Utilization of Coal Slurry Waste as an Alternative Raw Material in Portland Cement Clinker Production

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Abstract

Coal slurry is the liquid coal waste and was produced by mining activities such as coal washing. After mining, coal is crushed and washed. The washing process generates large amounts of liquid waste and solid waste. This paper is aimed to investigate the potential use of Turkish Coal Enterprises (TCE) coal slurry waste as an alternative raw material in laboratory and industrial scale Portland cement clinker production. The results showed that new raw material mixes containing coal slurry waste can be technically suitable and economic. The coal slurry waste was mixed into raw mixture with different proportions such as 1% wt., 2% wt. and 3% wt. The particle size distribution, chemical composition, clinker main phases, free lime, density, burnability index and gaseous emissions quality properties of coal slurry waste containing clinker were compared with the properties of clinker manufactured with conventional raw materials. The test results showed that the particle size distribution and chemical composition of coal slurry waste is compatible with raw material grain size and chemical compositions. Clinker main mineral phases as alite (C_3S), belite (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) was found at the desired value range of normal clinker. Portland cement clinker prepared without coal slurry waste free lime and burnability index test results were higher than coal slurry containing clinker. These findings suggest that coal slurry waste facilitate burnability of raw mix. Furthermore, the incorporation of coal slurry waste into the raw mix of clinker shows no significant effect in the emissions quality when compared with the values obtained in normal Portland cement clinker conditions. It was seen that 3 wt. % coal slurry waste replacement as an alternative raw material has good effects in Portland cement clinker production.

1. Introduction and purpose

It is a common knowledge that manufacturing of various construction raw materials such as lime and cement continuously increase the atmosphere emission of high concentration of carbon monoxide, sulphur oxides, nitrogen oxides etc. These toxic gases are one of the main reasons of air, water and soil pollution [1]. In recent years, huge amount of solid wastes are recycled and used in various construction materials production as a result of environmental concerns. One of the types of these industrial pollutant solid wastes is coal slurry wastes.

Coal slurry is the liquid coal waste and is produced by coal preparation and washing processes at coal enrichment plants. After mining process, coal is crushed and washed. The washing process generates large amounts of liquid and solid waste. There are lots of studies to utilize coal slurry in various industrial and building materials production. Because of consisting of high amount of clay minerals, using of coal slurry was frequently investigated in brick production as raw materials [2-5]. However, utilization of coal slurry in cement production was rarely researched and it was seen that literature and industrial studies for using in cement production was limited.

The most detailed investigation was conducted by Erkan et al. (2004) and evaluation of tailings obtained from coal preparation plant waste water was utilized as cement raw material. According to the sieve analysis, it was seen that original tailing (>0.045 mm) composed of mostly coal, on the other hand; undersize grain fractions of the tailing (<0.045 mm) contained kaolin, illite, muscovite and quartz minerals. Then, raw meal was produced with mixing of <0.045 mm sized coal tailing (21.31 wt. %) and limestone (78.69 wt. %). When properties of obtained raw meal were analyzed, it was seen that SR was supplied the reference values. However, AR value of the cement produced from coal tailings was seen slightly above from the limit values with 2.7. Finally, it was indicated that mixing of lime stone and coal tailing at proper ratios provided a suitable cement production and supplied the required cement standards like silicate ratio and hydraulic module [6].

The main reason of the using of coal wastes in the cement production is usually because of having high calorific values of these wastes. Galos et al. (2014) researched usage area of the hard coal mining and processing waste in Poland. According to the study, the most common usage area of the coal shale obtained from the company Haldex S.A. (the larger coal producer in Poland) is cement industry. The coal shale used as raw material was consumed 150,000 – 200,000 t/year in cement industry. It was indicated that usage of coal shale obtained from this region supplied less fuel consumption in cement clinker production because of having high calorific values [7]. Hlavata et al. (2014) researched about coal mining wastes usage in cement clinker production. It was indicated that calorific value was 17 $MJ.kg^{-1}$ and ash content was higher than 40% of coal waste used in the experiments. There was not seen that any negative results on the final cement products, also it was specified that these coal slurry wastes can be used as both raw material and fuel sources [8].

It is important that following the changing of product quality when adding a waste material into cement production raw meal. Within this scope, it is continuously searched the changing of characteristic properties of cement during production process. For this reason, some cement standards like silica ratio (SR), aluminum ratio (AR) and lime saturation factor (LSF) are measured to determine a material suitability for using as cement raw material. A high SR means that more calcium silicates but less aluminate and ferrite exist in the clinker. Also, high SR causes difficulty in burning of clinker, using high amount of fuel, difficulty in sintering and decreasing in cement resistance. Low SR derives easily sintering of raw meal, and then quick-resisting and easily hardened cement can be produced. SR is usually required in the range of 2.0 and 3.0. AR is directly associated with clinker heat. Low AR supplies a reduction in clinkering heat and also fuel usage. Thus, AR value of raw meal is required in between 1.5 - 2.5. In addition, AR increasing means that more aluminate and less ferrite present in the clinker. High AR causes quick-freezed and high resistance cement production. LSF is a ratio of CaO to the other three main oxides (SiO_2, Al_2O_3 and Fe_2O_3); moreover, it controls the alite and belite ratio in the clinker. Increasing in LSF causes higher proportion of alite to belite, also, it is an important parameter to measure raw meal of Portland cement clinker and it is quite related to SR and AR. LSF values in the clinkers is usually in between 0.92 – 0.98; however, LSF values of some regions in the clinker can be a little below or a little above because of mixing of raw materials is never perfect in the practice. The LSF value higher than 1.0 is means that free lime presents in the clinker [6, 9].

In this study, a potential usage area of coal slurry wastes obtained from Turkish Coal Enterprises (TCE) was investigated in laboratory and industrial scale Portland cement clinker production. After waste materials characterization, laboratory scale clinker production was researched by mixing of coal slurry wastes and cement raw mixture with different proportions. To prove the laboratory results, industrial scale clinker was produced with same mixing ratios. Results showed that obtained clinker products with adding coal slurry waste were supplied the required cement standard limit values.

2. Material and method

Coal slurry waste (CSW) is taken from Omerler Coal Preparation Plant of Turkish Coal Enterprises. Omerler Coal Plant produces approximately 200 tons coal slurry waste per year. The coal slurry has 80 % wt. humidity and 2400 kcal/kg calorific value. It is heated in drying oven to reduce humidity value from 80 % wt. to 10 wt. %. Then, dried coal slurry waste was transferred to CIMSA Inc. for laboratory and industrial scale clinker production.

3. Results and discussion

3.1. Laboratory Scale Clinker Production

In laboratory scale clinker production, CSW was added 2 wt. % and 3 wt. % amounts into the raw meal composition. The chemical composition of raw meal and CSW for Portland cement clinker production, mineralogical compositions and grain size distributions are given in Table 1, Table 2 and Table 3, respectively.

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

Compound	Raw Meal (%)	Coal Slurry Waste (%)
SiO_2	12.96	42.7
Al_2O_3	3.38	12.8
Fe_2O_3	2.13	5.2
CaO	42.90	1.5
MgO	1.22	3.1
Na_2O	0.26	0.2
K_2O	0.45	1.4
TiO_2	0.25	0.5
SO_3	0.03	1.4
P_2O_5	0.07	0.5
MnO	0.0395	0.08
Cr_2O_3	0.024	0.07
Cl	0.011	0.02
LOI	35.5	30.3
Humidity (%)	0.5	2.20
$CaCO_3$ (%)	77.2	2.79

Table 2. Mineralogical composition of raw materials.

Raw Meal	Coal Slurry Waste
Calcite, $CaCO_3$	Quartz, SiO_2
Quartz, SiO_2	Kaolinite, $Al_2Si_2O_5(OH)_4$
Dolomite, $CaMg(CO_3)_2$	Magnesite, $MgCO_3$
Feldspar, $(K,Na)AlSiO_3O_8$	Dolomite, $CaMg(CO_3)_2$
Chlorite, $(Mg,Al,Fe)_6(Si,Al)4O_{10}(OH)_8$	Clinochlore, $(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$
Muskovite, $(K,Na)Al_2(Si,Al)_4O_{10}(OH)_2$	Illite, $(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$
	Anhydrite, $CaSO_4$

Table 3. Grain size distribution of raw materials.

Sieve Opening Size, µm	Acceptable Ranges of % Passing by Mass	
	Raw Meal	Coal Slurry Waste
416	98.39	100
200	89.97	98.9
125	79.99	97.74
90	74.61	95.55
63	66.89	91.62
53	64.55	90
45	62.36	87.71
32	56.68	79.76
11	44.45	50
2	15.15	10

The burnability of a raw mix for Portland cement production can be defined as the case with which free calcium oxide (free CaO) derived from limestone calcination reacts in the kiln with silicon, aluminum and iron oxide [10]. The burnability test was carried out in an electrical furnace kiln according to the following regime: first step 100ºC for 24 h ; second step at 1000ºC 30 min and finally 30 min up to 1400ºC, 1450ºC and 1500ºC. The burnability index (B.I) is calculated by the Eqs. (1);

$$\text{Burnability Index (B.I)}=100*\frac{\left(\frac{\text{Free CaO}_{1400ºC}}{3.6}+\frac{\text{Free CaO}_{1450ºC}}{2.6}+\frac{\text{Free CaO}_{1500ºC}}{1.6}\right)}{3} \quad \text{Eq. (1)}$$

Calculated burnability index was evaluated according to the given values. If,

B.I. $\leq$ 83 Easy burnability
83 $\leq$ B.I. < 120 Normal burnability
B.I. $\geq$ 120 Hard burnability

In order to see the effect of CSW incorporation, the burnability of 3 mixtures were compared. The first mixture (reference raw meal) was based on a currently used at the industrial scale in cement production. The second and the third mixtures are prepared by using 2 wt. % and 3 wt. % CSW addition to the reference raw meal.

Burnability test results are given in Table 4. It can be seen that the addition of 2 wt. % and 3 wt. % CSW to the raw meal make the burnability easier than reference raw meal.

Table 4. Burnability test results.

		Raw Meal (Reference)	Coal Slurry Waste	
Raw Meal (%)		100.00	98	97
CSW (%)		--	2	3
	1400ºC	3.70	1.84	1.55
Free CaO	**1450ºC**	2.97	1.70	1.43
	1500ºC	2.16	1.44	0.83
B.I.		117.34	68.83	49.98
Result		Normal Burnability	Easy Burnability	Easy Burnability

3.2. Industrial Scale Clinker Production

Industrial scale clinker production studies are carried out in CIMSA Inc. Eskişehir Company. Turkish Coal Enterprises Company sent approximately 500 tons of dried CSW to CIMSA. The chemical composition of each raw material is shown in Table 5.

Table 5. The chemical composition of raw materials.

Compound	**Limestone (%)**	**Shale (%)**	**Sand (%)**	**Bauxite (%)**	**Iron source (%)**	**Raw Materials Mix (%)**
SiO_2	3.16	44.40	82.57	10.30	28.4	15.58
Al_2O_3	0.65	11.17	5.53	50.90	5.71	3.66
Fe_2O_3	0.29	9.93	5.10	24.02	54.63	1.81
CaO	53.15	15.20	0.58	3.03	0.70	42.24
MgO	0.33	6.10	0.28	0.65	0.57	1.32
SO_3	0.09	0.14	0.04	0.28	0.28	0.029
Cl^-	0.006	0.004	0.001	0.001	0.002	0.001
Na_2O	0.014	1.46	0.032	0	0.04	0.13
K_2O	0.43	0.30	0.64	0.44	0.30	0.44
LOI	41.9	10.8	5.1	10.2	9.4	34.6
TOTAL	**100.02**	**99.504**	**99.873**	**99.821**	**100.032**	**99.81**
H_2O	2.4	6.5	11.5	4.7	13.6	5.6

After chemical composition determination of raw materials, industrial raw meal and clinker productions were done respectively.

3.3. Raw Meal Production

In raw meal production, raw mix, limestone and CSW materials were used in the average percentages as given in Table 6.

Table 6. Raw meal mix composition (wt. %).

Limestone+Clay (Mix) (%)	**Limestone (%)**	**Feldspar (%)**	**Iron source (%)**	**Coal Slurry Waste (%)**
87.17	11.83	0	0	1.00
79.20	15.58	2.40	0.72	2.10
78.84	15.24	2.31	0.56	3.05

The chemical compositions of CSW containing raw materials are given in Table 7. LSF, SR and AR values are calculated by using Eq. (2), Eq. (3) and Eq. (4):

$$LSF\ (\%) = \frac{(CaO)}{2.8\ (SiO_2)+1.18\ (Al_2O_3)+0.65\ (Fe_2O_3)} \quad \text{Eq. (2)}$$

$$SR\ (\%) = \frac{(SiO_2)}{(Al_2O_3+Fe_2O_3)} \quad \text{Eq. (3)}$$

$$AR\ (\%) = \frac{(Al_2O_3)}{(Fe_2O_3)} \quad \text{Eq. (4)}$$

Table 7. The chemical composition of CSW containing raw mixture (%).

Compound	Limestone + Clay (Mix)	Limestone	1 wt. % CSW	2 wt. % CSW	3 wt. % CSW
			25 wt. % CSW + 75 wt. % Limestone	50 wt. % CSW + 25 wt. % Feldspar + 25 wt. % Iron Source	70 wt. % CSW + 20 wt. % Feldspar + 10 wt. % Iron Source
SiO_2	15.45	1.15	10.57	42.79	42.69
Al_2O_3	3.68	0.49	3.32	15.59	16.48
Fe_2O_3	2.45	0.15	1.88	17.56	11.66
CaO	42.15	53.51	41.42	3.27	3.75
MgO	1.48	0.41	0.56	0.52	0.53
K_2O	0.45	0.06	0.39	2.00	2.02
Na_2O	0.23	0.03	0.02	0.76	0.61
SO_3	0.03	0.01	0.02	0.08	0.09
LSF	**85.68**	**1373.57**	**119.28**	**2.18**	**2.56**
SR	**2.52**	**1.80**	**2.03**	**1.29**	**1.52**
AR	**1.50**	**3.27**	**1.76**	**0.89**	**1.41**
Equivalent Alkaline	**0.53**			**2.07**	**1.93**

Limestone and mix (limestone+clay) components are crushed to reduce particle size 0-50 mm and mix homogenously for sending to rotary kiln in the compositions as given in Table 6.

3 different kinds of CSW containing raw meal produced and chemically analyzed as given in Table 8 and compared commercial CIMSA Inc. Factory raw meal results.

Table 8. The chemical compositions of CSW containing raw meal.

Compound	Raw Meal			CIMSA Inc. Factory Raw Meal (%)
	1 wt. % CSW	2 wt. % CSW	3 wt. % CSW	
Al_2O_3	3.40	3.17	3.31	3.07
CaO	43.13	42.99	43.02	42.81
Cl^-	0.007	0.007	0.006	0.007
Fe_2O_3	2.24	2.28	2.29	2.09
K_2O	0.41	0.45	0.45	0.47
MgO	1.29	1.53	1.28	1.55
Na_2O	0.16	0.28	0.2	0.26
SiO_2	12.76	12.38	12.56	12.72
SO_3	0.34	0.29	0.32	0.14
LOI	35.3	35.8	35.7	35.90
TOTAL	**99.037**	**99.17**	**99.14**	**99.01**
Lime Saturation Factor (LSF)	104.65	107.8	106.1	105.46
Silica Ratio (SR)	2.26	2.27	2.24	2.46
Alumina Ratio (AR)	1.52	1.39	1.45	1.47

3.4. Clinker Production

CSW containing raw meal compositions are used in clinker production. In clinker production, the feed rate of raw meal to rotary kiln is 130-140 ton/hour, calcination ratio 94-96 %. The photos for production of CSW containing clinkers are given as below (Fig.1-2).

Fig.1. Clinker production in rotary kiln.

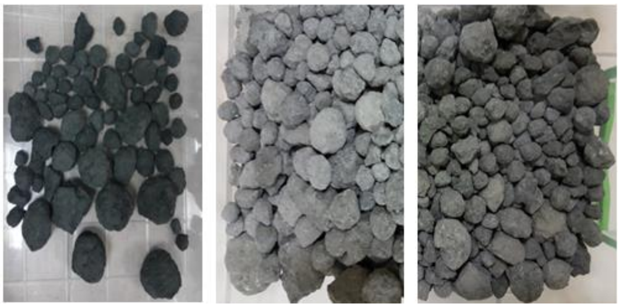

Fig.2. Clinker samples produced from 1 wt. %, 2 wt. % and 3 wt. % CSW containing raw meal, respectively.

Clinker quality control tests are done according to the density determination. In density determination 2 kinds of sieves with 5.6 mm and 12.2 mm sizes are used. In general, density values are desired between 1260-1280 g/l. If this value is less than 1200 g/l, it can be said that, clinker indicates free lime. Density measurement was illustrated in Fig.3.

Fig.3. Sieve analysis for density measurement.

The composition of the clinker was adjusted by varying the lime saturation factor (LSF) as well as the alumina and silica ratios (AR and SR, respectively). In Portland type, these parameters can be varied from 100 to 103 for LSF, 2.35 to 2.45 for SR and 1.40 to 1.50 for AR. In this work, the values of above parameters were assumed with using Eq. (3), Eq. (4) and Eq. (5).

The composition of the clinker was calculated to provide the same phases as the main phases of a real Portland clinker. Using the Bogue's calculation, the amount of C_3S, C_2S, C_3A and C_4AF were determined according to the ASTM C 150-92 [11]. The main phases are given in Table 9 with their abbreviated symbols. In Portland cement production, C_3S phase is reported to be the main compound.

Table 9. Main clinker phases and abbreviations.

Abbreviation	**Compound**	**Formula**
C_3S (Alite)	Tricalcium silicate	$3CaO.SiO_2$
C_2S (Belite)	Dicalcium silicate	$2CaO.SiO_2$
C_3A (Aluminate)	Tricalcium aluminate	$3CaO.Al_2O_3$
C_4AF (Ferrite)	Tetracalcium aluminoferrite	$4CaO.Al_2O_3.\ Fe_2O_3$

CSW containing clinker chemical and physical analysis results are given in Table 10 and main phases are given in Table 11.

Table 10. The chemical and physical analysis results of CSW containing clinker.

Compound	Clinker			CIMSA Inc. Factory Values (%)
	1 wt. % CSW	2 wt. % CSW	3 wt. % CSW	
CaO	65.50	65.67	65.74	65.94
SiO_2	21.25	20.91	21.21	21.23
Al_2O_3	5.63	5.39	5.46	5.25
Fe_2O_3	3.40	3.36	3.40	3.44
MgO	2.00	2.49	1.96	2.18
K_2O	0.63	0.62	0.65	0.66
Cl	0.006	0.007	0.005	0.008
Na_2O	0.25	0.38	0.32	0.28
TiO_2	0.15	0.20	0.20	
SO_3	1.08	0.81	1.07	1.00
Undefined	0.10	0.16	0.19	
TOTAL	**99.99**	**99.84**	**100.0**	**99.99**
LSF	95.81	97.9	96.6	97.40
SR	2.35	2.39	2.39	2.44
AR	1.60	1.6	1.61	1.53
Free lime	1.93	2.34	2.10	1.65
Density (g/l)	1230	1230	1210	1250

Table 11. The main phases of CSW containing clinker.

Main phases	Clinker			CIMSA Inc. Factory Values (%)
	1 wt. % CSW	2 wt. % CSW	3 wt. % CSW	
C_3S	57.53	57.72	64.76	55-65
C_2S	19.80	16.43	11.98	11-20
C_3A	8.16	8.6	8.72	7-9
C_4AF	10.37	10.25	10.36	10-15

4. Conclusion

From the laboratory and industrial clinker studies, it can be concluded that the incorporation of Turkish Coal Enterprises coal slurry waste in clinker production is technically viable and does not present appreciable environmental effects. The main conclusions of the work are summarized below.

1. Coal slurry waste can be evaluated as raw materials for Portland cement clinker according to the chemical composition analysis.
2. Burnability index test results showed that the addition of 2 wt. % and 3 wt. % CSW to the raw meal make the burnability easier than reference raw meal.
3. According to the chemical composition of the clinker obtained, the CSW with up to 3 wt. % addition in clinkers show acceptable phase compositions and many of the major phases which are comparable with CIMSA Portland cement clinker.
4. High humidity and volatile material content prevents the usage of CSW in different sectors. So that, it needs to dehydration process for a kind of application. In cement industry, CSW humidity value has to lower than 10 %.
5. The other important parameter is high volatile material content (30 %) in CSW because of carbon content. In cement production, high volatile material content reduce the capacity of clinker production because of volume decreasing during the raw meal calcination stage.

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