Technological Options for Effective Utilization of Bauxite Residue (Red Mud) – A Review

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INTERNATIONAL SEMINAR ON BAUXITE RESIDUE (RED MUD)

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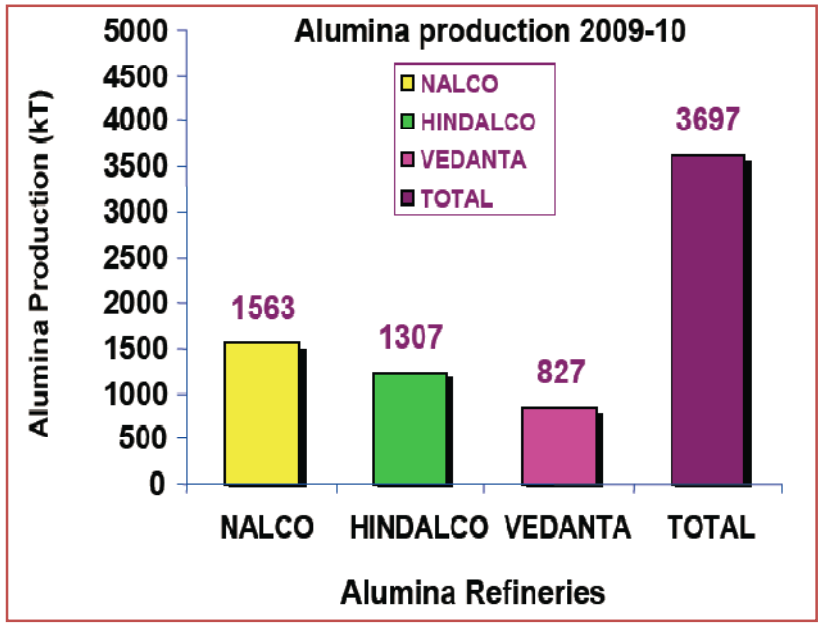
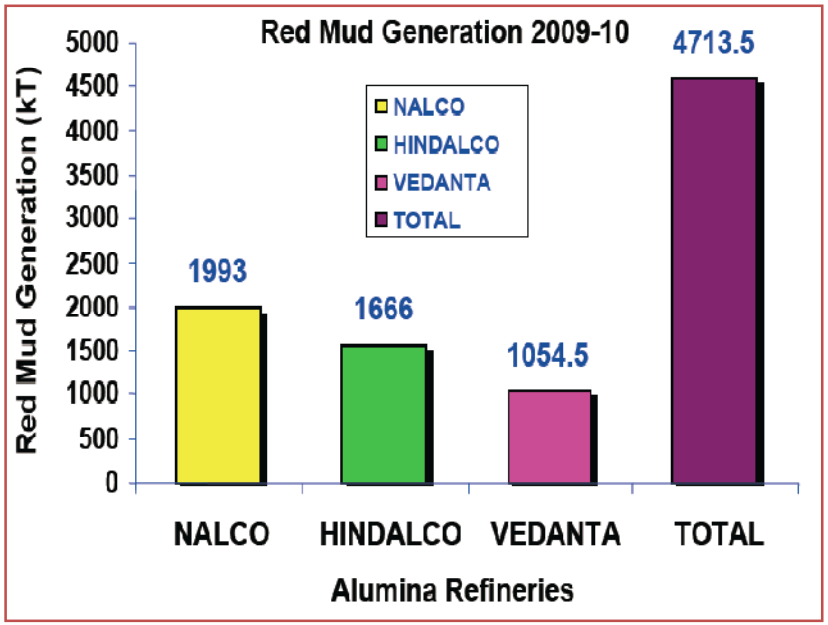
Generation of Red Mud in India





- 4.71 Million TPA……. 6.25% of world's total generation
  - **1.2–1.5 times the alumina extracted**
  - **4 times of aluminium produced**
- Likely to increase three fold with the setting up of new production facilities and decreasing ore quality.

Trigger to figure out the problem with Red Mud

- The accident in Red Mud storage area in Hungary in October'10

- High Volume and Highly alkaline waste
- Large area required for containment
  - approximately 30 million sq. m or 3000 Hectares for entire generation by 2014-15 (for containment of 3-5 years)
- Disposal of Red Mud accounts for 5% of production cost
- Less than 5% of red mud is being utilized in the world with the remainder disposed in storage areas.

Characteristics of Red Mud

Table 1: Characteristics of Red Mud - India and World wide					
Companies	**Fe2O3 (%)**	**Al2O3 (%)**	**TiO2 (%)**	**SiO2 (%)**	**Na2O (%)**
Al. Corp	20.26	19.6	28	6.74	8.09
MALCO	45.17	27	5.12	5.7	3.64
HINDALCO	35.04	23	17.2	5	4.85
BALCO	33.8	15.58	22.5	6.84	5.2
NALCO	52.39	14.73	3.3	8.44	4
Hungary	38.45	15.2	4.6	10.15	8.12
Jamaica	50.9	14.2	6.87	3.4	3.18
Surinam	24.81	19	12.15	11.9	9.29
ALCOA Mobile	30.4	16.2	10.11	11.14	2
Arkansas	55.6	12.15	4.5	1.5-5	Traces
Sherwon	50.54	11.13	Traces	2.56	9
FRG Baudart	38.75	20	5.5	13	8.16
Lowest Value	**20.26**	**11.13**	**3.3**	**2.56**	**2**
Highest Value	**55.6**	**27**	**28**	**13**	**9.29**
Range	**20-26 to 55.6**	**11.13 to 27**	**3.3. to 28**	**2.56 to 13**	**2 to 9.29**

Characteristics of Red Mud

- Red Mud contains
  - Silica, Alumina , Fe_2O_3, CaO , TiO_2, and in minor quantities, Na, K, Cr, V, Ni, Ba, Cu, Mn, Pb, Zn etc.
  - Particle size: 90 volume % below 75µm
  - The specific surface : 11m2/g and
  - the specific weight : 3.4 g/cc
- Vast variation in chemical composition between different Red Muds worldwide
- Repeatedly rinsed red mud suspension, of a density between 1.2 and 1.3 g/cm3 and dry matter concentration from 250 to 350 g/l, is disposed as a waste .

Mineral Constituent of Red Mud

- Diaspore $Al_2O_3.H_2O$
- Gibbsite $Al_2O_3.3H_2O$
- Calcium Aluminum Iron Silicate Hydroxide $[Ca_3AlFe(SiO_4)(OH)_8]$
- Cancrinite $[Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2 \cdot 2H_2O]$
- Hematite Fe_2O_3
- Calcite $CaCO_3$
- Quartz SiO_2
- Perovskite $CaTiO_3$ and
- possibly Goethite,$FeO(OH)$, Sodium-Aluminium-Silicate Hydrate $(1.0Na_2O \cdot Al_2O_3 \cdot 1.68SiO_2 \cdot 1.73H_2O)$

Prevalent Methods of Disposal

- Seawater Discharge via pipeline to deep sea locations after reducing caustic soda levels
- Lagooning/Ponding with naturally impervious layers or sealants
- Dry Stacking or 'Sloped Deposition',
- Dry Disposal where the red mud is filtered to form a dry cake (>65% solids)
- Neutralization by seawater lowering the pH of the residue.
  - The sea water after neutralization is treated with concentrated H2SO4 (0.05 liters of conc. H2SO4 per 1,000 liters of red mud) and put back to ocean

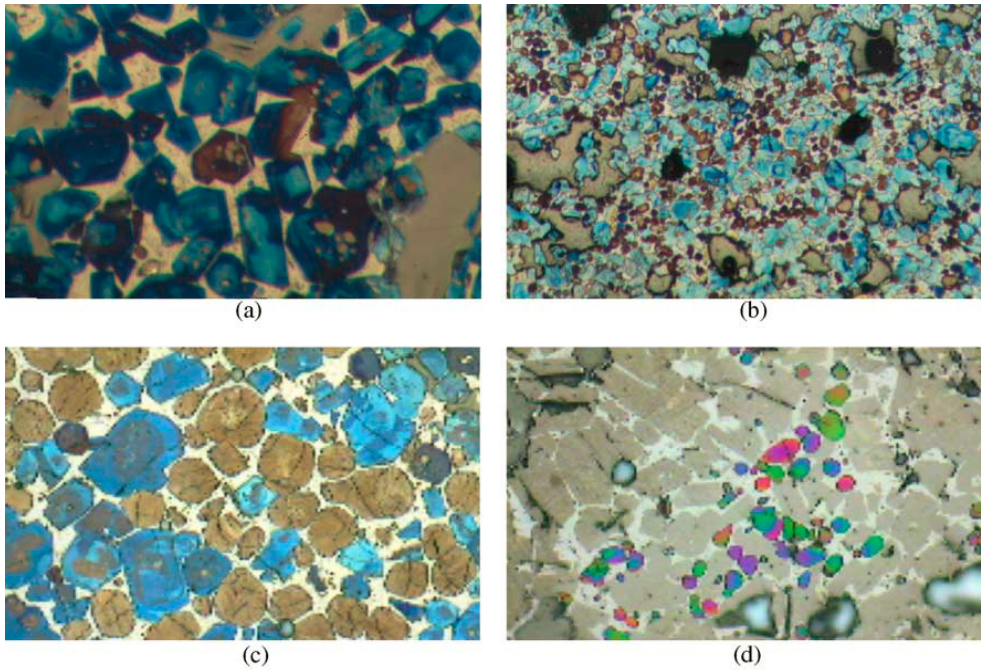
Methods of Disposal in India

Red Mud Generation In India- Present and Projections & Present Dumping Procedure				
Company	**Present Generation in TPA**	**Additional Generation by 2014-15 in TPA**	**Total Generation by 2014-15 in TPA**	**Dumping Procedure**
NALCO	1.99	0.65	2.64	Red Mud after 6 stage washing sent to pond. The bottom and sides of the pond is covered by impervious and semi-pervious clay and base filters
HINDALCO	1.67	0.455	2.125	Muri: Wet slurry disposed in unlined pond Belgaum: Red Mud after 6 stage washing and filtration sent to pond. Dry portion of the pond covered with 15 cm black soil for vegetation. Renukoot: Red Mud after 5 stage washing and filtration sent to pond.
VEDANTA	1.05	1.82	2.87	Red Mud after 6 stage washing and filtration sent to pond. Pond dyked with stone and protected with polythene and clay liner
UTKAL	0	1.95	1.95	Not Applicable
RAYKAL	0	1.82	1.82	Not Applicable
ADITYA	0	1.82	1.82	Not Applicable
JSW	0	1.82	1.82	Not Applicable
Total	**4.71**	**10.335**	**15.045**	Not Applicable

Source: JNARDDC, Nagpur, January, 2011

Use of Red Mud as Raw Meal in Cement

- 3.5% by weight of red mud was used in raw mix for production of Portland cement clinker without any impact on clinker quality
  - No appreciable difference seen in chemistry, mineralogy, grind ability, setting time, compressive strength and expansibility.

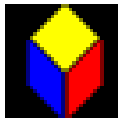


Microstructure of Portland cement clinker with red mud residue: (a) well-formed alite crystals (×500), (b) crystals C2S scattering among alite showing that the raw mix was homogenous (×100), (c) high percentage of C4AF (×500), (d) Free CaO scattering among alite (×500)

- Similar results seen for up to 5% by wt usage of de-watered Red Mud (60-65% solid) known as FA/Ferral

Use of Red Mud as Laterite Corrective in Cement

- Lab Scale trial of Red Mud done as a lateritic substitute by utilizing up to 2.5 – 3 % by weight of Raw Mix by discussing 2 case scenarios
- **Case – I : Cement Plant Using Cement Grade Limestone as the main Limestone Source.**
  - Usage of 2% Red Mud leads to increase of HGLS (High Grade Lime Stone) by 5% with no significant substitution of high Alumina Laterite or Iron Ore.
  - The clinker Fe_2O_3 tends to go higher above 4.5% which is not desirable.
- **Case – II : A Cement Plant with Purer Quality of Limestone**
  - Consumption of Iron ore and high Alumina laterite increases
- In cement plants using marginal quality of Limestone and high ash Coal (~ash = 34 – 35%), use of Red Mud would not be economically viable as it results in increased consumption in purchased HGLS



Cement Raw Mix with Red Mud

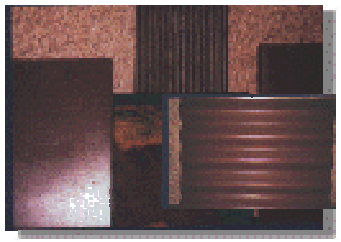
Use of Red Mud for making Special Cement

- Special Cement Production Using Red Mud
  - Calcium Aluminate Cement: Not exactly from Red Mud but by precipitating the spent liquor by lime and sintering it in 1000 ^{0}C
    - CAC contains 70-80% alumina and major phases are CaO.Al2O3 and CaO.2Al2O3
- BHU-Hindalco study of producing
  - Aluminoferrite (C4AF) - belite (β-C2S) using lime + red mud + fly ash
  - Aluminoferrite (C4AF) - ferrite (C2F) - aluminates (C3A & C12A7) utilizing lime + red mud + bauxite; and
  - Sulfoaluminoferrite (C4(A,F)3S) - aluminoferrite - ferrite using lime +red mud + bauxite + gypsum.

- Strength comparable to OPC is obtainable from Lime, Red Mud, Gypsum and Bauxite mixture
- Replacement of Bauxite by Fly ash reduces strength
- F/A ratio of 0.8-1.2 in the raw mixes + firing temperature of 1250 oC for 1.0-1.5 h give the best results for preparing the special cements.

Use of Red Mud for making Ceramics, Bricks and Composites

- Ceramics and Bricks Production from Sintered Red Mud Compact
  - Moderate reactivity up to 900°C
  - At higher temperatures, higher strength, lower porosity and immobilization of heavy metals can be achieved
  - In the sintering process, Iron Oxide of Red Mud acts as a filler or a flux, Alumina Oxide as fillers and Calcium Oxide acts as mineralizer.
  - Addition of 50% Red Mud and 50% clay mixture has shown improvements in water absorption and bending strength



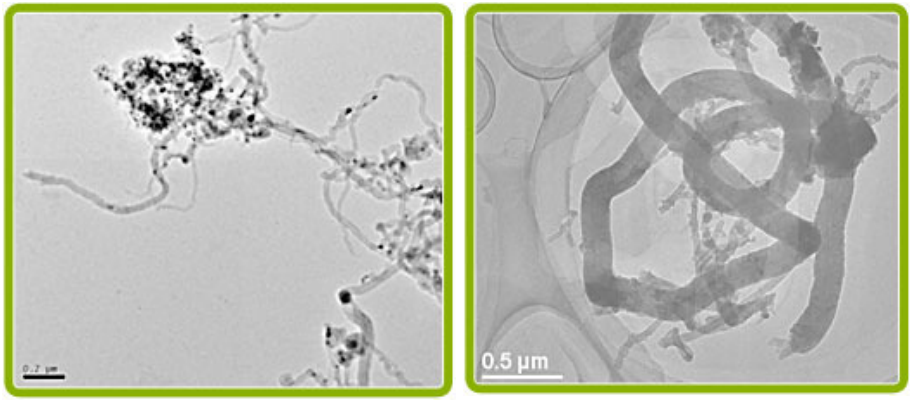
- Production of Composites from Red Mud
  - BMTPC, India has produced a composite from red mud, polymer and natural fibers, which is a substitute of wood based panel products
  - AMPRI, India, has developed fiber Reinforced Red mud composite doors

Recovery of Metals from Red Mud

- Extraction of Iron and Titanium from red mud.
  - smelting in a blast/electric/low shaft furnace (with or without pre-reduction) to produce pig iron
  - Slag from smelting may contain up to 50% TiO2 (especially for Indian Red Mud) which may be recovered by chlorination
  - Environmentally benign as it avoids the stages of coking and sintering
- Extraction of Sodium and Aluminium from red mud
  - Red Mud-BaO-Na2CO3 mix (in ratio of 1:0.15:0.25) sintered at 1000 ^{0}C
- Extraction of Iron and Alumina
  - Reduction-sintering, leaching and then magnetic beneficiation for recovery of alumina and ferric oxide
  - alumina recovery of Bayer red mud can reach 89.71%, Fe recovery rate can reach 60.67%

Use of Red Mud in Catalysis

- For recovery of fuel and gas from mixture of waste oil and MSW
- As a Chlorine scavenger for recovery of oil from PVC
- As a substitute of Cu-Cr-Ti commercial catalyst (Calcined Red Mud)
- For acid neutralization in excess of 15 moles of acid/kg
- As a flocculent having application in STPs (Phosphate binder)
- For the synthesis of Multi-Walled Carbon Nano Tubes (MWCNTs) by fluidized bed chemical vapor deposition



TEM images of carbon deposit from decomposition of methane and butane on red mud

Conclusions

- The utilization of red mud is of great significance from the point of view of resource conservation and sustainability of the aluminium industry.
- Red Mud use (lab scale and plant scale) has been successful for making cement, ceramics, bricks, catalysts and for recovery of metals
- However, the reuse of red mud for any application should have following four criteria:
  - Volume: The application should have **high volume usage**
  - Performance: It should be a **low cost substitute** with same performance
  - Cost: It should be **cost effective**
  - Risk: There should be **no environmental, health or safety risk** associated with its use

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Questions / remarks ?