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Utilization of Incineration Waste Ash Residues in Portland Cement Clinker

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MSWI (municipal solid waste incineration) ash and sewage sludge ash are used in part as raw materials for cement clinker production by taking advantage of the high contents of SiO_2, Al_2O_3 and CaO. It is necessary to establish a material utilization system for the incineration waste ash residues instead of disposing these ashes into landfill. This paper is aimed to study the feasibility of replacing clinker raw materials by waste ash residue for cement clinker production. Sewage sludge ash, MSWI bottom ash and MSWI fly ash are the three main types of ashes being evaluated. The ashes were mixed into raw mixture with different portions to produce cement clinker in a laboratory furnace at approximately 1400 ^{o}C. X-ray diffraction and X-ray florescence techniques were used to analyze the phase chemistry and chemical composition of clinkers in order to compare these ash-based clinkers with commercial Portland cement clinker.

1. Introduction

The generation of solid waste has been rapidly increasing due to the growth of population, rising of living standards and industry growth around the world. Thousands of million tons of municipal solid waste (MSW) are produced every year. Waste management and utilization strategies are the main concern in many countries. Usually, incineration is a common technique for treating waste as it can reduce 70% by mass and reduce up to 90% by volume of waste as well as providing recovery of energy from waste to generate electricity. Incineration ash contain toxic substances such as dioxin, heavy metals and chloride, proper treatment should be consider for utilizing it. A possible technology is to fix the toxic substance in incineration ash into cement clinker by replacing part of the clinker raw material (Chen and Juenger, 2009). This process can be sustainable if waste ash is fully utilized into clinker.

Portland cement clinker is produced from high temperature firing and grinding of mineral deposits such as limestone, sand and copper slag. It contains four primary phases: Ca_3SiO_5 (C_3S), Ca_2SiO_4 (C_2S), $Ca_3Al_2O_6$ (C_3A), $Ca_4Al_2Fe_2O_{10}$ (C_4AF). Calcium oxide-bearing waste materials such as fly ash from municipal solid waste incineration can reduce CO_2 emissions from Portland cement manufacturing by reducing the use of limestone, replacing it with materials high in CaO rather than $CaCO_3$ (Chandra, 1997).

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2. Experimental

2.1 Material

Bottom ash (BA) and fly ash (FA) of municipal solid waste is collected from the co-combustion pilot plant in Green Island Cement (GIC) Ltd. The sewage sludge is collected from Stone cutter's Island waste water treatment plant and heated in muffle furnace in 850 ^{o}C for two hours to become sewage sludge ash (SSA). The chemical compositions of raw materials for clinker production are shown in Table 1.

Table 1 Chemical compositions of raw materials (wt %)

	BA	*FA*	*SSA*	*Limestone*	*Sand*	*Copper Slag*	*Pulverized-fuel Ash*
CaO	30.3	70.3	12.9	52.0	0.8	1.0	5.8
SiO_2	21.5	1.1	16.3	5.7	70.0	6.7	48.0
Fe_2O_3	7.4	0.3	14.9	0.8	15.0	1.4	26.1
Al_2O_3	6.9	0.4	7.9	0.3	5.0	89.7	10.4
SO_3	2.1	2.1	19.5	0.2	0.0	0.8	0.2
Cl	0.8	1.8	3.2	0.4	0.0	0.0	0.0
K_2O	0.6	0.2	1.7	0.2	2.5	0.3	0.8
Na_2O	2.1	0.3	6.8	0.0	0.0	0.6	0.2
MgO	1.1	0.4	3.2	0.3	0.9	0.8	1.0
P_2O_5	12.9	0.1	9.2	0.1	0.5	0.4	1.4
LOI	11.7	22.8	3.0	40.4	8.6	0.2	4.5

2.2 Raw mix

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 in raw meal after the heating process was calculated (Hewlett, 1998).

Bogue's equations:

$$C_3S\,(\%) = 4.071(CaO) - 7.602(SiO_2) - 6.718(Al_2O_3) - 1.43(Fe_2O_3) \quad (1)$$
$$C_2S\,(\%) = 2.87(SiO_2) - 0.754(C_3S) \quad (2)$$
$$C_3A\,(\%) = 2.65(Al_2O_3) - 1.692(Fe_2O_3) \quad (3)$$
$$C_4AF\,(\%) = 3.043(Fe_2O_3) \quad (4)$$

In order to ensure the clinker quality, the following composition parameters are controlled. Typically, the clinker controlled at the lime saturation factor (LSF) values around 0.92 to 0.96, hydration modulus (HM) values around 1.7 to 2.4, silica ratio values around 2.35 to 2.6 and alumina ratio (AR) values around 1.2 to 1.9.

$$LSF\,(\%) = \frac{(CaO)}{2.8(SiO_2) + 1.18(Al_2O_3) + 0.65(Fe_2O_3)} \quad (5)$$

$$HM\,(\%) = \frac{(CaO)}{} \quad (6)$$

$$\overline{(SiO_2 + Al_2O_3 + Fe_2O_3)}$$

$$SR\ (\%) = \frac{(SiO_2)}{(Al_2O_3 + Fe_2O_3)} \quad (7)$$

$$AR\ (\%) = \frac{(Al_2O_3)}{(Fe_2O_3)} \quad (8)$$

Table 2: Mixture composition of Ash clinkers (wt %)

Type	*Limestone*	*Sand*	*Copper Slag*	*Pulverized-fuel Ash*	*Waste Ash*
BA2C	74.50	15.03	2.30	6.16	2.00
BA4C	73.42	14.42	2.05	6.11	4.00
BA6C	72.35	13.80	1.80	6.05	6.00
BA8C	71.63	13.72	0.97	5.68	8.00
SSA2C	75.70	15.68	1.29	5.33	2.00
SSA4C	74.84	15.04	0.78	5.34	4.00
SSA8C	72.98	14.26	0.23	4.54	8.00
FA2C	73.36	15.29	2.29	7.06	2.00
FA4C	71.18	15.57	2.30	6.95	4.00
FA8C	67.22	16.62	1.59	6.56	8.00

For the clinker production, a high temperature muffle furnace was used. First of all, the 150 g of raw mixture (Table 2) was put into an alumina crucible and loaded into the furnace at 900 °C. The preheating process of the raw meal was 15 min. Then the temperature of the furnace was raised to 1400°C with a heating rate 10 °C /min for the calcination process. Finally, the temperature of the furnace was maintained at 1400 °C for 90 minutes for the sintering and clinkerization process. The crucible was taken out from furnace immediately after the heating process and cooled down to room temperature. After the clinker production, the clinkers were ground to ASTM 200 mesh for analysis and the analysis results were compared to the properties of standard Ordinary Portland cement (OPC) clinker.

2.3 Analysis

A JEOL JSX-3201Z X-ray Fluorescence Spectrometer was used for the qualitative elemental composition determination. The crystalline phase of clinker samples were analyzed by a Philips Powder X-ray diffractometer PW1830 using CuK_{α} radiation and identified from the JCPDS-ICDD database. Finally, the Toxicity characteristic leaching procedure was performed according to USEPA Method 1311. The heavy metal contents in the TCLP extract of lab-clinkers were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using Perkin Elmer Optima 3000XL.

3. Results and discussion

3.1 XRF analysis on clinker compositions

The chemical compositions and clinker phase compositions are shown in Table 3. The MSWI bottom ash clinkers show acceptable phase compositions which are comparable with OPC. The effective C3S (free lime content deducted) of bottom ash clinkers is varies from 37 to 47 wt%. The free lime content in BA8C is quite high, it may due to the phosphorus content and metal ions in bottom ash that hinder the formation of C_3S. Sewage sludge ash clinkers show relatively good correlation with OPC when 2 wt% of ash is added. However, the effective C_3S value drops to 19.3 wt% when the ash addition increased to 8 wt%; extremely high free lime content (8.79 wt%) is found in SSA8C indicated that decomposition of C_3S or formation of other compounds may occur in this situation. High phosphorus content and sulfur trioxide content in SSAC may suppress the formation of the main phases, thus, the phases must have been influence by the incorporation of sewage sludge ash. Pre-treatment of sewage sludge ash may be an option for the removal of influence materials and enhance its feasibility for clinker production. MSWI fly ash clinkers do not show good correlation with OPC, the LSF of fly ash clinkers is relatively low which may lead to insufficient of CaO for alite formation, this problem could be solve by modifying the raw mix composition and by addition of raw material.

Table 3 Chemical and phase composition of Ash clinkers (wt %)

Type	*OPC*	*BA2C*	*BA4C*	*BA6C*	*BA8C*	*FA2C*	*FA4C*	*FA8C*	*SSA2C*	*SSA4C*	*SSA8C*
Al_2O_3	5.13	5.53	5.53	5.56	5.38	5.34	5.57	5.83	4.89	4.75	4.55
SiO_2	23.3	22.6	22.4	22.2	23.0	23.9	23.8	24.0	23.7	23.8	23.0
CaO	66.2	65.0	64.9	64.5	64.8	64.9	64.6	64.1	65.2	65.2	65.6
Fe_2O_3	3.53	3.74	3.62	3.71	3.42	3.68	3.65	3.61	3.21	3.54	2.80
P_2O_5	0.17	0.40	0.57	0.94	1.27	0.28	0.36	0.40	0.58	0.92	1.58
SO_3	0.27	0.13	0.18	0.19	0.23	0.12	0.14	0.24	0.18	0.30	0.93
Cl	0.00	0.02	0.02	0.02	0.03	0.03	0.04	0.05	0.01	0.01	0.01
MgO	0.83	0.56	0.60	0.54	0.63	0.71	0.61	0.70	0.83	0.74	0.87
Free lime	0.61	0.98	1.04	1.23	2.31	0.49	1.41	1.55	2.17	3.82	8.79
Total Alkali	0.23	0.80	0.78	0.98	0.94	0.34	0.36	0.61	0.52	0.34	0.61
Effective C_3S	50.0	46.4	46.6	46.0	37.9	39.5	33.6	27.0	38.9	30.9	19.3
C_2S	27.3	26.4	25.6	24.7	29.7	36.9	38.1	43.2	31.4	32.6	22.4
C_3A	7.62	8.33	8.54	8.44	8.48	7.91	8.59	9.34	7.51	6.61	7.32
C_4AF	10.8	11.4	11.0	11.3	10.4	11.2	11.1	11.0	9.8	10.8	8.5
LSF	89.8	90.2	90.5	90.8	88.8	86.0	85.6	83.8	88.0	87.4	91.7
HM	2.07	2.04	2.05	2.05	2.04	1.97	1.96	1.92	2.05	2.03	2.16
SR	2.69	2.43	2.45	2.39	2.61	2.65	2.57	2.54	2.92	2.87	3.13
AR	1.45	1.48	1.53	1.50	1.57	1.45	1.53	1.61	1.52	1.34	1.63

3.2 XRD patterns of clinkers

The clinkers produced with MSWI bottom ash are shown in Figure 1 together with the pattern of Ordinary Portland Cement. For MSWI bottom ash clinkers, many of the major phases are found and comparable with Ordinary Portland Cement. However, for sludge ash clinker and MSWI fly ash clinker, most of the major phases are absent and strong peak of C_2S is observed. It may due to high sulfur trioxide content and metal ions in sewage sludge ash that suppress and hinder the phase formation.

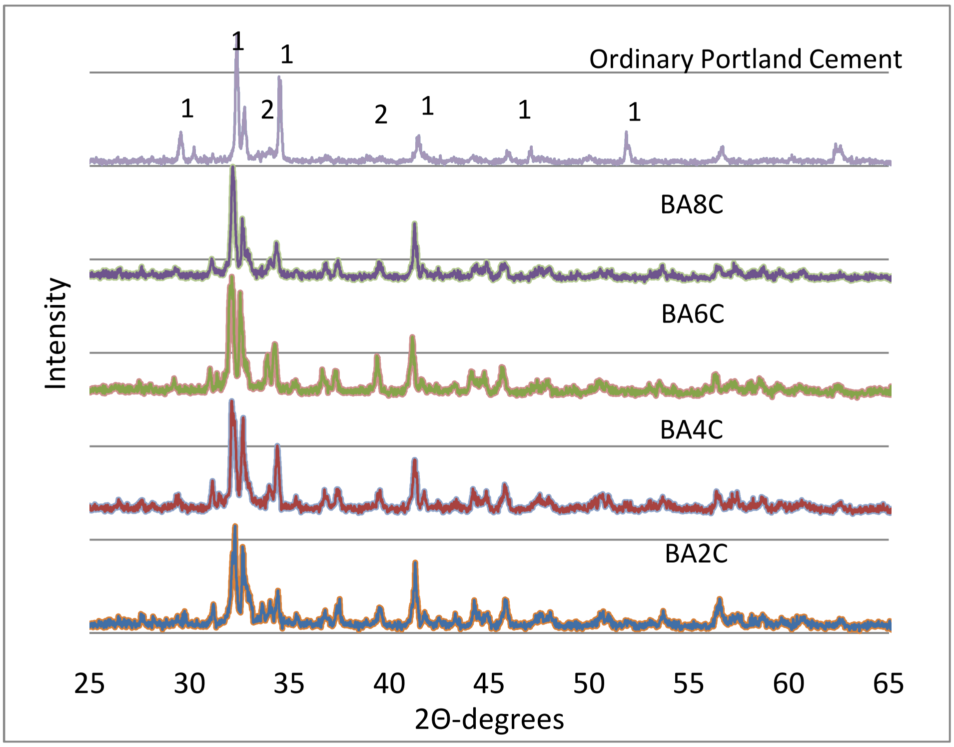

Figure 1: X-ray diffraction patterns of clinkers; 1=C_3S, 2=C_2S.

3.3 TCLP

Table 4 TCLP results of ash clinkers (ppm)

	FAC8	SAC8	BAC8	Standard GIC Clinker	TCLP Limit
Ag	-	-	-	0.06	50
As	-	-	-	0.004	50
Ba	2.19	0.6	3.841	1.327	1000
Be	-	-	-	-	10
Cd	-	-	-	-	10
Cr	-	-	2.4015	0.263	50
Cu	-	-	-	-	250
Hg	-	-	-	0.001	1

Ni	-	-	-	-	250
Pb	-	1.121	3.412	-	50
Sb	-	-	-	-	150
Se	-	-	-	-	1
Sn	-	-	-	-	250
Tl	1.17	0.431	0.872	0.056	50
V	-	-	-	-	250
Zn	-	-	-	0.065	250

The TCLP of ash clinkers are shown in Table 4, all of them are well below the TCLP disposal limits. The results show that most of the heavy metals are concentrated and stabilized in the clinker matrix with low leachability. Comparing with commercial clinker product, the ash clinkers have similar leaching behavior. Therefore, the waste ash could be used as cement raw material with excellent leaching behavior comparable to normal clinker product.

4. Conclusion

MSWI (municipal solid waste incineration) bottom ash and fly ash and sewage sludge ash are evaluated as raw materials for Portland cement clinker according to the chemical composition analysis. According to the phase and chemical composition of the clinker obtained, the MSWI bottom ash with up to 6 % addition in clinkers show acceptable phase compositions and many of the major phases which are comparable with ordinary Portland cement clinker. High phosphorus content and sulfur trioxide content in sewage sludge ash may suppress the formation of the main phases. Fly ash clinkers may lead to insufficient CaO for alite formation. A proper pre-treatment would be required to use fly ash or sewage sludge ash. The heavy metals are concentrated and stabilized in the clinker matrix with low leachability. Further tests on the physical properties of the clinkers should be taken to fully understand the feasibility of ash based clinker.

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