
UTILIZATION OF BASALT ON THE CLINKERIZATION OF ORDINARY PORTLAND CEMENT CLINKER

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Abstract

This study comprises the effect of basalt as a flux and mineralizer on the formation of Portland cement clinker, where it used instead of sand, iron and clay at constant lime saturation factor. Three mixtures were prepared, the first formed from original raw materials, in second mixture the sand and iron replaced by basalt and in the third mixture the clay, sand and iron replaced by basalt. All these mixtures prepared at same lime saturation factor. Firing all these mixtures at same temperature 1350 °C with heating rate 10°C/min and for one hour as a soaking time. The chemical and x-ray analysis of the different raw materials such as original raw mix, limestone, clay, and basalt were determined. Also physical and chemical changes during heating up the mixtures were studied by the aim of DSC technique. The degree of formation of the clinker was studied by the determination of insoluble residue, free lime contents, identification of the cement phases such as C₃S, β-C₂S, C₃A., and C₄AF by the aid of the XRD technique, and SEM. The potential phase composition of clinker was calculated by Bouge's equations.

Keywords: Basalt, Clinkerization, Ordinary Portland Clinker

Introduction

The additions of small amount of some substances that are not normal clinker raw meals may distinct alter the progress rate of the clinkerization processes, these substances that have the capacity to intensify the rate of clinker formation are called fluxes or mineralizers ^[1].

A fluxing agents or fluxes are substances that accelerate the formation of clinker by decreasing the temperature at which a melt starts to be formed in the system and by an increase the amount of the liquid phase formed at any temperature above. Under these conditions, tricalcium silicate (C₃S) starts to form at a lower temperature; the reaction progresses faster and the clinkerization process may be completed at a temperature much lower than that need in the absence of these fluxing agents ^[2].

Unlike fluxing agents, mineralizers are substances which accelerate the rate of solid state reaction or reactions that take place within the liquid phase or at liquid-solid interface without significantly altering the temperature of melt formation and the amount of melt present ^[3].

Basaltic rocks have been widely used as aggregate for various purposes. They show a variety of textural and mineralogical characteristics that may affect their physico-mechanical properties as well as their use as construction material ^[4].

This Study shows that the basalt is by far one of the most reactive aggregate in the cement clinkerization process.

Materials And Methods Of Investigation

The materials used in this investigation were limestone, clay, sand, iron, basalt and raw meal (kiln feed)- These materials were supplied by NLSupervision Operation & Maintenance- The materials were separately dry ground in a disk mill to a grain size that pass through 90 μm sieve size. The chemical analysis of the raw materials was determined using conventional wet method, as well as X-ray fluorescence technique (XRF) as shown in Table (1).

Table (1): Chemical analysis of starting materials, mass % .

| Material Oxide | Lime Stone | Clay | Sand | Iron | Basalt | Raw meal |
|--------------------------------|---------------|-------|-------|-------|--------|----------|
| SiO ₂ | 0.650 | 60.89 | 93.64 | 3.02 | 58.50 | 13.86 |
| Al ₂ O ₃ | 0.134 | 19.53 | 2.00 | 0.78 | 14.43 | 3.49 |
| Fe ₂ O ₃ | 0.093 | 7.41 | 0.53 | 92.29 | 8.57 | 2.40 |
| CaO | 55.55 | 0.32 | 1.58 | 1.65 | 4.70 | 43.62 |
| MgO | 0.568 | 0.24 | 0.11 | 0.27 | 4.35 | 1.44 |
| SO ₃ | 0.021 | 0.01 | 0.02 | 0.30 | 0.00 | 0.07 |
| K ₂ O | 0.046 | 0.72 | 0.23 | 0.06 | 0.87 | 0.07 |
| Na ₂ O | 0.013 | 0.47 | 0.45 | --- | 2.40 | 0.13 |
| Cl ⁻ | 0.016 | 0.508 | 0.059 | 0.044 | 0.015 | 0.06 |
| LOI 950°C | 42.93 | 10.00 | 1.35 | 1.60 | 6.24 | 34.84 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

The chemical composition of ingredient components which are seen in Table (1), shows that, the clay contains high amount of SiO₂, in combined and most in free status (quartz), this confirmed by XRD pattern, also, it contains small amount of Fe₂O₃ and other oxides which are known as fluxing oxides such as MgO and Na₂O. On the other side basalt contains silica lower than in clay, and contains higher amount of Fe₂O₃, FeO, alkalis and MgO which act as fluxing oxides.

The mineralogical composition of the limestone, clay and basalt are identified by using X-ray diffraction (XRD). Figure (1) shows the mineralogical composition of limestone sample; it is clear that it is mainly composed from calcite. Figure (2) shows the mineralogical composition of basalt; it is also, clear that it composes from muscovite, tremolite, albite and very little amount of quartz.

Figure (3) shows the mineralogical composition of clay; it composes from kaolinite, quartz, iron oxide, and a little amount of halite. However clay contains higher amount of Al_2O_3 contents, but clay is in less reactive state due to its mineralogical composition, confirmed by XRD pattern Fig. (3), and basalt is more reactive due to its mineralogical composition, which confirmed by XRD pattern Fig. (2), meaning most of SiO_2 present in clay in the form of quartz, while the SiO_2 present in basalt is in combination form. XRD pattern shows that the basalt contains Na, K, Si, Ca, Al, Fe, Mg, Mn, in the form of Muscovite, Terolite, Albite.

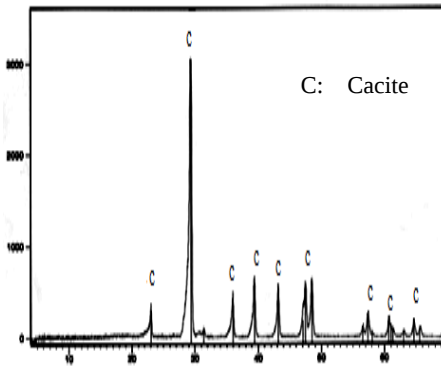


Figure (1): XRD pattern of limestone

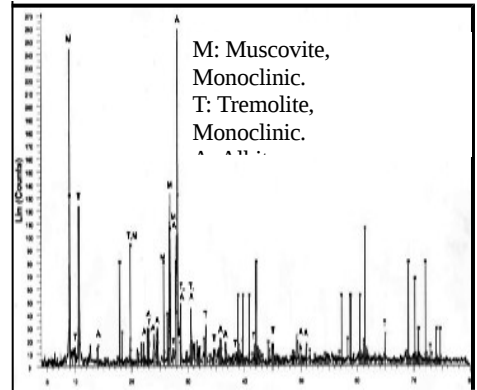


Figure (2): XRD pattern of basalt rock

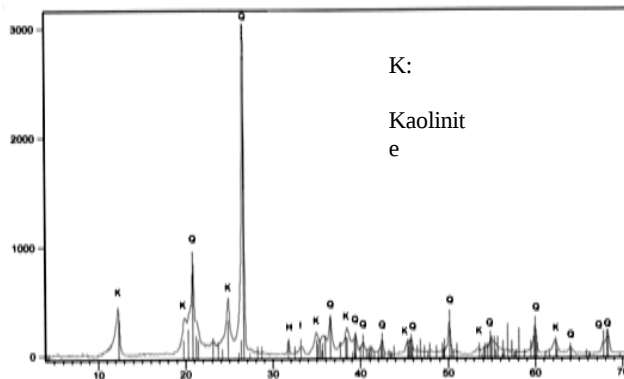


Figure (3): XRD pattern of clay

Preparation of Mixtures

Three mixtures have the same lime saturation factor 98% were prepared. The first mixture is the raw mixture (kiln feed) and the other two mixtures were prepared by substitution the corrective ingredient (iron, sand and or clay) with basalt. The ratio of each component in each mix was calculated from two or three component equations ^[5], the chemical analysis of these mixes are listed in Table (2).

Table (2): The composition and chemical analysis of prepared mixtures, mass %

| Ingredient | Mix | | |
|--------------------------------|-------|-------|-------|
| | Mix 1 | Mix 2 | Mix 3 |
| Lime stone | 78.51 | 78.7 | 76.7 |
| Clay | 18.00 | 19.27 | -- |
| Sand | 1.04 | -- | -- |
| Iron | 2.45 | -- | -- |
| Basalt | -- | 2.03 | 23.3 |
| SiO ₂ | 13.49 | 13.36 | 13.57 |
| Al ₂ O ₃ | 3.40 | 4.15 | 3.33 |
| Fe ₂ O ₃ | 2.34 | 1.67 | 1.99 |
| CaO | 42.45 | 42.52 | 42.35 |
| MgO | 1.40 | 1.24 | 1.40 |
| SO ₃ | 0.07 | 0.19 | 0.23 |
| Na ₂ O | 0.07 | 0.057 | 0.55 |
| K ₂ O | 0.13 | 0.056 | 0.02 |
| Cl ⁻ | 0.06 | 0.015 | 0.02 |
| LSF | 98.0 | 98.0 | 98.0 |
| SM | 2.35 | 2.30 | 2.55 |
| AM | 1.45 | 2.49 | 1.67 |
| LOI 950°C | 33.9 | 34.29 | 35.52 |
| % > 90 μm | 0.00 | 0.00 | 0.00 |

About 300 gm from each mixture, was mixed using a ball mill; each mixture from the above mixes was molded in one inch cylindrical bar at 500 kg/cm². Ten cylindrical bars from each mix (30 g) were fired in a muffle furnace at same firing temperatures 1350°C, with a heating rate of 10 °C/min., for 1 hr as a soaking time. The fired clinker was quenched in the air to prevent the dissociation of the formed clinker. The clinker

was ground in a disk mill to pass completely through 90um sieve size. Small amounts from each clinker were taken for the free lime, insoluble residue determinations and X-ray diffraction analysis as well as SEM.

Results And Discussion

Phase composition and microstructure

The phase composition of fired mixes was identified using X-ray diffraction (XRD) analysis, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM)

X-ray diffraction (XRD) ^[6,7]

XRD diffractograms of the fired clinkers at 1350°C for 1hr as a soaking time of all prepared mixes are shown in Figure (4). The Figure illustrates the XRD patterns of the fired clinkers Mix 1, 2 and 3 fired at 1350°C for 1hr as a soaking time. The results indicate the main characteristic peaks of all clinker phases such as calcium silicate Ca₃SiO₅ (alite), Larnite Ca₂SiO₄ (belite), Calcium Aluminum Oxide Ca₃Al₂O₆ and Iron Aluminum Calcium Oxide Fe₂O₃Al₂O₃(CaO)₄ (ferrite) in addition to presence free lime. The XRD diffractograms of Mix 3 and Mix 2 show increasing in presence alite more than in mix 1 due to presence 2.03 in mix 2 and 23.3% basalt in mix 3, also the XRD diffractograms show decreasing in free lime content in mix3 and mix 2 compared to mix 1 due to addition basalt in mix 2 and mix 3. These results confirmed using XRF analysis for the fired clinker for determining free lime and clinker phases as showed in Table (3)

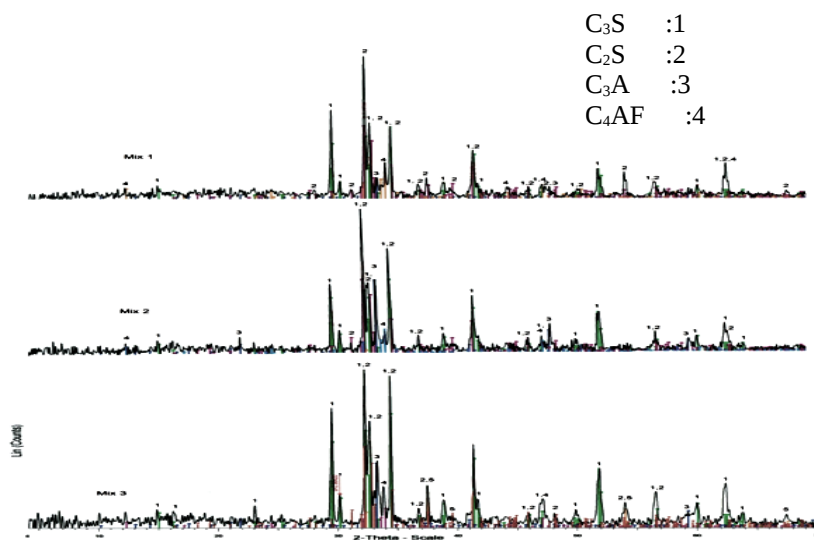


Figure (4): XRD patterns for clinker of mixes 1, 2 & 3**Table (3): XRF analysis for clinker fired for 1 hr at 1350 °C**

| Phases | Mixture | | |
|-------------------|---------|-------|-------|
| | Mix 1 | Mix 2 | Mix 3 |
| C ₃ S | 56.72 | 57.91 | 71.63 |
| C ₂ S | 18.50 | 13.73 | 2.32 |
| C ₃ A | 7.61 | 14.00 | 7.77 |
| C ₄ AF | 11.38 | 9.62 | 11.56 |
| FCaO | 2.0 | 1.1 | 1.55 |
| Insoluble residue | 0.19 | 0.16 | 0.17 |

Differential scanning calorimetry (DSC)^[8,9]

The results of DSC analysis of prepared mixes are shown in Figs 5, 6 and 7. Figure 5 illustrate an endothermic peaks at 725-800 and 824-830 °C for decomposition of calcium carbonates, and endothermic peaks at 1162-1209, 1247- 1260 °C for intermediate products formation CA.C₁₂A₇ and C₂F + C₄AF, C₃A , C₂AS respectively, and finally the liquid phase endothermic peak at 1344-1371 °C.

Figure 6 illustrate an endothermic peak at 64-184 °C for H₂O evaporation and loss of adsorbed water, endothermic peaks at 315-352 and 430-480 °C for removal of structural H₂O (H₂O and OH groups) from clay minerals, endothermic peak at 700-795 °C for decomposition of calcium carbonates, endothermic peak at 1145-1192°C for intermediate products, and finally the liquid phase endothermic strong peak at 1287-1294 °C.

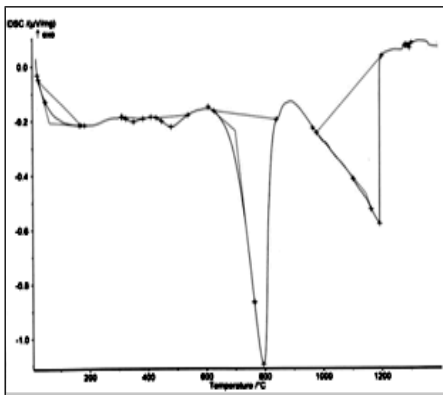


Figure (5): DSC chart for mix 1

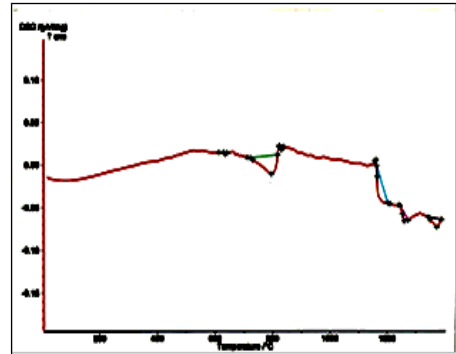


Figure (6): DSC chart for mix 2

Figure (7) illustrate an endothermic peak at 493-526 °C structural change in basalt mineral, exothermic peak at 658-688 ° C formation of intermediate products for belite these due to basalt contains a calcium oxides, iron oxides, silica and alumina oxides, so it's ready for such previous reactions, endothermic peak at 744-789 °C for decomposition of calcium carbonates, endothermic peak at 1192-1205 °C for intermediate products, and finally the liquid phase endothermic strong peak at 1209-1211°C. So the first melt started in mix3 earlier than other, in addition that part of the intermediate products (belite, aluminate and ferrite) also started earlier, which changed to liquid phase as the reaction proceeded. These results are in good agreement with that of the XRD analysis.

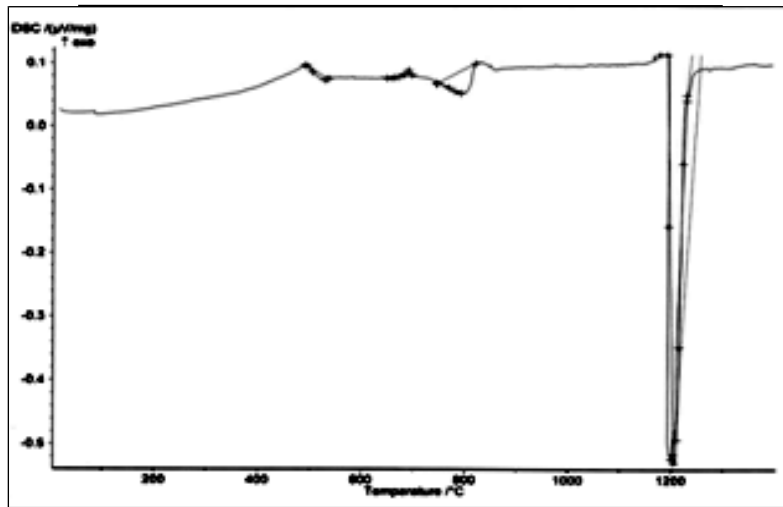


Figure (7): DSC chart for mix 3

Scanning electron microscopy ^[10]

The microstructure of the fired mixes at 1350°C for one hour as a soaking time has been undertaken using scanning electron microscopy (SEM) are shown in Figures (8 – 10). It is clearly from the Fig. (8) presence of all characteristic phases in the Mixture 1, such crystals of alite (dark, angular) and belite (less dark, rounded) embedded in a matrix of interstitial material, itself composed mainly of dendritic ferrite (light) and aluminate (dark)s, beside presence of these phases the figure (8) shows liquid phase with limited amount, the appearance of liquid phase increase in mixtures containing

basalt (mix2 and mix3) specially mix 3 as shown in Figures (9 and 10). Also the amount of alite crystals increases in samples contain basalt in their composition as in mixes 2 and 3 as shown in Figures 9 and 10. These SEM images confirm the result obtained in XED, XRF and DSC.

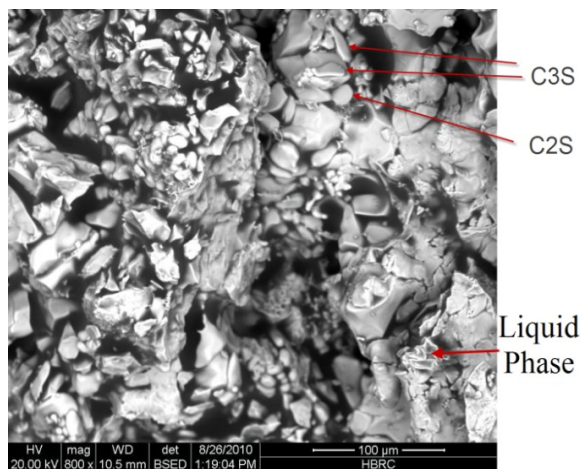


Figure (8): Clinker minerals of mix 1

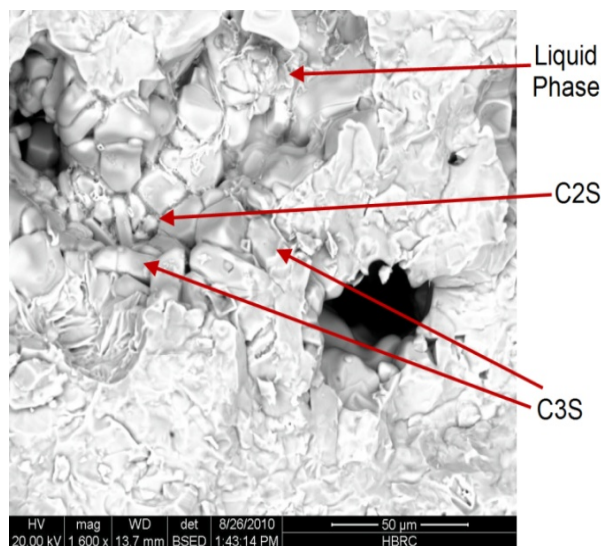


Figure (9): Clinker minerals of mix 2

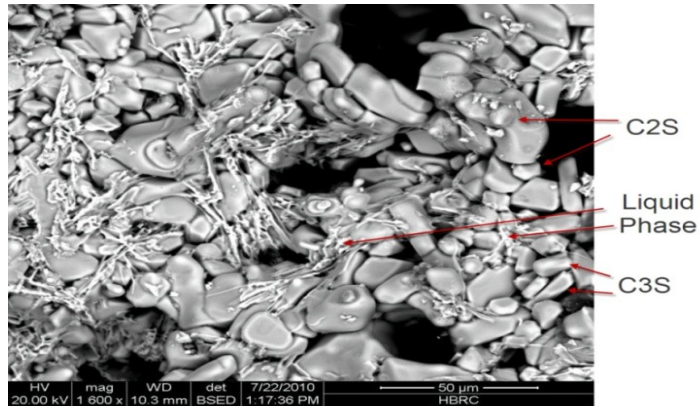


Figure (10): Clinker minerals of mix 3

The theoretical calculations for liquid phase content^[11], clinkering temperatures and Bogue equations for clinker phase composition for three fired mixtures were done. The results are listed in the tables (4-6). The theoretical results show the percentage of liquid phase higher in first mixture than other two mixtures as shown in Table (4). The Table (5) shows that the clinkering temperature for the first mixture lower than other two mixtures containing basalt. These results are different from the results obtained by XRD, DSC and SEM because the theoretical results ignored the effect of mineralogical composition of basalt on clinker and phase formation of prepared mixtures. But the Bogue equations for phase composition calculation confirm the results obtained by instrumental analysis (XRD, DSC and SEM) especially for mix 3 as shown in Table (6).

Table (4): The liquid phases content in clinker

| Mix Temp. | Mix 1 LP % | Mix 2 LP % | Mix 3 LP % |
|-----------|------------|------------|------------|
| 1338 °C | 25.0 | 18.0 | 22.4 |
| 1400 °C | 26.0 | 27.2 | 25.6 |
| 1450 °C | 27.0 | 27.6 | 26.0 |

Table (5) Clinkering temperature (°C)

| Mix Temp | Mix 1 | Mix 2 | Mix 3 |
|-----------|---------|---------|---------|
| Temp (°C) | 1409.16 | 1413.40 | 1429.69 |

Table (6): Clinker minerals calculated by Bouge's equations

| Mix Mineral | Mix 1 | Mix 2 | Mix 3 |
|-------------------|-------|-------|-------|
| C ₃ S | 61.87 | 57.86 | 62.29 |
| C ₂ S | 13.68 | 16.14 | 13.72 |
| C ₃ A | 7.88 | 12.74 | 8.51 |
| C ₄ AF | 11.11 | 7.90 | 9.45 |

Conclusion

The results show that the burnability of raw mixes improves if we substitute the corrective ingredient (iron and sand), and clay with basalt, which acts as a fluxing and mineralizer due to the basalt contain higher percentages of alkali oxides and iron oxides which act as fluxing oxides. Also the basalt contains SiO₂ in amorphous form have higher reactivity than SiO₂ in clay, thus the calcium silicate formation formed in mixes 2,3 which have basalt in their composition is higher in amount than mix 1.

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