

Red mud turns from waste to raw material for cement industry in joint effort by JP Cement-Dalla and Hindalco-Renukoot

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Abstract

All alumina refineries the world over are painfully aware that more than the alumina, they are producing red mud in a typical ratio of 1.5, depending upon the bauxite quality. Though various R&D efforts are being employed to find economically feasible uses for red mud, the results have not been coming so far. Various uses have been indicated, but either they fail the economy test or industries do not dare to take them forward for the fear of technical or economic failure. In this paper, we describe a step wise approach on the successful journey of red mud waste from plant to laboratory and then to becoming an additive in the raw feed mix to the cement industry as the result joint efforts of Hindalco-Renukoot and JP Cement-Dalla. In this paper, we study the use of Red Mud as an alternate raw material in place of iron ore or laterite.

1. Introduction

Hindalco Renukoot have long been in pursuit of an application for the utilization of Red Mud with the help of various research institutes. One such study showed positive results for the cement industry. In the cement industry, laterite is used as an additive for producing cement clinker and our Red Mud happens to have a similar composition to laterite. We needed a cement partner for plant scale trials, and since the Dalla Cement Factory is located in the periphery of 30 km, it emerged as a natural choice for plant scale trials.

The Dalla Cement Factory (DCF) at Dalla, Sonbhadra district, Uttar Pradesh, was established in 1971-72 by Uttar Pradesh Cement Corporation Ltd., and was declared sick in the year 1997, led to winding up of the company in 1999. It was taken-over by the Jaypee Group in 2006, who revived the existing clinker line no. K4, with a capacity of 0.5 Mtpa, and installed new clinker line K5 with a capacity of 1.5 Mtpa.

Hindalco approached the Dalla cement factory for a collaborative project, and conducted preliminary trial study of 5 days with red mud as per the guide lines of co-processing in cement/power/steel issued by CPCB, dated February 2010.

The trial study was conducted for co-processing of red mud in a kiln with a clinker capacity of 4500 MTD from 05th Dec to 09th December 2013. The chemical characteristics of laterite envisaged to be used up to 2 to 3 % are listed in Table 1, and the characteristics of Red Mud, in Table 2.

Table 1. Chemical characteristics of laterite.

Oxides	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	CaO	MgO
%	38.48	21.43	26.03	0.91	0.56

Table 2. Chemical characteristics of red mud.

Oxides	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	CaO	TiO ₂
%	40.4	16.46	8.34	2.46	14.84

2. Use of Industrial waste as alternate raw material

Cement kilns traditionally use laterite/iron ore to fulfill the requirement of iron oxide in raw mix. The adequate percentage of iron oxide present in red mud provides potential to use it in the cement raw mix for the manufacturing of cement clinker. This leads to the conservation of minerals like laterite and iron ore, and utilization of industrial waste which otherwise has a cost to manage and has an environmental impact. In other words, the use of red mud as an alternate raw material also offers conservation of traditional raw materials.

3. Present study

The trial for co-processing of red mud in the K-5 kiln was conducted between the 5th and 9th December 2013. Kiln process parameters, stack emissions and product quality parameters were observed closely for the 5 day trial period. Of the 5 days, one day was without feeding red mud, three days with red mud during trial run, and one day after the trial run without feeding red mud. See schedule trial schedule laid out in Table 3.

Table 3. Schedule of trial run with raw mix.

Particulars	Duration	Raw Mix
Pre trial study	1st day (05/12/2013)	Limestone with Laterite
Trial co-processing with Red Mud	2nd day (06/12/2013)	Limestone with Red Mud
	3rd day (07/12/2013)	
	4th day (08/12/2013)	
Post trial study	5th day (09/12/2013)	Limestone with Laterite

Red mud was fed along with limestone to raw meal grinding, and stored in the raw meal silo, from where it was fed into the preheater for clinkering. The feed rate of red mud was targeted at approximately 2.0 % i.e. 150 TPD. The exact feed rate was monitored on hourly basis and recorded. Presently DCF is using approximately 1.5 to 2.0 % i.e. 100 to 150 TPD of additive; however this requirement may vary up to 4.0 % with changes in iron oxide in limestone and change in the quality of Red Mud. In this study, emission of various pollutants such as SO₂, NO_x, HCl, HF, hydrocarbons, CO, TOC, PAH, VOC, dioxins and furans etc. were monitored during co-processing of waste, as well as pre and post co-processing.

During the study period, consistency in process and quality parameters were maintained as represented in Tables 4 and 5. It was also observed that when the additive is changed from laterite to red mud, there has been no change in % of various oxides in clinker, or significant changes in the various ratios such as LSF (lime saturation factor), SM (silica modulus) and AM (alumina modulus). Percentages of the various phases like C3S, C2S, C3A and C4AF are also more or less similar in all the cases. Liquid content is also the same as when laterite is used.

4. Methodology of trial study

When clinker is ground along with 30 % fly ash and 3 % gypsum, no change in the quality of cement before and after use of red mud was found. There has been similar strength measured after one day, 3 days, 7 days and 28 days.

Table 4. Process parameters observed during trial study.

Sr. No	Parameter	Pre Trial Run			Trial Run with Solid Waste			Post Trial Run		
		05.12.2013			06.12.2013 to 08.12-2013			09.12.2013		
		Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.
1	Kiln speed, rpm	3.25	4.30	4.09	4.10	4.33	4.31	3.62	4.30	4.24
2	Kiln Torque, Amp	516	720	640	530	828	686	582	650	640
3	Kiln feed, TPH	280	336	311	305	331	321	303	325	320
4	BZ Temp °c	1180	1263	1240	1202	1306	1276	1179	1248	1234
5	Secondary Air Temp °c	997	1110	1052	1012	1120	1070	1007	1098	1062
6	Tertiary Air Temp °c	902	998	945	915	1025	958	904	1022	962
7	O2 % Kiln string	2.5	5.0	4.5	2.8	5.2	4.4	3.0	4.9	4.4
8	CO PPM kiln string	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 5. Quality test parameter of clinker during trial run of red mud.

Trial Condition	Raw Materials	Additive Used	Date of Trial	LOI (%)	SO ₃ (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	Na ₂ O (%)	K ₂ O (%)	Total Alkali as Na ₂ O (%)	Cl ⁻ (%)	Free Lime (%)	LSF	SM	AM	C3S	C2S	C3A	C4AF	LIQ
Before Study	Laterite	2%	05.12.13	0.3	0.82	21.61	4.87	3.56	61.95	5.13	0.52	1.03	1.20	0.010	0.69	0.90	2.56	1.37	47.28	26.56	6.89	10.83	26.99
During Study	Red-Mud	2%	06.12.13	0.3	0.89	21.4	4.83	3.44	62.12	5.21	0.55	1.04	1.23	0.020	1.09	0.91	2.59	1.40	48.38	25.14	6.99	10.47	26.71
	Red-Mud	2%	07.12.13	0.4	0.94	21.36	4.83	3.5	61.84	5.44	0.54	1.03	1.22	0.020	1.01	0.91	2.56	1.38	47.78	25.47	6.88	10.65	26.88
	Red-Mud	2%	08.12.13	0.3	0.91	21.32	4.8	3.45	62.01	5.41	0.56	1.02	1.23	0.020	1.03	0.92	2.58	1.39	48.97	24.46	6.89	10.50	26.65

Table 6. Quality test parameter of cement during trial run of red mud.

Test Results of Cement (PPC)	Trial Condition	Ratio			Normal Consi.	Fineness	Residue	Setting Tie		Compressive Strength				Expansion		
		Clinker (%)	Flyash (%)	Gypsum (%)		Blaine (M ² /Kg)	R 45 μ (%)	R 90 μ (%)	IST (Mints.)	FST (Mints.)	1 Day (M.Pa.)	3 Days (M.Pa.)	7 Days (M.Pa.)	28 Days (M.Pa.)	Autoclave (%)	Lecha telier (mm)
		Before Study	64.23	31.94	3.83	31.50	375	28.60	9.20	260	290	9.20	26.30	39.60	53.00	0.12
During Study	06.12.13	64.18	32.02	3.80	31.00	365	29.80	9.40	200	250	9.52	25.80	37.95	51.76	0.12	0.75
	07.12.13	64.32	31.94	3.74	31.00	357	28.80	8.80	220	270	11.58	25.59	37.64	48.94	0.18	0.5
	08.12.13	66.18	30.01	3.81	31.00	370	28.00	8.60	180	235	11.42	26.22	36.90	49.00	0.15	0.5

5. 24-hourly sampling frequency and parameters monitored

Parameter like SO₂, HCL, CO, NO_x, TOC HF, particulate matter, HC, VOC, PAH, metals, dioxins and furans, cyanides were monitored and analyzed. The frequency of sampling was four samples per day during the trial study of red mud. Results are summarised in Tables 7, 8 and 9.

Table 7. Summary of average level of emissions during trial study of red mud test method: USEPA SW-846, Method 1311.

Sample No.	Parameter	UOM	Pre Trial		Trial with Red Mud		Post Trial	
			Ave	Range	Ave.	Range	Ave.	Range
1	Particulate Matter	mg/Nm ³	32.5	30.7-35.1	30.1	26.5-33.2	29.0	27.6-30.0
2	Sulphur dioxide	mg/Nm ³	6.7	6.2-7.1	6.0	5.3-6.5	5.7	5.3-6.0
3	Oxides of Nitrogen (NO _x)	mg/Nm ³	853	798-882	830	814-854	820	786-848
4	Hydrocarbons	mg/Nm ³	121	112-130	112	97-126	111	109-112
5	Carbon monoxide	mg/Nm ³	56.6	48.9-60.7	48.4	36.8-56.5	42.0	35.6-45.6
6	Hydrogen Chloride (HCl)	mg/Nm ³	11.6	10.1-12.5	11.3	10.5-12.0	11.0	10.5-11.5
7	Hydrogen Fluoride (HF)	mg/Nm ³	1.8	1.5-2.1	1.5	1.2-2.0	1.7	1.2-2.2
8	TOC	mg/Nm ³	5.2	5.2	4.5	4.2-4.8	4.6	4.6
9	PAH	µg/Nm ³	0.71	0.70-0.72	0.5	0.4-0.7	0.7	0.5-0.8
10	VOC	µg/Nm ³	4.4	4.2-4.5	4.3	4.0-4.5	4.3	4.1-4.5
11	Cyanide	mg/Nm ³	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
12	Mercury	mg/Nm ³	0.0168	0.0168	0.0140	0.013-0.014	0.0151	0.0151
13	Cadmium + Thallium (Cd + Tl)	mg/Nm ³	0.029	0.014	0.021	0.017-0.026	0.025	0.025
14	Total Metals	mg/Nm ³	0.322	0.322	0.308	0.301-0.318	0.308	0.308
15	Total Dioxins and Furans	ng/Nm ³	0.0354	0.0354	0.0323	0.0316-0.0332	0.0346	0.0346

Table 8. Heavy metals in clinker.

Sr. No.	Parameter	UOM	05.12.2013	06.12.2013	07.12.2013	08.12.2013	09.12.2013
			RESULTS				
1	Antimony as Sb	mg/kg	5.6	6.5	7.2	8.0	7.5
2	Arsenic as As	mg/kg	0.56	0.45	0.53	0.47	0.39
3	Cadmium as Cd	mg/kg	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
4	Chromium as Cr	mg/kg	17.8	19.9	15.3	18.6	13.6
5	Cobalt as Co	mg/kg	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
6	Copper as Cu	mg/kg	46.5	53.2	59.0	52.6	54.1
7	Lead as Pb	mg/kg	23.2	25.0	21.5	24.0	26.5
8	Manganese as Mn	mg/kg	254.98	255.48	289.06	288.89	261.44
9	Mercury as Hg	mg/kg	0.13	0.20	0.15	0.17	0.18
10	Selenium as Se	mg/kg	0.12	0.10	0.11	0.08	0.10
11	Thallium as Tl	mg/kg	2.0	2.2	1.7	4.1	2.5
12	Tin as Sn	mg/kg	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
13	Vanadium as V	mg/kg	7.2	6.5	7.5	7.2	6.7
14	Zinc as Zn	mg/kg	63.5	70.5	63.6	68.5	65.5

Table 9. Clinker TCLP analysis

Sr. No.	Parameters	UOM	Pre Trial	During Trial	Post Trial
1	Antimony as Sb	mg/kg	< 0.01	< 0.01	< 0.01
2	Arsenic as As	mg/kg	< 0.01	< 0.01	< 0.01
3	Cadmium as Cd	mg/kg	< 0.01	< 0.01	< 0.01
4	Chromium as Cr	mg/kg	< 0.01	< 0.01	< 0.01
5	Cobalt as Co	mg/kg	< 0.01	< 0.01	< 0.01
6	Copper as Cu	mg/kg	< 0.01	< 0.01	0.04
7	Iron as Fe	mg/kg	< 0.01	< 0.01	0.11
8	Lead as Pb	mg/kg	< 0.01	< 0.01	< 0.01
9	Manganese as Mn	mg/kg	0.02	0.03	0.02
10	Mercury as Hg	mg/kg	< 0.001	< 0.001	< 0.001
11	Nickel as Ni	mg/kg	< 0.01	< 0.01	0.02
12	Selenium as Se	mg/kg	< 0.01	< 0.01	< 0.01
13	Thallium as Tl	mg/kg	< 0.01	< 0.01	< 0.01
14	Tin as Sn	mg/kg	< 0.01	< 0.01	< 0.01
15	Vanadium as V	mg/kg	< 0.01	< 0.01	< 0.01
16	Zinc as Zn	mg/kg	0.01	0.01	0.01

It is evident from the above Tables 7, 8 and 9, that during trial co-processing of red mud:

- The particulate emissions were always less than 50 mg/Nm³, the maximum observed was 30.1 mg/Nm³;
- Sulphur dioxide emissions were observed to be ranging between 5.3 - 6.5 mg/Nm³;
- Oxides of nitrogen emissions, which are much dependent on the temperature, were ranging between 814 to 854 mg/Nm³;
- HCL and HF emissions values were found to be 10.5 – 12.0 mg/Nm³ and 1.2 – 2.0 mg/Nm³;
- Volatile organics were generated between 4.0 – 4.5 µg/Nm³;
- Polynuclear aromatic hydrocarbon emissions were observed in the range of 0.4 to 0.7 µg/Nm³;
- Dioxins and furans were found to be 0.0354 ng/Nm³ during pre-trial period, 0.0316 – 0.0332 ng/Nm³ (compared to 0.0346 ng/Nm³ during post trial period);
- The total heavy metals and mercury emissions values are 0.236 – 0.243 mg/Nm³ and 0.0156 – 0.0183 mg/Nm³;
- Total organic carbon was 4.2 – 4.8 mg/Nm³;
- Ambient air quality was found to be normal considering the industrial activities.

6. Conclusions

Based on the results achieved during trial run of red mud, the team found that there was no process problem in the pyro-section, and no deterioration in the quality of clinker and cement during the trial.

Dalla cement did not find any changes in emission level from stack and ambient. Therefore, the joint study concluded that red mud can be utilized by the cement industries in place of the usual laterite additive, to protect the environment, conserve natural resources and produce cost benefits.