places relict structure (Fig-10) of belite inside the alite and well-developed belite with multidirectional lamella were observed. Then on Gaussian type alite crystal size distribution (Fig. 11) with a modal value of 12 to 18 micron indicates increased feed volume through kiln, burner pipe retraction and increase in primary air. The non-Gaussian type grain size distribution curve for belite (Fig. 12) crystals with modal value of 12 to 15 micron indicates that clinker is burned under high temperatures and quick cooling. The occurrence of coalescent clusters of belite at some of the places with adequate liquid phase, indicates the presence of coarse quartz in the mix. However, in comparison to C8 to C17 clinker, there is certainly a decline in belite clustering which may due to finer raw material, especially the lower size of coarse grain.

The microstructural analysis of all clinker shows highly irregular shapes and moderately grown crystals of Alite (with every possible morphological instability) from cellular to skeletal) and Belite embedded in between a sufficient amount of fine crystalline interstitial matter. Alite mostly occurred in subhedral to anhedral form and predominately occurs as smaller to medium grains with an average grain size of 16.2 to 20.8 µm in C1 to C7 and 15.2 to 20.9 µm in C8 to C17 clinker. In C1 to C17 clinker most of the alite crystals are in medium size i.e. within 15-30µm range and belite crystals are in smaller size i.e. <15 µm. The unstable growth of alite is indicated by the entrapment of small amount of interstitial matrix and heavy metal oxides. The presence of relatively bigger belite along with numerous smaller alite hints at possible hindered growth of alite due to increased melt viscosity owing to alkalies without sulphate. The decreasing trend of alite size (Fig. 11) indicates higher LSF and rapid burning, resulting in growth rate of crystals slower than the formation of nuclei. Micro-fine crystalline Aluminate crystals (Fig. 2) well dispersed throughout the matrix preferentially at the alite and belite grain boundaries depict moderate cooling and declining reactivity of C3A. To some extent the alumina ratio can be related to the alite size growth, in general, lower A.R. with a more mobile liquid phase produces larger alite crystal and densifies the clinker at higher burning temperatures. However, the lower crystal size of alite and the presence of some dark color phases (possibly Alkali Sulphates) in &around the matrix, further substantiate the hindered growth of alite crystal due to some alkalies (Figs. 3 and 4). The ratio of silicate to fluxes in C1 to C7 clinker is more comparable to C8 to C17 clinker by XRD technique, but by Bogue calculation, there is no significant difference observed (Table 4). All micrographs are taken in 400 Representative photographs from all clinkers are shown as below.

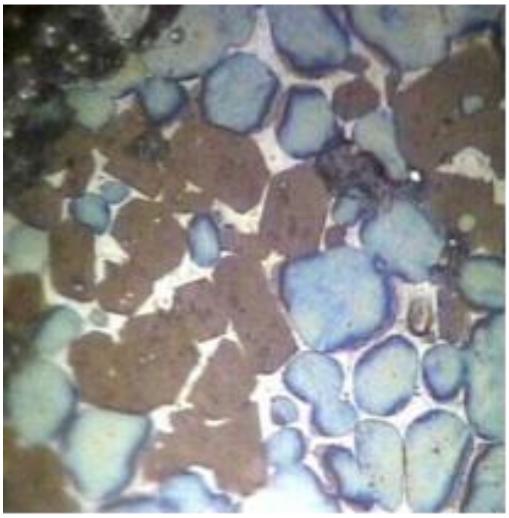


Fig. 6. Distinct morphology of silicates.

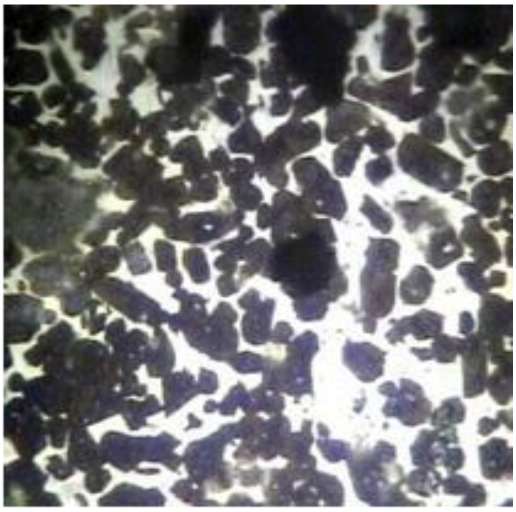


Fig. 7. Smaller discrete primitive form of alite.

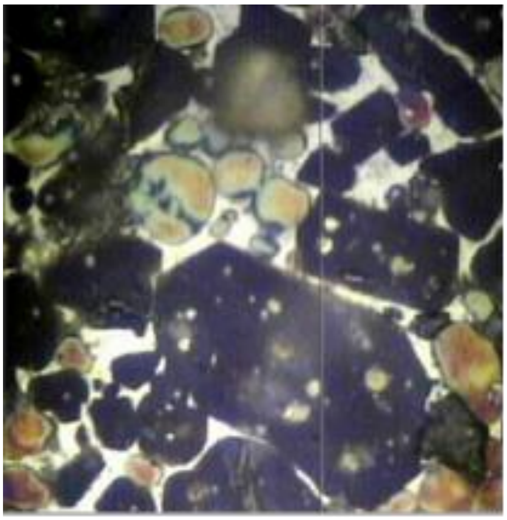


Fig. 8. Inclusions of belite inside alite.

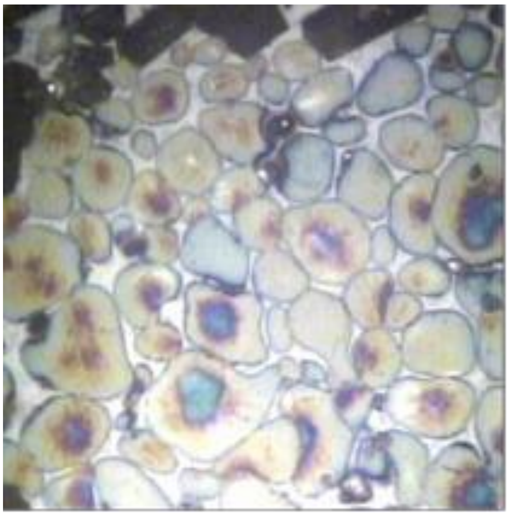
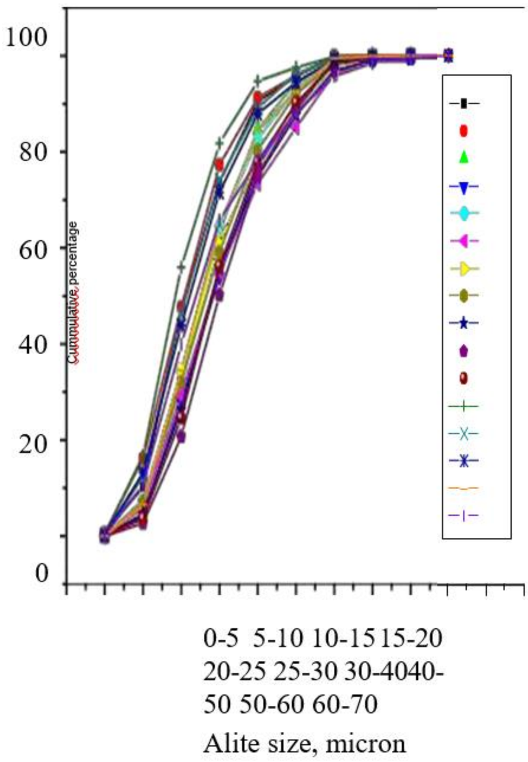


Fig. 9. Close packed belite structure.

Table 4. Phase proportion of C1 to C17 clinker by different technique (Wt%).

	Bouge calculation				XRD				Ratio of Silicates to fluxes	
	C_3S	C_2S	C_3A	C_4AF	C_3S	C_2S	C_3A	C_4AF	Bouge	XRD
C1	49.8	24.6	6.2	14.2	56.2	24.9	2.4	15.8	3.65	4.46
C2	52.1	22.2	6.1	13.9	57.7	23.7	2.4	15.9	3.72	4.45
C3	51.2	23.5	5.9	14.5	56.1	24.5	2.1	17.0	3.68	4.22
C4	54.2	18.3	7.0	15.9	57.6	23.2	3.2	15.7	3.19	4.28
C5	51.5	21.3	7.2	15.3	57.6	23.8	2.2	15.2	3.29	4.68
C6	54.6	21.5	6.7	13.0	59.9	18.1	5.9	15.7	3.87	3.61
C7	50.4	23.7	4.0	16.4	50.9	30.7	2.0	15.9	3.66	4.56
C8	42.0	31.6	8.0	14.8	52.4	25.6	5.2	16.3	3.23	3.63
C9	51.7	24.6	6.7	12.8	59.7	19.4	5.8	14.6	3.90	3.88
C10	49.9	24.5	6.9	14.4	59.6	19.7	6.1	14.3	3.49	3.89
C11	49.2	24.6	6.6	14.5	57.6	21.8	5.1	15.4	3.49	3.87
C12	52.8	21.2	5.9	12.9	59.2	20.6	1.4	16.2	3.96	4.53
C13	54.9	19.6	5.8	12.7	59.5	20.6	1.4	16.3	4.05	4.53
C14	44.6	29.6	8.4	13.8	53.9	24.7	4.2	16.9	3.31	3.73
C15	45.4	29.2	7.9	14.5	58.5	18.0	5.3	18.0	3.33	3.28
C16	46.0	28.8	8.4	13.4	54.3	23.4	4.6	16.6	3.40	3.67
C17	ND									



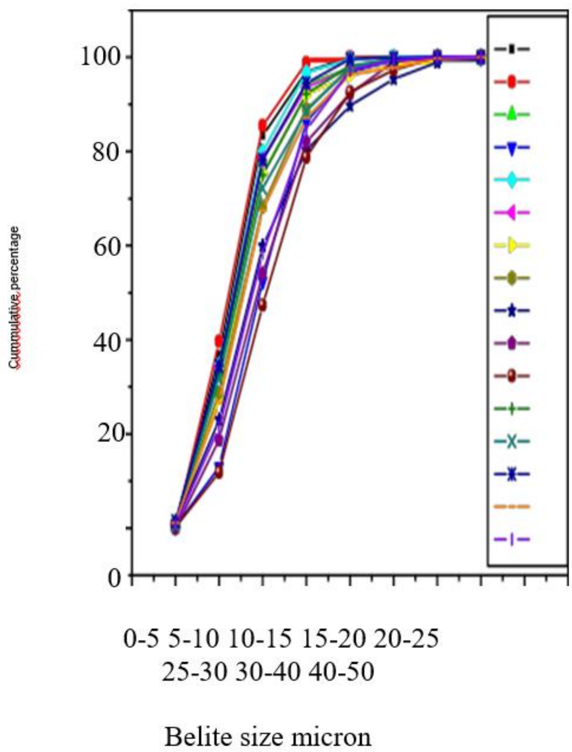


Fig. 10 and 11. show size distribution of alite and belite crystals in C1 to C16 clinker.

Results and Discussion

Typical elemental substitution in alite and belite phases as given by Taylor in Table 1 shows Al2O3 and Fe2O3 as the major and Na2O, P2O5, SO3, and K2O as the minor impurities present in the structure. Similar trends have been observed in our study (Table 2) but the value (quantity) is higher than the proposed value of Taylor. This may be due to change in fuel quality and raw materials. CaO/SiO2 molar ratio is calculated from actual value given by EDX which shows higher range (3.01 -

3.11) in alite structure of C1 to C7 clinker and lower ratio in C8 to C17 clinker. The molar ratio of belite crystals in all set of clinker shows higher range than the stoichiometric value. The impurity level is also more in clinker due to an increase in Fe2O3 and Al2O3 %. Mathematically CaO and SiO2% as calculated from XRD value shows no significant variation in CaO% and SiO2% present in silicate phases. The percentage of SO3 is higher in belite phase in all sets of clinker. Heavy metal concentration in silicate phases of C1 to C7 clinker is more as compared to C8 to C17 clinker. The percentage of Sc and Ba is on higher side in all clinker which is coming from municipal waste and limestone. But there is no significant effect observed from regression analysis. Oxides of Cu, Zn, Ba and Pb mainly incorporated into belite phase gives an indication of decreasing hardness of crystal. The bond work index of C1 to C7 clinker is more as compared to C8 to C17 clinker except C6.

The SEM microstructural study by back-scattered electron shows that Na and K is mainly associated with S and form Na2SO4 and K2SO4 in the edges of alite crystals and the flow of the S elements are towards Na and K which is confirmed from scatter plot analysis by taking Na, K & Sin ternary system. Elemental mapping of the all clinkers shows that the heavy metals are distributed uniformly throughout the crystal in both sets of clinker. From Optical Microscope study, it is found that alite crystals are in low to medium size range while most of the belite crystals are smaller in size in both types of clinkers. The standard deviation value shows that there is a slight variation in the sizes of the alite and belite indicating crystal homogeneity. There is no significant variation in phase proportion as observed by bogue calculation, XRD and OM method. OPOCZKY and Gavel, 2004 reported that the inclusion of transition metals shows favorable influence on grindability, by reducing their hardness. Tsivilis and Kakali, 1997 observed that the order of decreasing of grindability as: MnO, Cr2O3, Ni2O3, ZrO2, CuO, Co2O3, V2O5, MoO3, TiO2, ZnO. Kim, Chu, Lee, Song, 1997 found that clinker grindability became worse as ZnO content increased.

Conclusions

ESEM and EDS quantitative microanalysis of 17 industrial clinkers indicate a significant influence of heavy metal oxide and impurities on the phase composition of alite and belite. CaO/SiO2 molar ratio of C1 to C7 clinker increases due to presence of impurities in crystal lattice. On the other hand, entrapment of ZnO especially in belite crystal decreases the grindability of clinker. The x-ray mapping shows a homogeneous distribution of elements in clinker. There is no significant influence of heavy metal oxides on phase proportion and size of the silicate phases. The distinct morphology of silicate phases is due to the different burning and cooling conditions of clinker.

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