Light Metals 2013 *Edited by: Barry Sadler*
TMS (The Minerals, Metals & Materials Society), 2013

MANAGEMENT OF INDUSTRIAL WASTE: THE CASE OF EFFECTIVE UTILIZATION OF RED MUD AND FLY ASH AT VEDANTA ALUMINIUM LIMITED - LANJIGARH

Dr. Mukesh Kumar, Bimalananda Senapati & C. Sateesh Kumar
Vedanta Aluminium Limited, Lanjigarh – 766 027, Odisha – INDIA

Keywords: Brick, Mineral Cementation, Red Mud

Abstract

Red mud is the major waste produced during the production of alumina through Bayer's process. Its disposal remains a worldwide issue because of huge land requirement and associated environmental concerns. Substantial R & D activities are going on around the world to find its effective utilization, including development of various products and byproducts. At present, the setting up of materials industries is taking place at a rapid pace which necessitates the availability of enormous amounts of raw materials. The use of red mud and fly ash in building material production is one viable option for conservation of natural resources and effective utilization of hazardous industrial effluents.

The present paper intends to put forth a perspective view based on real-facts, information and data on the enterprise of VAL's Refinery towards the utilization of the industrial wastes being generated by the set up with special reference to red mud and fly ash.

Introduction

Mining and industrialization processing of different raw materials, a lot of unutilized materials are being generated and discarded as solid wastes. Disposal of these materials not only occupies the valuable land but also causes environmental pollution. At present, the building materials industry is a fast growing sector, where a significant quantity of natural resources is being used to meet the requirement. Utilization of waste materials from industrial process in making building materials has been paid more attention to conserve natural resources and minimize the environmental pollution.

Red mud is the major waste material produced during the digestion of bauxite ores with caustic soda in alumina production following the Bayer's process. Currently about 2.7 billion tones of red mud are accumulated in the world with a growth of over 120 million tons per year. In India, generation of red mud from the aluminium refinery industries is about 3 million tones. (Indian Aluminium Industry "Indian Primary Aluminium Market", 2009). This makes red mud as one of the largest industrial by-products in modern society and highlights the importance of effective storage and remediation strategies.

Alumina refineries having captive thermal power plants generate both red mud and fly ash as a major waste. In addition to this, a substantial amount of lime grit is also generated in the Bayer's process to produce the alumina. Major quantities of these wastes such as red mud, fly ash and lime grit are being disposed without proper utilization.

Utilization of waste resources is one of the opportunities in building material industries to save the natural resources and to minimize disposal problem and environmental pollution which is a need of the hour. One of the economic ways is utilization of red mud in building material production such as brick, block and aggregate. Building brick is common useable housing materials and it has enormous application in the construction sector. Many processes such as firing route (Dass A, 1990) and cold setting method such as geo-polymerization path (Peter N, 1997) have been developed in manufacture of building bricks. The firing process in the production of red mud building brick is cost-intensive and causes environmental pollution as the bricks are produced by firing between 900^0C-1100^0C. The cold setting process is one of the options to save the burning of fuel in production of building brick. There are many options of cold setting process where the cementation bonding matrix is created to develop strength suitable for making building materials. In the non-fired process, attempts have been made in production of red mud building bricks by adding cement (Liu W, 2009), lime and Gypsum (Jiakuan Yang, 2008) and sodium silicate (Peter N,1997) as a binder. These non-fired methods demonstrate the utilization of red mud 25-40% by wt in production of building brick. Still there remains a challenge for development of economical process for bulk utilization of red mud along with fly ash that generates as a waste in the aluminium refinery plant in production of building material products.

M/s Vedanta Aluminium Limited, Lanjigarh. Odisha, India produces 1.6 Million Tonnes of red mud along with fly ash (0.35Million tons) and lime grit (0.012 million tons) per year as waste material. A mineral cementation process has been developed at CSIR-IMMT, Bhubaneswar to utilize the red mud, fly ash and lime grit of the alumina refineries wastes in development of building materials such as brick and block. Mineral cementation is an innovative and green process of making cementing mineral phases by chemical reaction of oxides and hydroxides of silica, alumina, calcium, magnesium, iron, alkali, sulphate bearing minerals in atmospheric temperature and develops binding property like Portland cement. The mineral constituents present in red mud, fly ash and lime grit are best suited to develop cementation phases by cold setting reaction in the production of building materials in an economical manner. The present paper describes the scope for utilization of red mud, fly ash and lime grit in the cold setting cementation process for manufacture of brick, block etc.

Materials and Methods

Raw Materials

The raw materials such as red mud, fly ash and lime grit of M/s Vedanta Aluminium Limited, Lanjigarh are used in the mineral cementation process for manufacture of cold setting building brick and blocks in a pilot plant scale.

The red mud is a semi-wet material and contains 10-15% free moisture in which about 80% by wt of the size fractions are below 45 micron. The specific gravity of red mud is 2.90. The chemical constituents present in the red mud by mass is 12.0% SiO_2, 20% Al_2O_3, 2.8% CaO, 39.1% Fe_2O_3, 8.6% TiO_2, 0.15% K_2O, 5.75% Na_2O, 0.40% MgO, 0.05% MnO, 0.56% V_2O_5, 0.08% ZrO_2, and 8.6% Loss on ignition.

The captive power plant of 70MW capacity generates fly ash and it is collected in dry condition from Electro Static Precipitator. The fly ash contains maximum size fractions up to 250 micron in which fractions below 75 micron is about 80% by wt. The specific gravity of fly ash is 2.05 and contains 51.3% SiO_2, 27.8% Al_2O_3, 1.5%CaO, 10.9% Fe_2O_3, 1.2% TiO_2, 0.9% K_2O, 0.6%Na_2O, 0.5%MgO, 0.05% MnO, and 4.6% LOI.

The lime grit is a granular material and contains particles up to 10mm sizes. The waste lime grit contains 12-20% CaO. It is used after chemical activation as a binder in brick production with red mud. The lime grit is chemically activated in presence of chemical gypsum and alkali metal sulphates in preparation of activated sulphated lime (ASL) by thorough mixing and grinding to a fine powder. The activated sulphated lime (ASL) powder prepared from the lime grit contains about 28% CaO and 25% SO_4 as the major constituents.

The other raw materials such as sand as a filler and Portland slag cement as a binder is used with the red mud mix in brick production. The fineness modulus of the sand is 2.94. The cement is Portland slag or any other cement as per the availability in the market.

Manufacturing Process

The brick manufacturing plant consisting of pan mixer, conveyer belt and rotary hydraulic press having on line production capacity 500 bricks per hour is used in production of red mud building bricks. On dry condition, the red mud with additives are mixed in the pan mixer for 5 minutes and then water is added as per the desired quantity and then it is mixed for 10 minutes in preparation of the wet mix. Then the wet mixture from the pan-mixer is conveyed for feeding to the brick press machine for casting of brick. The different raw mix designs of red mud prepared on 200 kg scale is used in the production of (230x100x75) mm size bricks at 25 ton pressure. The bricks after 12 hours of casting are stacked exposed to the atmosphere for drying and water curing. The bricks are water cured in three days of interval for hydration reaction and development of bonding strength. The drying and curing period is continued up to 14 days for completion of the curing. Then the bricks are evaluated for determination of various properties.

Manufacture of Building Brick

The raw materials used along with red mud are fly ash, sand, slag cement and activated sulphated lime (ASL). The slag cement and activated sulphated lime are the cold setting binders. Different experimental mix designs have been made to optimize the use of red mud, fly ash and lime grit in the production of building brick. Effort has been made to maximize the utilization of red mud with and without the combination of sand and fly ash in building brick production. The mixtures of cement and activated sulphated lime (ASL) termed as binder is used along with the raw mix in brick production. The binder consists of 1:1 weight ratio of slag cement and activated sulphated lime. About 16 mix designs of 200 kg each (Mix-1 to Mix-16) of red mud consisting of sand, fly ash and binder have been used in the production of brick. The mix compositions used in brick production with and without sand and fly ash consist of 50 to 90% red mud by weight. The raw mix proportions of different mix designs used in brick production are (a) Red mud – binder, (b) Red mud – Sand – binder (c) Red mud – fly ash – binder (d) Red mud – fly ash – sand –binder. All the bricks produced from different compositions are cured for 14 days as per the procedure and then tested to summarise the properties.

Test Procedures

The properties of building bricks are determined following procedures of Bureau of Indian Specification (BIS) IS 3495(Part-1) for compressive strength, IS 3495(Part-2) for water absorption, IS 3495(Part-3) for efflorescence etc. In addition to the above test, water resistance, leaching and heat tolerance capacity of the red mud bricks are also determined.

Leaching Test

The red mud contains Na_2O as alkali material about 5.75% by weight. Most of the alkalis are water leachable. On hydration the sodium oxide is prone to leach out from the red mud and this may affect the strength and durability of the bricks. In order to examine the effectiveness of Na_2O stabilization in the brick, the leaching test has been carried out. The full size brick sample has been immersed in water to maintain S/L ratio 1:5. For example a brick of 3.0 kg wt. is immersed in 15 liters of water. The leaching of sodium oxide from brick to water has been determined by measuring the changes in pH of the water up to 30 days. The portable water of pH 6.8 has been used for leaching test. The effect of leaching on strength of the brick has been determined.

Heat Resistance Test

Heat resistance property is one of the aspects of building brick for resistance to any events of firing. In order to determine this property, the bricks are fired in the electrically heated furnace at 200^0C, 400^0C and 600^0C temperature by soaking in the respective temperature for 30 and 60 minutes. Then the bricks are tested for the determination of compression strength on hot condition immediately after removing from the furnace. The strength of the heat soaked brick has been compared to the normal strength of the brick to see the effect of deterioration of strength property.

Results and Discussion

The properties of bricks determined from the different combinations of raw mix such as (a) Red mud – binder, (b) Red mud – Sand – binder (c) Red mud – fly ash – binder (d) Red mud – fly ash – sand –binder have been given in Table-1,2,3 and 4 respectively. The bricks produced from compositions of Mix-1 to Mix-4 contain 83 to 90% of red mud and 10 to 17% of binder (Table-1) and Mix-5 to Mix-8 contains 68 to 75 % of red mud, 15% sand and 10 to 17% of binder (Table-2). The bricks after 14 days of curing attain 86 to 130 kg/ cm^2 dry crushing strength and 76 to 120 Kg/cm^2 wet crushing strength. The use of sand with red mud increases the crushing strength of the bricks. In these mix compositions with and without sand, the red mud brick weight remains above 3.5 kg. The water absorption of the bricks ranges from 8 to 14%. Although dry and wet crushing strength of the bricks are satisfactory but these mix composition bricks contain

free soda as observed in the leach test results (Table-5). The pH of the water consisting of these bricks has reached to 10.06 which are close to the leaching of free soda from the red mud. The red mud bricks produced from red mud and binder shows significant reduction of strength due to the leaching of soda as compared to the original strength of these bricks (Table-5). The efflorescence property of these bricks is not controlled due to the leaching of soda. These mix composition bricks consisting of 68 to 90% red mud with and without sand are not satisfactory in respect to the efflorescence property and durability for use as a construction material. Considering this aspects of soda leaching problems, the red mud is used along with fly ash for brick production. The mix compositions of red mud consisting of 33 to 40% fly ash (Mix-9 to Mix-12) and 18 to 25% fly ash and 15% sand (Mix-13 to Mix-16) are tested in brick production. The properties of red mud brick with the combination of fly ash and fly ash-sand have been given in Table-3 and 4. The red mud bricks produced from the combination of fly ash and binder range in crushing strength from77 to 120 kg/cm^2 and water absorption 10 to 16%. The unit weight of the bricks remains below 3.2 kg. Similarly the red mud bricks produced from the combination of fly ash-sand and binder range in crushing strength from 85 to 130 kg/cm^2 and water absorption 4 to 10%. The unit weight of the bricks produced from the mix of fly ash and fly ash-sand remains below 3.3 kg. It is observed that the brick crushing strength in all the mix compositions increases with the increase of binder from 10 to 17%. The use of sand with red mud and fly ash shows the increase of crushing strength in the bricks. These red mud bricks in presence of fly ash drastically decrease the leaching of soda and also retain the strength after immersion of 30 days in water Table-5. The efflorescence property as well as other physical properties like strength, water absorption of the fly ash blend bricks is quite satisfactory and confirm the requirements of building brick specification IS 12894:2002.

The binder is a mix combination of cement, lime grit, gypsum and alkali metal sulphate. The cementation property of the binder proceeds through hydraulic reaction in atmospheric temperature. The reactive sulphate and lime present in the binder plays a significant role in consolidation of red mud and development of binding strength in the brick. SO_4 is an effective ion of higher hydration energy which promotes the hydraulic reaction of silicates, aluminates and alkalis in formation of alumino-silicate chain structures of geopolymer minerals as the cementation phases. Alumino-silicate and silica minerals of fly ash in presence of binder, activated sulphated lime, reacts with soda of the red mud to form the stable mineral phases. The cold setting strength of the red mud building bricks are due to the formation of calcium bearing hydraulic phases and sodium bearing silico-aluminate phases. The use of fly ash with red mud significantly improves the brick property and reduces the leaching effect of soda.

Heat resistance property is one of the aspects of the building brick for their survival against any fire accidents. The effect of heat on brick strength determined on hot condition after removing from the furnace fired at 200^{0}C, 400^{0}C and 600^{0}C temperature with soaking period of 30 and 60 minutes has been given in Table-6. It is observed that the bricks fired at all the temperatures on soaking for 30 minutes do not show any significant change in strength. The bricks after soaking of heat for 60 minutes in all the temperatures show the decrease of strength 20 to 35% as compared to the original strength. On firing condition at 600^{O}C temperature the hot brick retains about 63 kg/cm^2 crushing strength. This indicates that the red mud brick can withstand to the temperature without adversely affecting the structure.

Conclusion

The above experimental study reveals that red mud along with fly ash is very effective in production of cold setting and durable building brick as per the required standard IS:12894:2002. The cementation binder prepared from lime grit is effective in utilization of red mud for production of building brick without any adverse effects with respect to leaching of soda. The cold setting binding phases developed in the building bricks are lime and alkali bearing geopolymer phases which are very stable. The heat resistance properties of red mud brick are also very promising which can withstand the temperature up to 600^{0}C without any adverse effects in deterioration of strength. This paper illustrates the use of red mud and fly ash in building material production is one viable option for conservation of natural resources and effective utilization of hazardous industrial effluents.

Abbreviations used in the following Tables
DW - Dry Weight
DBD - Dry Bulk Density
WA - Water Absorption
DCS - Dry Crushing Strength
WCS - Wet Crushing Strength
E - Efflorescence
IS - Specification as per IS 12894: 2002 Fuel ash-Lime Bricks, (Wet Compressive strength)
RM-Red mud
FA-Fly Ash
S-Sand
B-Binder

Table 1: Properties of red mud- binder mix brick

Composition & Properties	Mix-1	Mix-2	Mix-3	Mix-4
Raw mix-wt% Red mud Binder	 90 10	 88 12	 85 15	 83 17
Brick Properties				
DW (Kg)	3.62-3.68	3.62-3.68	3.64-3.72	3.68-3.75
DBD (Kg/m^3)	1897-1939	1907-1939	1918-1960	1939-1976
WA (%)	10-14	10-14	10-13	10-12
DCS (Kg/cm^2)	86-90	87-92	88-92	118-124
WCS (kg/cm^2)	76-81	79-84	84-86	105-112
E	---Moderate---			
IS	Class-7.5	Class-7.5	Class-7.5	Class-10

Table 2: Properties of Red mud-Sand-Binder mix brick

Composition & Properties	Mix-5	Mix-6	Mix-7	Mix-8
Raw mix-wt% Red mud Sand Binder	 75 15 10	 73 15 12	 70 15 15	 68 15 17
Brick Properties				
DW (Kg)	3.65-3.75	3.68-3.75	3.72-3.83	3.72-3.78
DBD (Kg/m^3)	1924-1976	1940-1976	1960-2018	1960-2034
WA (%)	10-12	8-10	8-10	8-10
DCS (Kg/cm^2)	86-92	94-98	104-110	123-130
WCS (kg/cm^2)	82-85	84-87	100-104	110-120
E	---Moderate---			
IS	Class-7.5	Class-7.5	Class-10	Class-12.5

Table -3: Properties of Red mud- Fly ash -Binder mix brick

Composition & Properties	Mix-9	Mix-10	Mix-11	Mix-12
Raw mix-wt% Red mud Fly Ash Binder	 50 40 10	 50 38 12	 50 35 15	 50 33 17
Brick Properties				
DW (Kg)	2.75-2.85	2.80-2.92	2.95-3.10	3.00-3.20
DBD (Kg/m^3)	1449-1502	1475-1539	1555-1634	1581-1686
WA (%)	14-16	12-16	12-16	10-12
DCS (Kg/cm^2)	77-86	90-96	104-114	124-130
WCS (kg/cm^2)	75-80	85-87	100-108	120-127
E	---Nil---			
IS	Class-7.5	Class-7.5	Class-10	Class-12.5

Table-4: Properties of Red mud- Fly ash - Sand- binder mix brick

Composition & Properties	Mix-13	Mix-14	Mix-15	Mix-16
Raw mix-wt% Red mud Fly Ash Sand Binder	 50 25 15 10	 50 23 15 12	 50 20 15 15	 50 18 15 17
Brick Properties				
DW (Kg)	2.80-2.95	2.90-3.00	3.00-3.15	3.15-3.30
DBD (Kg/m^3)	1475-1555	1528-1581	1581-1660	1660-1739
WA (%)	8-10	8-10	6-8	4-6
DCS (Kg/cm^2)	85-95	96-102	116-124	126-130
WCS (kg/cm^2)	80-87	85-89	110-116	122-127
E	---Nil---			
IS	Class-7.5	Class-7.5	Class-10	Class-12.5

Table-5 Characteristics of leaching and effect on strength of red mud bricks

Brick composition (wt %)	pH of leaching water No of days						Crushing Strength Kg/cm^2	
	1	3	5	10	20	30	Leach	Dry
Red mud	9.0	10.8	11.2	12.1	12.2	12.2	-	-
Fly ash	8.0	8.2	8.3	8.3	8.3	8.3	-	-
Brick of Mix-3 RM-85 B-15	7.8	8.5	9.2	9.7	10.1	10.1	56-63	88-92
Brick of Mix-11 RM-50 FA-35 B-15	7.4	7.6	8.1	8.2	8.3	8.3	95-103	104-114
Brick of Mix-15 RM-50 FA-20 S-15 B-15	7.4	8.1	8.3	8..4	8.5	8.5	104-110	116-124

Table-6: Crushing strength of Heat treated brick

Brick composition (Mix-10)	Dry crushing strength (Kg/cm^2)	Heat soaked temperature of brick and Crushing strength (Kg/cm^2)			
		Soaking time(min)	200^0C	400^0C	600^0C
RedMud-50 Fly ash-38 Binder-12	91-94	30	88-90	80-82	77-80
		60	74-80	68-72	60-63

Acknowledgement

The author acknowledges the valuable and dedicated assistance of Dr. B.D. Nayak, Scientist, CSIR-IMMT, Bhubaneswar. Grateful thanks are also to all the colleagues of the institute who have directly or indirectly involved in this project with commitments and sincerity in completing this project work in time.

References

Klauber, C., Gräfe, M. and Power, G. Bauxite residue issues: II. options for residue utilization, Hydrometallurgy, V. 108, Issues 1-2, June 2011, Pages 11-32.

Amritphale S S. Patel M. Utilization of red mud, fly ash for manufacture of bricks with pyrophyllite. *Silicate Industries*. 1987; 52(3-4):31-35

Amritphale S S, Anshula A, Chandraa N and Ramakrishnana N. A novel process for making radiopaque materials using bauxite red mud. *Journal of European Ceramic Society*. 2007; 27(4):1945-1951

Dass A , Malhotra S K (1990) . Limestone stabilized red mud bricks. *Materials and Structures* 23:252-255

Gordon J N, Pinnock W R, Moore M M, A preliminary investigation of strength development in Jamaican red mud composites, *Cement and concrete composites*. 1996; 18(6):371-379

Indian Aluminium Industry "Indian Primary Aluminium Market" (2009) www.scribd.com/doc/.../19614972-Indian Aluminium Industry

Joaquin Yang and Bo Xiao (2008), Development of uninterred construction materials from red mud wastes produced in the sintering alumina process. Construction and Building materials 22(12)

Leonadou S A, Oustadakis P, Tsakiridis P E and Markopoulos C, "Titanium leaching from red mud by diluted sulphuric acid at atmospheric pressure," J. Hazard mater, Vol 157, pp-579-586, Sept 2008

Liu E W C, Yang J K. and B Xiao, "Application of bayer red mud for iron recovery and building material production from alumino-silicate residues," Journal of Hazardous Materials, Vol 161, pp-474-478, Jan 2009

Peter N (1997), IDRC Reports, Making brick with red mud in Jamaica, ,No.21(2). International Development Research Centre, Ottawa, Canada

Roskil reports, *The economics of bauxite and alumina, Available from http:// www.roskil.co.uk/index.html.access in 8/06/2010*

Ribeiro D V , labrincha J Z, and Morelli M R. Use of red mud as addition for poprtland cement mortars, Journal of material Science and Engineering.2010; 4(8):1-9

Singh M, Upadhaya S N and Prasad P M. Preparation of special cements from red mud, Waste Management.1996; 16(8):665-670

Singh M, Upadhaya S N and Prasad P M. Preparation of iron rich cements using red mud, *Cement and concrete research*, 1997; 1037-1046

Vincenzo M S, Renz C, Stefano M and Giovanni C , Bauxite red mud in the ceramic industry Part2: Production of clay based ceramics, *Journal of European Ceramic Society*, 2000; 20(3) : 245-252

Wang S B., Ang H M and Tade M O, "Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes," Chemosphere, Vol 72, pp-1621-1635, August 2008

Yang H Z, Chen, C P and Pan J, "Preparation of double-layer glass ceramics/ceramic tile form bauxite tailings and red mud," *Journal European Ceramic Society*, Vol.29, pp.1887-1894, July 2009

Zhong, Y F, Zhang and Zhang Y, "Extraction of alumina and sodium oxide from red mud by a mild hydro-chemical process," *Journal of Hazardous Materials*, Vol. 172, pp-1629-1634, Dec 2009