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Copper slag: An alternative raw material for the cement industry

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ABSTRACT

Copper slag is a by-product obtained during matte smelting and refining of copper. One of the greatest potential applications for reusing copper slag is in cement and concrete production. The use of copper slag in cement and concrete provides potential environmental as well as economic benefits for all related industries, particularly in areas where a considerable amount of copper slag is produced. The present research paper assesses the characteristics of copper slag and its utilization on clinkerization and cement manufacturing process. The paper is divided into two parts as (i) using copper slag as a raw mix component. (ii) using copper slag as a cementious material for manufacturing of OPC (ordinary portland cement). Characterization of copper slag indicates that it contains constituents compatible with manufacture of cement, along with the impurities of copper. The phase composition determined by XRD indicates that the quality of clinker is good and is capable of yielding good quality cement. As the copper slag is found to contain an appreciable amount of Fe_2O_3 (~58.96%) and SiO_2 (~32.26%), its extent of utilization as a raw mix component depends on the content of iron and silica in the parent limestone deposit. Copper slag also can be gainfully utilized up to 5% in the manufacture of OPC as supplementary cementious material.

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1. INTRODUCTION

While producing copper, the anode, a slag with rich iron and moderate silica content is also generated. Production of one tonne of copper generates, approximately 2.2-3 tons copper slag. In India, the amount of copper slag produced is about 13 × 10^5 ton per annum and accumulated stocks are about 40 × 10^5 ton. The slag also has latent hydraulic properties. One of the copper plants in India having copper smelter with a capacity of 1 × 10^5 ton per annum commenced production in May 1998. In 2001 the capacity was further increased to 1.5 × 10^5 ton per annum. The production capacity has been further increased to 5 × 10^5 ton per annum in two more stages. The approximate generation of copper slag is around 8 × 10^5 ton per annum as reported. From the chemical composition of copper slag, it is observed that the material is suitable for utilization in cement manufacturing (Supekar, 2007).

2. MATERIALS AND METHODS

2.1. Properties & characterization of copper slag

Copper slag is used as an alternative raw material for clinker & cement making. The physical and mechanical properties viz. Color, Grain shape, Bond's work index, Specific gravity, Bulk density and pH etc of copper slag were determined and the results obtained are given in Table 1.

Chemical analysis of the Copper slag carried out using XRF is given in Table 2. This was done

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Table 1. Physical & Mechanical properties of Copper slag.

BWI kWh/ton	Colour	Grain Shape	Sp.Gravity	pH	B.D(g/cc)
19.34	Black glossy	Multi faceted	3.71	5.70-6.5	1.93

Table 2. Chemical composition of Copper Slag (Wt%).

GOI	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	CuO	Na_2O	K_2O
5.63	32.26	58.96	4.92	1.00	0.9	0.50	0.65	0.44	1.03

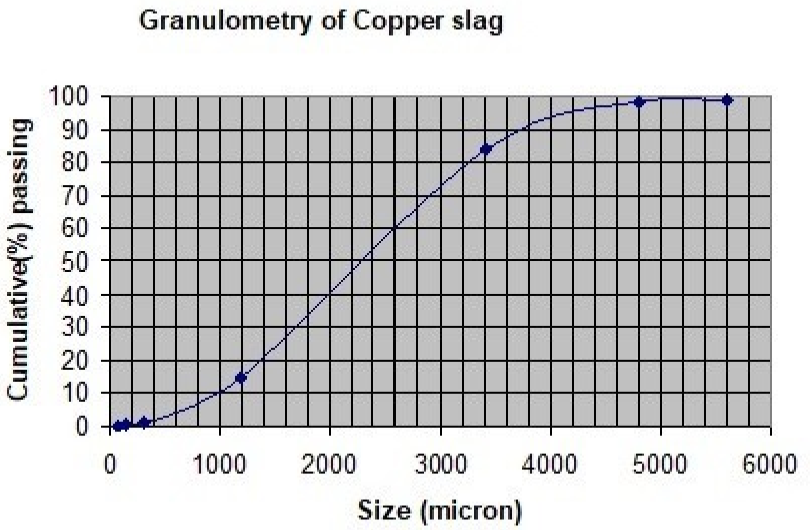

Fig. 1. Granulometry of Copper slag.

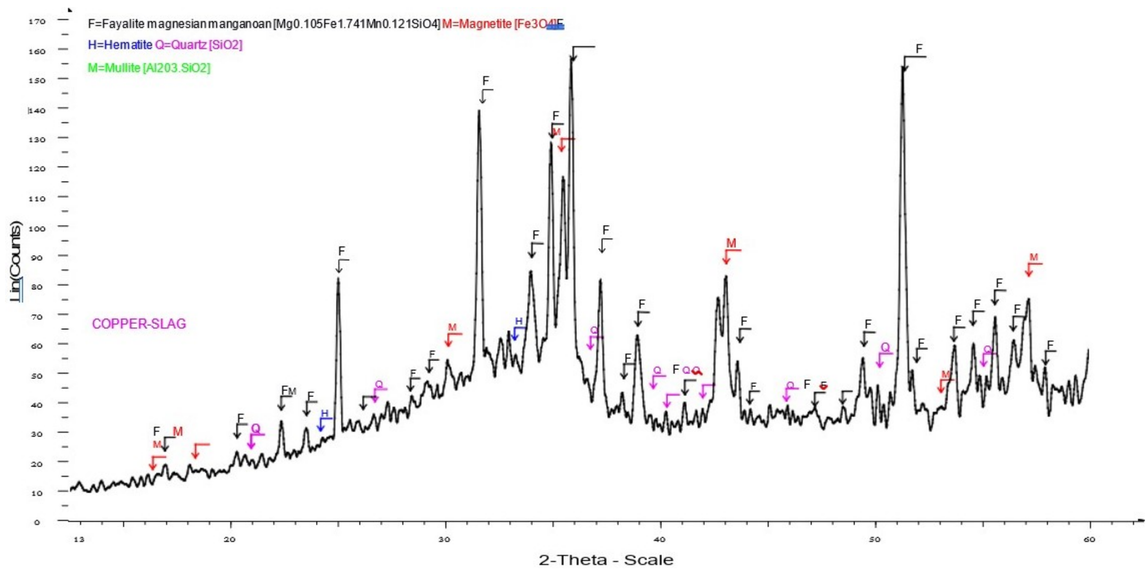

Fig. 2. X-ray diffractogram of copper slag.

primarily to understand its constituents and suitability for appropriate design of raw mix (Fig. 1).

The X-ray diffraction pattern of copper slag is shown in Fig. 2.

Diffractogram records the presence of the major mineral phases like Fayalite magnesian manganon [$MgO \cdot 105FeO \cdot 741MnO \cdot 121SiO_4$] , Magnetite [$Fe_3O_4$], Hematite[$Fe_2O_3$], Quartz [$SiO_2$], Mulllite [$Al_2O_3 \cdot SiO_2$]. The X-ray diffraction pattern indicates presence of a hump around 20–40°, which might be on account of glassy or amorphous phase. Glassy or amorphous mineral phases are more reactive than crystalline minerals. Apart from this, the minerals found indicate that the material is rich in Fe_2O_3 and SiO_2.

Scanning electron microscope with energy dispersive x-ray is used to know the microstructure and chemical composition of copper slag. From spot anal-

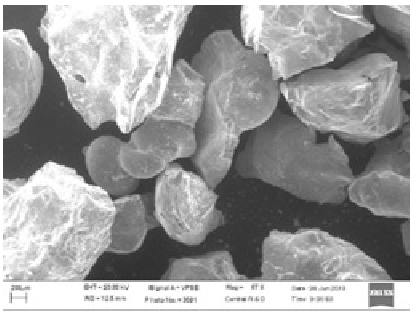

Fig. 3. Microstructure of Cu- Slag.

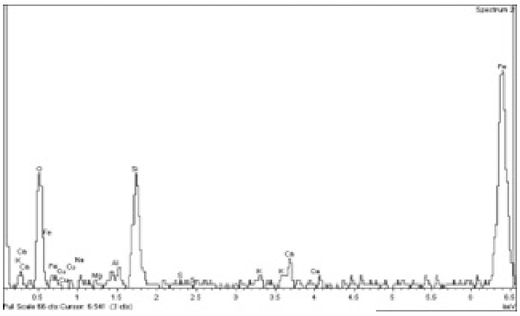

Fig. 4. Elemental analysis of Cu- Slag.

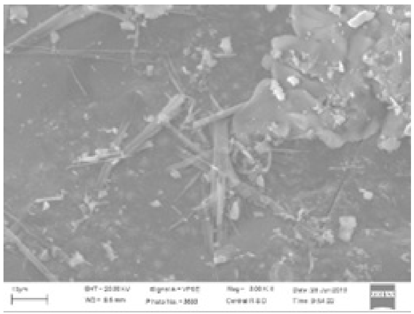

Fig. 5. Presence of Mullite.

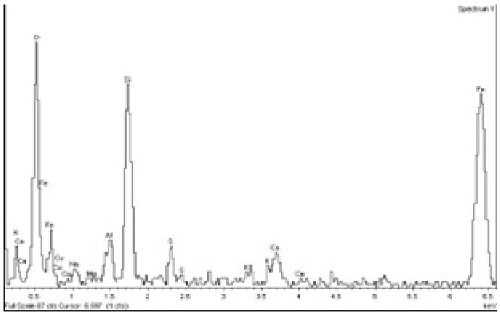

Fig. 6. Spot Analysis of Mullite.

ysis data it is observed that copper slag is consisting of iron and siliceous matter in nature. It is mostly crystalline nature during formation (Figs. 3–6).

2.2. Using Copper slag as a raw mix component

Different types of raw material like limestone, bauxite, Iron ore, coal ash and copper slag are used for raw mix design. Two types of raw mixes were prepared i.e. with and without copper slag. The raw mix constituents were thoroughly blended and ground to a fineness of 19.80% residue on 90µm and 1.08% residue on 212 µm Nodules of about 1.0 cm in diameter were prepared and dried in an oven at 105 ± 5°C for 2 hours before subjecting them to burnability studies. The nodules were fired at 1350°C, 1400°C and 1450°C respectively at a heating rate of 20°C/min with a retention time of 30 mins. The fired nodules were then taken out at 1200°C from the furnace and air quenched. The Clinkers CL-1 & CL-2 prepared respectively were finely ground and subjected to free lime determination by Ethylene glycol method. The free lime content determined in corresponding laboratory prepared clinkers and the lime combinability values are given in Fig. 7.The chemical analysis of the various materials viz. Limestone, Iron ore, Bauxite, imported coal ash and pet coke which are used for raw mixes are given in Table 3.

2.3. Raw mix design with & without copper slag

Two raw mixes were designed with the following raw materials (Table 4) keeping the coal ash absorption level at 0.88% on clinker basis, considering 60% South African coal and 40% Pet coke firing. The proportions of raw materials are given in Table 4.

2.4. Utilization of Copper Slag as a performance improver

An attempt has also been made to assess the technical suitability of Copper Slag as a performance improver for the manufacture of OPC. SO3 content in all set of samples are kept 2%. Summary of analyzed results are as given in Table 5.

The strength data shows that 1-, 3-, 7- and 28-days strength is at par with OPC 43 grade.

3. DISCUSSION

While designing the raw mixes, efforts were made to keep the level of utilization of copper slag to the maximum possible extent. However, due to presence of high Fe_2O_3 (58.96%) and appreciable amount of SiO_2 (32.26%), its proportion could not be increased beyond 1.0%. Further increase of copper slag lead to decrease in LSF of raw mix and resultant clinker. The results of free lime determination (Table 6) indicate

Table 3. Chemical composition of various materials used in raw mix (Wt%).

S N	Raw Material	LOI	SiO_2	Al2O3	Fe_2O_3	CaO	MgO	Na_2O	Ka_2O	SO_3
1	Avg grade L.S.	35.33	13.92	2.39	1.98	44.05	0.65	0.05	0.21	0.06
2	Iron Ore	3.18	9.95	6.47	78.47	0.57	1.01	00	0.10	00
3	Bauxite	21.60	18.59	43.26	8.56	2.91	0.48	00	0.18	0.02
4	Copper Slag	5.63	32.26	4.92	58.96	1.00	0.90	0.44	1.03	0.50
5	S.A. Coal	---	43	25.80	4.25	23.09	1.36	0.29	0.38	1.75
6	Petcoke Ash	---	33.61	15.12	9.13	40.20	1.23	0.13	0.17	18.00

Table 4. Raw mix design.

Parameters	**Raw Mix-1** (Control – No copper slag)		**Raw Mix-2** (1.0% Copper Slag)	
	RM	Clinker	RM	Clinker
LSF	0.94	0.92	0.93	0.91
SM	2.20	2.18	2.33	2.31
AM	1.19	1.21	1.25	1.28
C_3S%	-	50.06	-	48.81
C_2S%	-	24.11	-	25.98
C_3A%	-	6.82	-	7.11
C_4AF%	-	13.60	-	12.66
Liquid%	-	26.99	-	26.07
Heat of Reaction(Kcal/Kg)	-	411.74	-	410.27

Table 5. Different proportions of raw materials in raw mix (Wt%).

S N	**Raw Mix**	**Limestone**	**Iron Ore**	**Bauxite**	**Cu- Slag**
1	RM-1 (Control)	96.5	1.00	2.50	**0**
2	RM-2 (With Copper Slag)	96.60	0	2.40	**1.0**

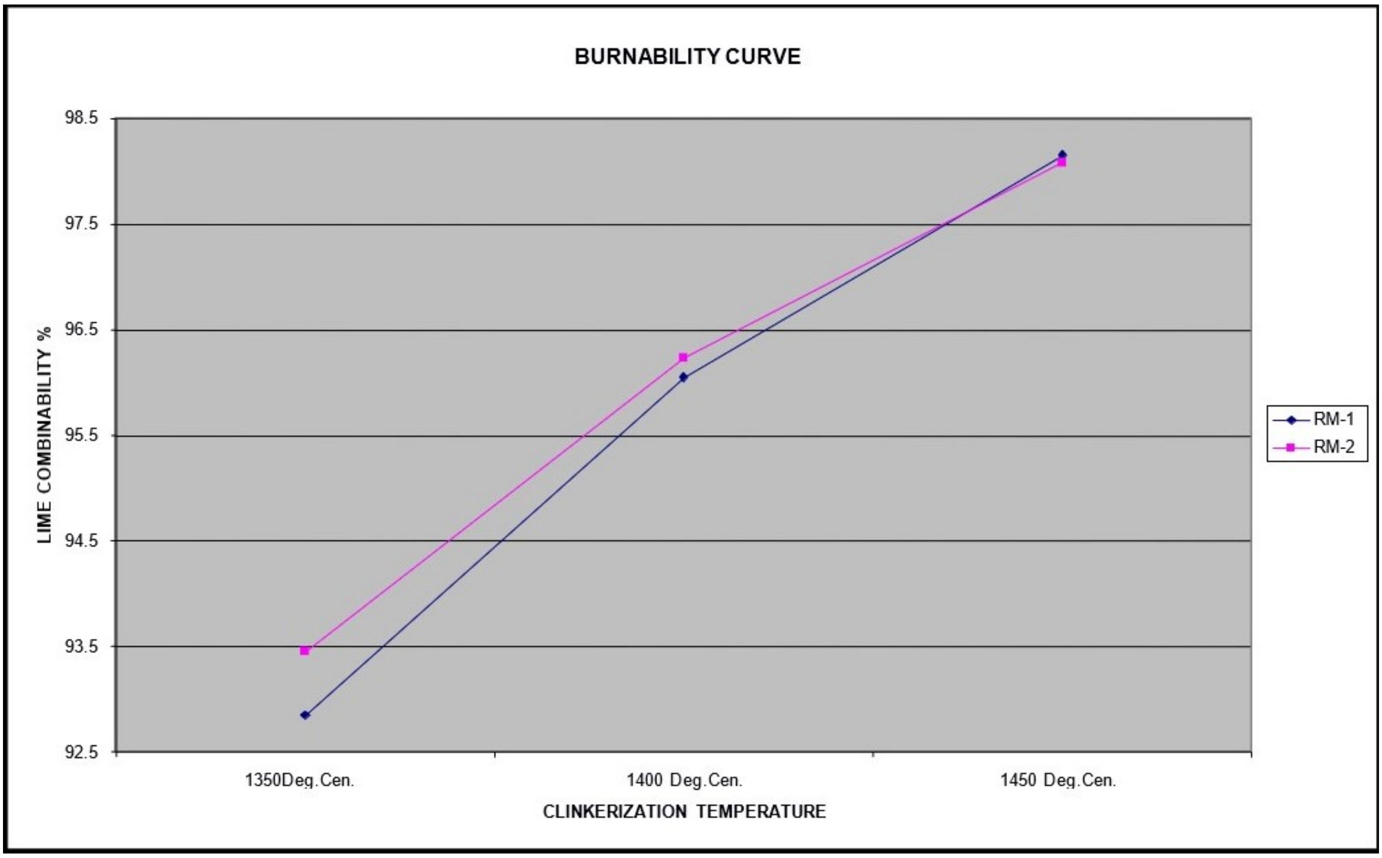

Fig. 7. Shows lime combinability of two raw mix samples.

that the two raw mixes have good burning characteristics and are capable of yielding quality clinkers when test fired at 1450°C with retention time of 30 minutes. It can be seen that burnability of the raw mixes, RM-1(control) and RM-2(containing Copper slag) are more or less similar at 1350, 1400 & 1450°C.

Table 6. Physical test results of ball mill ground sample using copper slag as PI.

Sample Description	SC (%)	Fineness m^2/kg	Setting time(minutes)		Strength (Mpa)			
			Initial	final	1 day	3 days	7 days	28 days
OPC-43 Control	23.50	310	145	170	26.4	41.6	54.5	70.2
OPC + 1% Cu-Slag	23.50	308	120	160	25.5	40.5	54.8	67.9
OPC + 2% Cu-Slag	23.75	307	110	155	27.2	41.8	53.6	71.6
OPC + 3% Cu-Slag	24.50	310	120	165	24.9	43.6	53.6	71.3
OPC + 4% Cu-Slag	23.50	309	125	175	25.5	40.8	54.4	66.3
OPC + 5% Cu-Slag	24.00	308	135	175	23.7	38.56	49.8	67.0

The effect of copper present in the copper slag is invisible in the formation of clinker as the quantity of copper slag used in the raw mix for clinkerization may not be enough to percolate the mineralizing effect of copper on the formation of clinker (Shi et al., 2008). However, its mineralizing action can be seen at such a lower addition also at 1350°C.

X-ray diffraction studies of laboratory made clinkers reveal that control clinker and Cu doped clinker are more or less similar in quality and both clinkers are good in quality and capable of yielding quality cement. Copper slag is hard to grind and its Bond's work index determined 19.34 kWh/ton. Such hard to grind material will increase raw mill grinding cost. We came to understand from plant official that Birla Copper-Dahej is going to install slag beneficiation plant after that copper slag size will become 60–100 micron, which will offset the increase in operating cost due to hardness. Characterization of copper slag indicates that it contains constituents compatible with manufacture of cement, along with the impurities of copper. The phase composition determined by XRD indicates that the quality of clinker is good and is capable of yielding good quality cement.

4. CONCLUSIONS

As the copper slag is found to contain an appreciable amount of Fe_2O_3 (58.96%) and SiO_2(32.26%), a maximum of 1.0% of copper slag may be used in the plant raw mix for manufacture of cement and the copper slag may replace presently used iron ore additive to the tune of around 1% in raw mix. The effect of copper present in the copper slag (0.65% only) is invisible in the clinker (CuO = 0.017%) as the quantity of copper slag used in the plant raw mix is only 1%.Copper slag can be gainfully utilized up to 3% as a performance improver in the manufacture of OPC-43 G.

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