

Raw Mix Designing for Coal as a Fuel in Cement Kiln as a Major Fuel and its Impact on Clinker Parameters

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Summary: In this paper the use of coal, found at Jabba Taar and Jabba Khushk Khyber Pakhtoon Khwa, in cement manufacturing as a major fuel and its impacts on the raw mix and clinker parameters has been discussed. The maximum amount of coal for pulverizing with raw mix was found to be 10% of the raw mix as calculated from the calorific value and the heat of clinkerization of coal. The coal residue left after burning was utilized in the cement raw material, for which a new raw mix was designed. The new raw mix was converted in to clinker. The resulting clinker was studied for all parameters as per British specification. It was found that the clinker obtained from the newly designed raw mix with coal ash, was in accordance to the British standard specifications.

Introduction

High strength Portland cement is recognized as the major construction material [1-3]. With the increase in population, the need and use of cement is increasing with tremendous speed. Therefore new plants are being installed with a high speed.

Portland cement is made by grinding clinker and gypsum together in the ratio of 95:5 by weight [3]. Clinker is made in a kiln and is composed mainly of calcium oxide (here noted as C), silica (S), alumina (A) and ferric oxide (F), manifested as four primary clinker compounds (C₃S, C₂S, C₃A and C₄AF) in the approximate ratios of 6:2:1:1, respectively [4]. Limestone is the major source of CaO and makes up to about 1.5 of the 1.7 tons of raw materials consumed per ton of clinker produced. A wide variety of secondary materials, such as coal combustion products can be used as partial substitutes for primary rock-based raw materials. Selection criteria of fuel include composition, energy and other cost savings and the potential to reduce carbon dioxide emissions. Calcination of limestone to yield CaO produces a lot of CO₂. The total production of CO_x from the calcination of raw material and fuel combustion is nearly 1 ton per ton of clinker and is the major reason, why kilns consume about 3–7 GJ of heat energy per ton of clinker, depending on kiln technology [5].

Some secondary materials are pozzolans; they become cementitious when reacted with lime [6]. Pozzolans can be mixed with Portland cement to make blended cements or can replace some of the Portland cement in concrete; in either case, the requisite lime is produced by the hydration of C₃S

and C₂S. Pozzolan addition generally improves the performance of concrete. Overall, secondary material usage by the cement industry is increasing and reached nearly 5% of total raw materials consumed in 2005. Coal combustion products accounted for 3% of total raw materials in 2005, including nearly 3 Mt of fly ash and about 1 Mt of bottom ash for clinker and about 0.5 Mt of synthetic gypsum (about 10% of total gypsum) for cement. Although only about 0.2 Mt of fly ash was used in 2005 as pozzolan in cement, the concrete industry itself used almost 14 Mt of fly ash (mostly as a pozzolan), as well as about 1 Mt of bottom ash as an aggregate[7]. Low-NO_x burners at power plants produce a high-carbon fly ash that, unless treated, is unsuitable as a pozzolan, but can still be used in cement kilns.

Coal is a combustible carbonaceous rock, containing many kinds of organic and inorganic material, formed from accumulated vegetable matter that has been altered by decay and various amounts of heat and pressure over millions of years[8-9]. Coal varies widely in its composition. It is composed chiefly of rings of six carbon atoms joined together in an extremely complex composition of layered arrangements that have in them, not only hydrogen but significant amounts of oxygen and nitrogen. The structure also includes varying amounts of sulphur and other environmental pollutants. Up to one tenth of the total mass of coal can be material with no fuel value. Coal is usually analysed for moisture, volatile matter, fixed carbon and ash. The sulphur and nitrogen content are important as emissions of their chemical oxides during coal burning can cause acid rain [10].

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The cement industry being the second biggest coal user in the country is important to the country [11-12]. Coal is found in all the four provinces of Pakistan. The country has huge coal resources, about 185 billion tones, out of which 3.3 billion tones are in proven/measured category and about 11 billions are indicated reserves.

The present work, deals with utilization of local coal, in cement manufacturing, its formulation for blending with raw mix and its impact on raw material and clinker parameters.

Results and Discussions

The chemical composition of normal raw mix for high strength Portland cement is shown in Table-1. Calculated amount of coal ash was added to the normal raw mix and pulverized thoroughly. The chemical analysis of this raw mix containing coal ash is shown in Table-2.

Table-1: Chemical analyses of normal raw mix for high strength Portland cement.

Contents	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃
Wt (%)	14.60	3.83	2.28	42.55	0.98	0.18	0.46	0.10

Table-2: Analysis of normal and designed raw mix containing coal residue.

	Normal raw mix with coal residue	Designed raw mix with coal residue
SiO ₂	17.86	14.63
Al ₂ O ₃	5.88	3.85
Fe ₂ O ₃	2.89	2.28
CaO	38.96	42.55
MgO	1.00	1.00
Na ₂ O	0.21	0.20
K ₂ O	0.60	0.50
SO ₃	0.16	0.16

The heat of clinkerization for one kg of clinker from 1.55 kg of raw mix is given in Table-3, which is the sum of different endothermic and exothermic processes, which absorb or evolves different amount of energies respectively. Evaporation of free water at 100 °C requires 538 cal/g. The heat absorbed in the dehydration of kaolin at 20 °C is 168cal/g. In the case of montmorillonite the corresponding value is 58.5 cal/g. and for illite 43 cal/g. The product of dehydration shows an exothermic reaction at about 900-950 °C arising from the crystallization of the amorphous material and amounting in the case of kaolin to 72 ± 10 cal/g dehydrated kaolin. The heat absorbed in dissociation of calcium carbonate is 422 cal/g at 20 °C and 393 cal/ g at 890 °C. For magnesium carbonate the values found by different investigations vary from 284–324 cal/g at 20 °C.

The reaction of the dehydrated clay products with lime is associated with a considerable evolution of heat, which varies with the cement composition and raw materials, but only about 50-70 cal/g when slag and limestone are used. A heat evolution of 100 cal/g, is sufficient theoretically to raise the temperature of the reacting masses by over 300 °C.

For different raw mixes and for slightly different data, different authors have calculated values from 400 to 430 kcal/kg clinkers [13]. The net heat of melting arises from the failure of all the glass to crystallize on cooling and is obviously a variable factor. The observed heat of clinkerization in the cement plant is 840-850 kcal /kg, which is almost double of the calculated heat of the clinkerization. The excess amount of heat is wasted from the kiln in different forms. The main loss is in the form of thermal radiations from the kiln shell and multicyclones. The shell temperature out side is about 400 °C, which is the clear evidence of loss of heat from the kiln. Secondly the temperature of the out coming clinker from the cooler is about 200-300 °C, which loses its heat to the open environment. The third loss of heat from the cement kiln is in the form of exit gases, from the chimney after multicyclones. So the heat required in practice of course become considerably greater than this theoretical value on account of the heat lost. With a wet process kiln thermal efficiencies are not much above 30 percent, but with special heat recuperators values approaching 50 percent are obtained in the semi dry and dry processes and rather more with shaft kilns.

Calculation of the Coal Quantity for Clinkerization

As clear from Table-4 that the calorific value of the coal under investigation is 5500 kcal/kg. One kg of clinker as clear from the Table-3 needs about 420 kcal/kg. This means that 5500 kcal is produced from the burning of 1000g coal; therefore 420 kcal of heat, which is needed for one kilogram of clinker, is obtained by burning 76.36g of coal.

From the above discussion, it is clear that 76.36 g of coal should be pulverized with raw meal to produce one kilogram of the clinker, which is equivalent to 1.55 kg of the raw mix. This can also be calculated that for one kilogram of raw meal, 49.27g of coal is required. But the observed heat required in cement kiln is 850 kcal/kg, which is almost double to that 420 kcal/kg. So the use of coal becomes up to 100 g per one kilogram of raw mix.

Table-3: Heat of clinkerization for one kilogram of clinker formation.

Heat absorbed	kcal/kg
Heating raw material from 20 °C to 450 °C	170
Dehydration of clay at 450 °C	40
Heating materials from 450 °C to 900 °C	195
Dissociation of calcium carbonate at 900 °C	475
Heating the decarbonated material from 900 °C to 1400 °C	125
Net heat of melting	25
Total	1030
Heat Evolved	kcal/kg
Exothermic crystallization of dehydration clay	10
Exothermic heat of formation of cement compound	100
Cooling clinker from 1400 °C to 20 °C	360
Cooling Carbon dioxide (CO ₂) from 900 °C to 20 °C	120
Cooling steam from 450 °C to 20 °C including condensation to water	20
Total	610
Net theoretical heat required to form 1kg of clinker	1030 - 610 = 420 kcal

Impact of Coal Residue on the Raw Mix Parameters

When coal is burnt with the raw mix, it produces heat which is utilized to convert the raw mix in to clinker. The residue/ash, left after burning of the coal disturb the composition of raw mix and clinker obtained from it. As clear from the Table-4, coal contains 19.32% ash, which contains maximum amount of silica (50.79%). With the addition of 100 g of coal with one kilogram of raw mix, all the parameters of the raw mix are changed. The chemical analysis of the resulting raw mix containing coal ash is represented in Table-2, which shows that silica contents is increased from 14.60% to 17.86% and lime contents from 42.55% to 38.96% (Table-2). The rest of elements are also disturbed. The net result of the coal used as a fuel is that, the composition of raw mix does not remains in the limits which may give clinker having all parameters not in accordance to the standard specifications. In order to bring, all the parameters of the resulting kiln feed and clinker to the normal range, new raw mix designing was performed, in which the required amount of coal ash has been incorporated in such a way that the composition of the final raw mix containing coal ash, remains within the specification.

Table-4: Physico-Chemical Parameters of studied Coal (%).

Moisture	Volatile Matter	Ash	Sulfur	Fixed Carbon	Hydrogen	Calorific Value kcal/kg
16.18	41.64	19.32	5.16	16.16	1.80	5500

The chemical analysis of the newly designed raw mix for coal as a fuel is given in Table-5. From the table it is clear that the newly designed raw mix in which coal residue has been used, contains almost the same composition as that of normal raw mix represented in Table-1. During the raw mix designing lime content has been increased and silica content decreased. The reason for this is that coal residue contains high silica and low lime content.

Table-5: Chemical Analysis of normal Clinker.

Contents	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃
Wt (%)	22.63	5.94	3.53	65.95	1.52	0.28	0.71	0.16

Impact of Coal Residue on the Clinker and Clinker Moduli

The chemical composition of normal clinker with out coal ash, prepared from normal raw mix in the furnace is shown in Table-5. When sufficient amount of coal residue was added with normal mix and was clinkerized, percentages of all the elements changed as clear from the Table-6.

Table-6: Chemical Analysis of Normal and newly designed Clinker containing coal residue.

	Normal clinker containing coal residue	Designed clinker containing coal residue
SiO ₂	27.68	22.67
Al ₂ O ₃	9.12	5.97
Fe ₂ O ₃	4.48	3.54
CaO	60.38	65.95
MgO	1.55	1.55
Na ₂ O	0.32	0.32
K ₂ O	0.94	0.94
SO ₃	0.24	22.67
MA	2.03	1.69
MS	2.04	2.38
LSF	0.66	0.90
C ₂ S	-32.90	50.32
C ₃ S	104.17	27.03
C ₃ A	16.58	9.84
C ₄ AF	13.64	10.77

According to British standards specification, MA ranges from 1.3 to 2.5, if it exceeds the upper limit, the viscous slag and high early strength is exhibited. Similarly if it is less than 1.3, then fluid slag, low early strength and low heat of hydration occur. The recommended and acceptable range of MS is 2-3. If MS goes below this range, burning become very easy but excessive liquid phase and low strength cement is obtained. At the upper limit of MS, the high strength cement is obtained but the burning become very difficult, if it crosses the upper limit, then no clinkerization take place at all. The normal and acceptable range of LSF is 0.90-0.98. It does not create any problem in cement manufacturing process

and its strength, even if reaches as low as 0.8, however, it should not be less than 0.8. From the results of the present study it is clear that the clinker moduli LSF is out of range. Moduli are the relationship among different oxides present in cement raw mix or clinker. These moduli are used to control the percentage of oxide of elements in raw mix during raw mix designing. Different cements have different ranges of moduli which have to be controlled during clinkerization. Therefore clinker moduli are very much important in quality control during cement manufacturing. The moduli of raw mix and clinker are almost the same. The moduli are classified as follow,

Alumina Modulus (MA)

Alumina modulus is the relationship between the oxide of aluminum and iron and is given as

$$MA = \frac{Al_2O_3}{Fe_2O_3}$$

Silica Modulus (MS)

Silica modulus is the relationship of the oxide of silica with aluminum and iron and is given as

$$MS = \frac{SiO_2}{Al_2O_3 + Fe_2O_3}$$

Lime Saturation Factor (LSF)

Lime saturation factor is the relationship of the oxide of calcium with silicon, aluminum and iron and is given as

$$LSF = \frac{CaO}{2.8SiO_2 + 1.2Al_2O_3 + 0.65Fe_2O_3}$$

Chemical composition of clinker obtained from the designed raw mix during this study is given in Table-6. From the close comparison of Table-6 and 2, it is clear that the composition of clinker obtained from the designed raw mix with coal residue is almost the same as that of normal clinker.

Experimental

Material and Methods

The chemical composition of the normal raw mix for high strength Portland cement, which was

used in this work, is given Table-1. The coal used in work was obtained from Jabba Taar and Jabba Khushk, Khyber Pakhtoon Khwa, Pakistan, whose analysis was carried out [14] in our previous work, as given in Table-4 and Table-7.

Table-7: Chemical analysis of coal ash.

Contents	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃
Wt (%)	50.79	26.62	9.08	2.61	1.20	0.50	2.06	0.72

Clinker Formation

The raw mix was converted into paste with small amount of water. Small granules in the range of 5-10 mm were manually made and dried in the oven at 110 °C. These granules were ignited in the muffle furnace at 1450 °C for one hour using nickel crucible for complete clinkerization. All the raw mixes were converted into clinker using the same procedure. The black color clinker was cooled in desiccators and stored in polythene bags. The clinker was studied for different physical and chemical parameters as per Pakistan standard specifications.

From the heat of clinkerization Table-3 and calorific value of coal samples Table-4, the amount of coal used for the clinkerization of one kilogram of the raw mix was calculated. Based on the calculation, new raw mix was designed with incorporating the exact amount of coal ash with the raw material. The raw mix designed and normal raw mix with which coal ash was mixed, were analyzed. Both the raw mixes were converted in to clinkers and were again analyzed using the same technique.

Conclusion

The results of the present study shows that coal of cherat mines can be used as a major fuel in cement kiln for clinkerization. The optimum amount of coal found during this study is 10% of the raw mix. The residue left after the burning of coal replaces some of the siliceous content of the raw material. With the proper raw mix designing, the use of coal in the kiln does not disturb any of the parameters of the clinker.

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