Chapter 1

Introduction

1.1 Background

One of the challenging problems that most of the nations especially the developing ones face is to meet the needs of the rapidly increasing populations, restricting the limits of capacity building increasing infrastructural facilities. As such, there is a need and demand for rapid urbanization and industrialization for economic development. Most of the activities to meet such demands generates huge amount of wastes such as industrial, agricultural or domestic in different forms (solid, liquid, semi-solid or their combinations). Most of these, if not appropriately treated and disposed of safely will adversely affect the ecology and environment. Thus it is necessary to assure that it is sustainable [1]. It has also sidelined the concept of sustainable development which requires the development of Eco-friendly technology for the optimal usage of the resources and the utilization and disposal of the industrial by-products. The present practice has created a severe threat to the environment due to exhaustive and uncontrolled use of natural resources [2]. On the other hand, it brings serious challenges around the globe regarding disposal, environmental and health problems due to the worldwide generation of the enormous quantity of waste. However, some of these waste has the potential to be used as a resource and can be utilized as raw materials or as additives in conjunction with other materials for the production of environmentally friendly construction and building materials. Thus, the governing bodies/policy makers, researcher community and the general public should play an appropriate constructive role in managing such wastes generated from various industrial units such as thermal power plant, alumina industries zinc industries, mine rejects, iron and steel industries, etc. An overview of the various industrial wastes and their major constituents are briefly summarized in Tables 1.1 and 1.2 respectively. From Table 1.1, it can be observed that fly ash, mine reject, blast furnace slag and red mud are the significant waste contribute most out of the total volume. From Table 1.1, it is also seen that India alone produces about 169 million tons of fly ash out of total of 777 million tons of fly ash produced all over the world, which is about 20% of the total production of fly ash. A part of the fly ash collected is used as a pozzolanic admixture in the cement but, the major portion is of F-class fly ash and is disposed of in ash ponds which needs a large area of land. Further, red mud produced from the alumina plants in India is about 14 million tons out of 400 million tons produced all over the world. Even though the share of red mud is only 4%, the total volume of the sum of 14 million tons annually is quite substantial. Therefore adequate attention should be paid to its management also. As such, its production in India is presented in Fig.1.2.

Presently, the total installed capacity of coal-based thermal plant in India is 158 gigawatts that using 510 million tons coal as fuel and generates 169 million tons fly ash annually (for year 2016–17). As per the government of India report [5], about 63.28% of total fly ash generated was now utilized in various applications such as construction and building (pavement materials, bricks, blocks and tiles) and as

TABLE 1.1: Overview of some of industrial wastes generated worldwide and in India

Sr. No	Industrial Waste	Ref.	Physical Form	Source	Estimated Annual Production (Million Tonnes),World	Estimated Annual Production (Million Tonnes),India	Disposal Method
1	Mine Rejects	[2]	Solid Lumps	Various Mining Operations	-	750	Open area dumping.
2	Fly ash	[3–6]	Powder	Coal Based Thermal Power Station	777.1	169.25	Wet /dry disposal in pond.
3	Red Mud	[7–10]	Paste or Cake	Alumina Industry	400	14	Dumping pond.
4	Blast furnace slag	[11, 12]	Fine or Solid Lumps	steel, zinc and phosphorous Industries	170-250	10	Dumping in open area
5	Phospho-Chalk and Phospho-Gypsum	[13, 14]	Slurry or Paste	Fertilizer Industry	280	6	Dumping pond.
6	Lime sludge	[15]	Slurry or Paste	Sugar Industry, Pulp and Paper Industry and Acetylene Industry	179	4.5	Stored in settling water ponds or wet/dry stacking.
7	Kimberlite	[2]	Solid Lumps	Diamond Mining	-	0.6	Open area dumping.
8	Jerosite	[16, 17]	Powder or Cake	Zinc Industry	2.5	0.45	Dumping pond.

Table 1.2: Major chemical composition of industrial wastes [5]

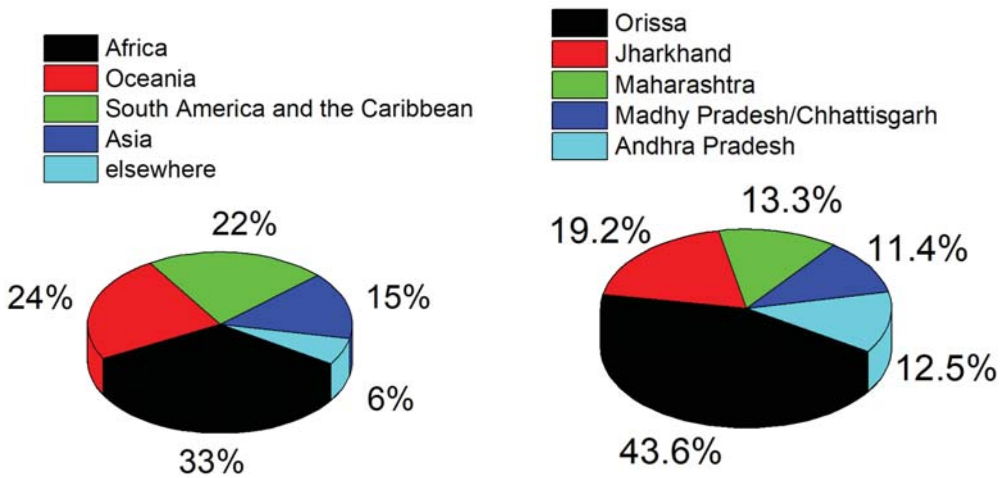
Sl. No.	Major Constituents (%)	Industrial Wastes					
		Fly ash	Granulated Blast Furnace Slag	Red Mud	Kimberlite	Mine Rejects	Jerosite
1	SiO_2	55.59	33.41	15.6	35.43	38.91	5.59
2	Al_2O_3	26.64	20.05	18.6	3.41	6.16	2.94
3	Fe_2O_3	9.5	0.89	26.65	11.81	4.49	25.56
4	CaO	2.3	34.24	15.44	8.3	24.4	11.34
5	MgO	0.6	8.86	0.8	28.47	2.25	Traces
6	SO_3	0.44	Nil	Nil	0.26	Nil	29.75
7	Na_2O	0.23	0.16	3.09	0.26	0.16	0.32

micro nutrients in agriculture . However, author could not find as such information in public domain about the exact utilization potential (percent of total generation) of other industrial wastes such as red mud and mine rejects. However, various attempts have been made by researchers worldwide and reported in the literature on the utilization of such waste in various civil engineering applications. In view of above, red mud, an alumina industries by-product has been considered as a base material for the present study for its economic and fruitful utilization.

1.2 General Overview of Red Mud

Red mud is a major industrial solid waste produced during the extraction of alumina from bauxite ores. The worldwide deposits of bauxite ore are estimated approximately to be 55 to 75 billion tonnes; whereas, India shares about 7% of global inventory [18]. The deposits of bauxite ore about the world and India are presented in Fig.1.1.

The average alumina refinery produces about 1.75 tonnes of red mud per tonne of alumina, depending on the source of bauxite ore and the extraction process [7]. Worldwide generation of this waste was about 4 billion tons per annum till 2016 [19]. Whereas, Indian alumina plants generate about 14 million tonnes of red mud



(a) (b)

FIGURE 1.1: Deposits of bauxite ore (a) world and (b) India [18].

every year. Fig.1.2 presents the generation of red mud by various Indian alumina industries.

It predominately contains minerals of ferrous (hematite, magnetite and goethite), silica (quartz and sodalite), alumina (gibbsite,diaspore, and boehmite), calcite, anatase, rutile, perovskite, water, oxilate, flocculants, some organic and inorganic carbon and some trace and rare earth elements [13, 21–25]. The major chemical composition of red mud of different industries located worldwide is summarized in Table 1.3 [18, 20, 26]. It appears from Table 1.3 that red mud predominately composed of oxides of iron, alumina, and silica. The availability of such elements is also one reason to select as base materials for present research. Initially, red mud in slurry form was disposed of either direct discharge in the sea or the ponds situated nearby the alumina plants. However, this conventional practice requires regular monitoring and maintenance activity and always prone to contamination of the surroundings. It was not also a sustainable and environmental friendly solution and sometimes create objectionable situations in the surroundings, on human health

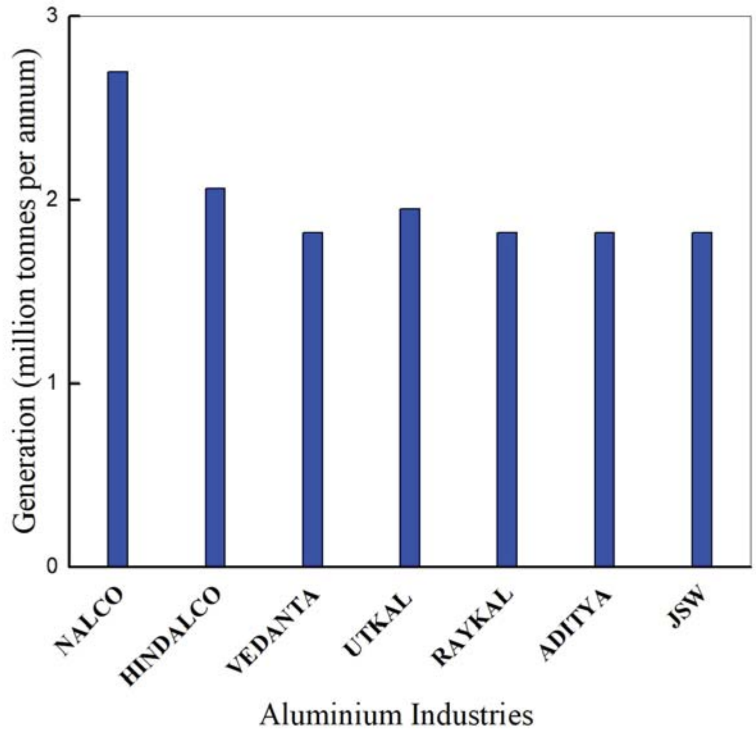


FIGURE 1.2: Red mud generation in India- present scenario [20].

and aquatic life when come in contact with land and water bodies [33–35]. Due to such limitations, now dry stacking and dry cake disposal methods are now practiced for safe disposal of residue. Dry stacking methods involve thickening and air drying process; whereas, dry cake disposal methods involves thickening and filtration process of residue before transfer to the disposal site. Filtration process helps in lowering the moisture content as well as reduces the losses of entrapped $NaOH$ in the residue that makes it more suitable for safer transportation, storage, and utilization in various engineering applications.

Further, engineered disposal area (EDA) with leachate collection and treatment facilities are being adapted along with the above techniques for red mud disposal [9, 10, 36]. At the same time, red mud has a massive problem of storage which requires a lot of space nearby alumina plant where it looks like huge mountain-size

TABLE 1.3: Chemical composition of red mud generated in different alumina plant

Country	Alumina Plant	Ref.No.	Major chemical composition (%)					
			Fe_2O_3	Al_2O_3	TiO_2	SiO_2	Na_2O	CaO
Italy	Eurallumina	[27]	35.2	20	9.2	11.6	7.5	6.7
Turkey	Seydisehir	[28]	36.94	20.39	4.98	15.74	10.1	2.23
UK	ALCAN	[29]	46	20	6	5	8	1
France	Aluminum Pechiney	[30]	26.62	15	15.76	4.98	1.02	22.21
Canada	ALCAN	[31]	31.6	20.61	6.23	8.89	10.26	1.66
Australia	AWAAK	[32]	28.5	24	3.11	18.8	3.4	5.26
Brazil	Alunorte	[32]	45.6	15.1	4.29	15.6	7.5	1.16
Germany	AOSG	[32]	44.8	16.2	12.33	5.4	4	5.22
Spain	Alcoa	[32]	37.5	21.2	11.45	4.4	3.6	5.51
USA	RMC	[32]	35.5	18.4	6.31	8.5	6.1	7.73
India	HINDALCO (used in present study)	[20]	21.9	28.1	7.5	15.6	10.2	4.5
	INDAL	[20]	24.3	24.5	6.2	18	-	5.3
	BALCO	[20]	19.4	27.9	7.3	16.4	11.8	3.3
	NALCO	[20]	14.8	54.8	6.4	3.7	2.5	4.8
	INDAL	[20]	19.2	44.5	7	13.5	0.8	4
	MALCO	[20]	14	18	56	50	2.0–4.0	6.0–9.0

mounds. Nowadays, lots of alumina plants are running out of space for the dumping of red mud. Thus, it is now essential to develop environmental friendly and sustainable cutting-edge technology to reduce, reuse and safe utilization of such industrial reject. Although, red mud has some environmental and logistical concerns with handling, storing and disposal due to its characteristics such as high alkalinity ($pH10 - 13.5$), sodicity, fine particles, heavy metals content [8]. Thus, red mud can not be used without treatment/stabilization and requires pre-treatment before civil engineering application. Stabilization is simply a method/technique of improving/modifying the basic properties of materials to satisfy the specific engineering requirements. It is needed when the available material does not meet the criteria such as stability, strength, compressibility, permeability, and durability for construction and building materials. Also, it should be environmental friendly and safe for the human being, aquatic life etc [37].

1.3 Overview of Stabilization Methods

Generally, mechanical, chemical, biological, thermal, electrical or in the combination of processes are used to improve the soil. Mechanical techniques include earth reinforcement, densification, and dewatering, etc whereas chemical process uses various traditional and non-traditional additives such as lime, cement, sodium silicate, calcium chloride, sodium hydroxide, sodium chloride, Xanthan gum, guar gum and many more [38, 39]. Thermal method and electrical methods are expansive and required skilled supervision thus these methods are not practiced frequently. In general, chemical soil stabilizers are categorized as being either traditional or nontraditional additives [40, 41]. Traditional additives embody cement, lime, bituminous materials, and industry by-products whereas nontraditional additives includes enzymes, polymers, resins, acids, silicates, ions, and lignin derivatives [42, 43]. Lime and cement are commonly used for stabilization purpose. Whereas, lime is one of the oldest and widely accepted traditional chemical stabilizer for construction purposes such as road, railroad, and airport, embankments, canal linings, the soil beneath foundation and slope stability. It has long history from ancient Mesopotamia, Egypt, Greeks and Romans to modern day construction [44–46].

1.3.1 Lime Stabilization

When the soil is treated with lime, it exhibits various changes in the lime- treated soil such as an increase in the plastic limit, decrease in plasticity indices, effective grain size increases, decrease in volume change, increase in strength, decrease in maximum dry density and increase in optimum moisture content.

1.3.1.1 Mechanism of Lime Stabilization

The changes mentioned above are attributed to one or more reactions, such as cation exchange, flocculation-agglomeration, cementing and carbonation, when the soil is treated with lime. Ion exchange, flocculation-agglomeration and carbonation occurs in the first stage, while pozzolanic reaction occurs in the second stage. In ion exchange, flocculation-agglomeration, calcium cations of lime replace metallic cations (sodium and hydrogen) on the surface of a clay particle and additional calcium ions are attracted to the surface which results lower plasticity and more friable soil. Whereas in carbonation, the available carbon dioxide in the air reacts with calcium or magnesium in the lime to form calcium or magnesium carbonate which imparts minor strength in the soil. However, these carbonates deter pozzolanic action and impede strengthening of soil. Cementing action is usually attributed to a pozzolanic reaction in which the aluminous and siliceous minerals in the soil react with lime in presence of sufficient moisture produce a gel of calcium silicates hydrate, calcium aluminate hydrate or calcium aluminate silicates hydrate. This gel cements the soil particles in a manner similar to that of hydrated cement [47–55] and reactions occur during this stage is as follows:

$$Ca(OH)_2 + SiO_2 \rightarrow CaO - SiO_2 - H_2O\,(C - S - H) \tag{1.1}$$

$$Ca(OH)_2 + Al_2O_3 \rightarrow CaO - Al_2O_3 - H_2O\,(C - A - H) \tag{1.2}$$

In addition to above, small amounts of C_4AH_{13}, C_3AH_6 and C_2ASH_8 (where, C is CaO, A is Al_20_3, H is H_2O and S is SiO_2) are also developed during the reactions [56–58]. These cementing action involving soil particles and lime causes increase in the strength. However, the degree of modification of lime stabilized soil depends on the several other factors such as type and amount of lime, soil type, moisture content, time between mixing and compaction, mixing, compactive effort curing time, conditions and temperature. Several researchers have studied the behavior of lime stabilized soil and found that the strength of stabilized soil increases with the increase in lime content, density, molding moisture content in the range below optimum, curing time and temperature.

Although, use of traditional additives such as lime and cement are considered as the less environmental friendly solution for soil stabilization as it will increase the pH of the soil after treatment and release extensive quantities of carbon dioxide during production which cause disturbances to the ecosystem [59, 60]. In general, 1 t CO_2 is released to the atmosphere and about 1.5 t by-products and approximately 3630 MJ energy is consumed during the production of 1 t of ordinary Portland cement that is added to increase the greenhouse emissions. With the limitations of traditional stabilizers, non-traditional stabilizer is now encouraged to help the CO_2 emission reduction strategies. Non-traditional additives are also called green materials which commonly include biopolymer and geopolymer which neither release carbon dioxide nor create a problem for the ecosystem. However, it is not popular methods due to unavailability of long term studies which could assure the performance of the stabilized materials.

1.3.2 Biopolymer Stabilization

Biopolymer is naturally occurring materials or water-insoluble gel-forming biopolymers of microbial origin produced in the industry using a natural process. Commonly used biopolymers include xanthan gum, guar gum and diutan gum biopolymers. However, Xanthan gum is frequently used due to its unique characteristics such as pseudo-plasticity,anionic and hydrophilic surface characteristics, high stability under a broad range of temperature and pH [61–63]. It is produced by fermentation of glucose or sucrose by the Xanthomonas campestris bacterium. Xanthan gum is a hetero-polysaccharide; its structure consists of two glucose, mannose, and one glucuronic acid (penta-saccharide). It is an anionic biopolymer which easily adsorbs water molecules via hydrogen bonding [64]. Its anionic and hydrophilic surface characteristics react with cations and forms higher gelation. When Xanthan gum is mixed with soil, it behaves differently with different types of soils. In case of cohesionless soil, it simply coats the grain surfaces and extends the area of contact among the soil particles whereas direct interaction through hydrogen bonding takes place between Xanthan gum and clay particles due to the electrically charged clay particles [65].

1.3.3 Geopolymer Stabilization

Geopolymers are inorganic polymers produced by polymerization of silicon, aluminum and oxygen species to form an amorphous three-dimensional structures. It is made with the dissolution of an alumino-silicate materials in the alkaline environment. In this process, firstly alumino-silicate materials are dissolved in the alkaline solution which create AlO_4^- and SiO_4^- tetrahedral and finally a gel phase regarding different types of monomers are formed which depends on the availability (concentration) of silica in the solution. The molecular arrangement in geopolymer process are summarized in Fig 1.3.

The methodology as stated above is available in literature [67–71] . For the sake of brevity these are not described here in detail. Various types of industrial wastes, their source, estimated annual generation with reference to world and India and their utilization rate and various techniques used for stabilization have been briefly discussed in this section. In the next section, review of literature available in public

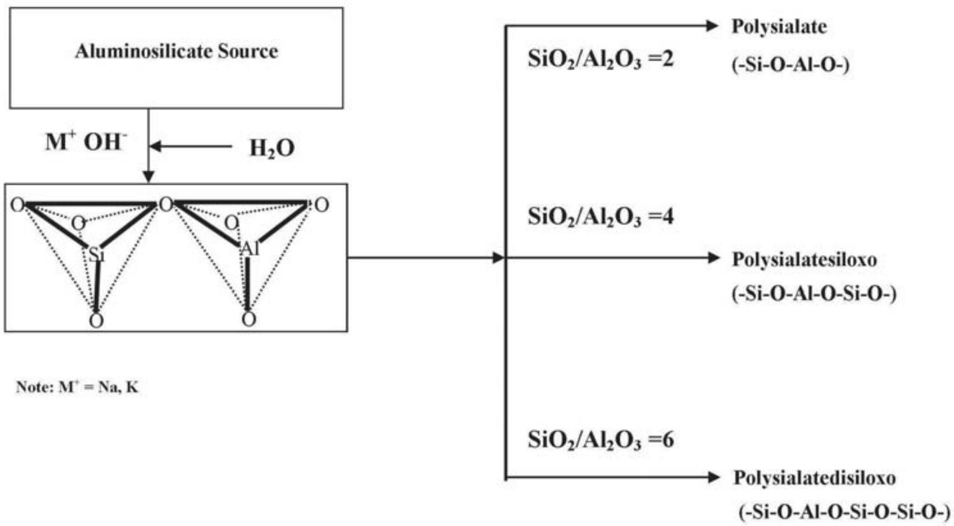


FIGURE 1.3: General framework molecular arrangement in geopolymer process [66].

database on utilization of red mud is presented in detail to establish the level of knowledge as a foundation for the present research .

1.4 Previous Studies

Researchers have carried several studies covering various aspects that explore disposal and utilization of red mud as resource material. The review of literature's are systemically presented herein to identify the gap of the reported work and to set the basic objectives of the present work and a Part of the work has been published as [1].

[1] **S. Kumar and A. Prasad**, "Civil engineering application of artificially cemented red mud: state-of-the-art review," *Recent trends in civil engineering and water resource engineering*, RTCWRE-17, Hyderabad, pp. 138-140, 2017.

1.4.1 Recovery of Components

Red mud primarily contains a significant amount of oxides of iron, aluminum, silica, and titanium and other valuable rare earth metals like Ga, Sc, Li, V, Rb and Ti [72]. Therefore, it is of great significance to recover metals from red mud. Due to the characteristics of high iron content and valuable metals, extensive research have been carried out in this areas by the researchers worldwide. About 83 numbers of patent has been found in these areas between the year 1964 to 2008 and details are shown in Fig1.4.

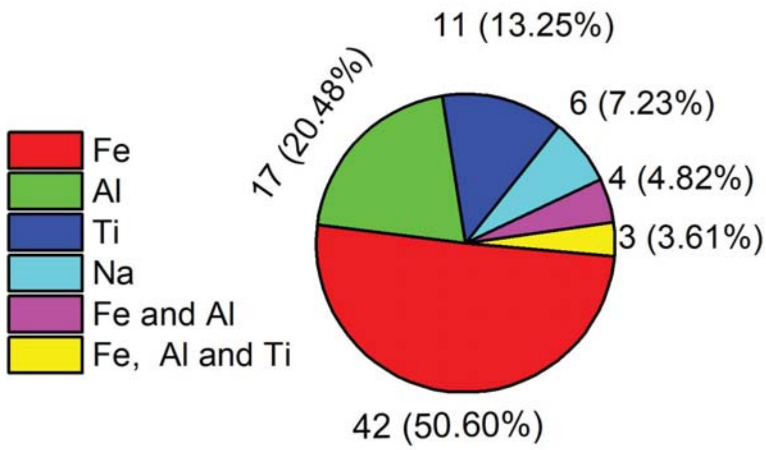


Figure 1.4: Overview of some patents on metals recovery from red mud [36, 72]

From Fig 1.4, it appears that most of the patents awarded for recovery of iron and few patents have also been awarded for recovery of aluminium, titanium and sodium. Further, the detailed literature on recovery and different methods adopted for various metals are briefly summarized in Table 1.4.

from the Table 1.4, it appears that direct magnetic separation, pyrometallurgy methods are used for iron recovery whereas hydochemical and bio leaching process is adopted for aluminum recovery from red mud. For example, hydro chemical process is an easy process that is frequently adopted for recovery of aluminum.

TABLE 1.4: Various studies on recovery/extraction of metals from red mud[36, 72]

Sr. No.	Title	Ref.	Recovery/ Extraction of Metals	Procedures adopted	Remarks
1	Method for recovering iron concentrates from alumina red mud	[73]	Iron	Direct magnetic separation	
2	Method for recycling iron from waste red mud in alumina production	[74]	Iron	Pyrometallurgical process	
3	A process for the production of direct reduced iron from red mud	[75]	Iron	Different preparation method is used	Graphane (accelerant) is mixed with red mud according specific ratio (red mud 85–99.5%, accelerant (0.5–15%).
4	Method of dealkalizing red mud and recovering aluminum and iron	[76]	Iron and Aluminium	Hydrometallurgy	
5	Processes for treating red mud	[77]	Fe, Ni, Co, Mg, and rare earth elements	Hydrometallurgy	
6	Conversion method of iron minerals in production process of alumina	[78]	Iron	Rcovery Process incorporated into the alumina Conversion method of iron minerals in refining process.	
7	Method for high-efficiency separation and comprehensive utilization of iron, aluminum and sodium in high-iron red mud	[79]	Iron, Aluminum and Sodium	Recovery process was incorporated into the iron ore smelting process	
8	Method for separating iron from raffinate in process of extracting scandium from red mud	[80]	Iron, Scandium	Iron is separated during the extraction of scandium	
9	Red mud harmless comprehensive recycling technology suitable for Bayer process	[81]	Iron and Aluminium	Various Process	First red mud is neutralized to pH 7.5–9 then it is separated into high specific gravity portion and low gravity portion by by gravity separation. Former is used for iron extraction and later is used for aluminium extraction.
10	Valuable products obtained from red mud	[82]	silicon dioxide, calcium sulphate, titanium dioxide, alums and ferrites (magnetite)	Various Process	A complex process for the usage of red mud to achieve zero waste.
11	Extraction process for reactive metal oxides	[83]	Iron, Aluminium and Titanium	Various Process	

Table **1.4 Continued..........**

Element recovered	Ref.	Study Type	Metallurgical process	Advantages	Disadvantages	Process adopted
Al	[31, 84–86]	Laboratory	Hydrochemical	Easy process	Poor efficiency and high costs.	Al2O3 extraction: 45% NaOH solution, CaO/red mud=0.25, Liquid/Solid=0.9.
		Laboratory	Bioleaching	Green process	Longer time periods.	Na_2O extraction: 7% NaOH solution, Liquid/Solid = 3.8.
Na	[85]	Laboratory	Pyro- and hydrometallurgy	High efficiency	high cost.	Reduction sintering, Hydrothermal treatment and temperature calcination.
		Laboratory	Hydrothermal treatment	Easy process	poor efficiency and high costs.	Soda-lime roasting, Roasting, quenching, magnetic separation and Calcination.
Fe	[31, 85–93]	Laboratory	Pyro- and hydrometallurgy	Less integrowth required	High energy consumption.	Roasting and Soda-lime roasting.
		Laboratory	Pyro- and hydrometallurgy			
		Laboratory	Magnetic separation	Low energy input.	Low efficiency.	
		Pilot	Pyrometallurgy		high energy consumption	
Ti	[94]	Laboratory	Bioleaching	Green process.	Longer time periods.	
		Laboratory	Pyro- and hydrometallurgy	Additional value as iron recovery.	High energy input.	Smelting,leaching with H_2SO_4.
V	[95]	Laboratory	Hydrometallurgy	High efficiency.	Secondary pollutants generate.	Ex traction with V_2O_5.
		Laboratory	Hydrometallurgy			
Sc	[96, 97]	Laboratory	Pyro- and hydrometallurgy			Leaching with acid.
Rare earth metals	[97–102]	Pilot	Hydrometallurgy	Improved efficiency.	Complex process.	Acid leaching 3 M H_2SO_4, solid to liquid ratio.
		Laboratory	Hydrometallurgy			

However it has poor efficiency and high operating costs. Similarly, the bio leaching is called as green process but it takes longer time periods for recovery of aluminum. Thus, every methods have their own merits and demerits regarding efficiency and costs.

1.4.2 Environmental and Agronomic Application

Red mud can also be employed in water and waste water treatments, treatment of acidic mine drainage, removal of acidic gases from waste streams, adsorption, and removal of trace metals, nutrient supplement and water holding capacity of soils [103–111]. It also works as a good heavy metal absorbent by changing the exchangeable heavy metal ions present in the contaminated soil into bonding oxides. Researchers [112–114] conducted laboratory tests on polluted soil and reported that red mud can reduce the heavy metal content of contaminated soil significantly . Work on environmental and agronomic applications reported by the researchers are summarized in the table 1.5.

1.4.3 Civil Engineering Application

Civil engineering is one of the promising areas where a large volume of different industrial waste can be used in various forms of construction and building materials such as pavement materials, bricks and paving blocks, embankment materials etc, with some modification in the properties of waste. Various attempts have been made by the researchers to incorporate them into the construction and building materials [21, 123–125]. Also, the behavior of the materials must be known. It helps us in deciding if the materials are suitable for various civil engineering applications. Several studies have been carried out on the basic geotechnical properties of red

Table 1.5: Previous studies on environmental and agronomic applications

Sr. No	Materials	Ref.	Fuctions	Applications	Study Type	Remarks
1	Red mud	[108]	Heavy metal removal and neutralization	waste water treatment	Pilot	Coagulant
2	Modified bauxite refinery residue (Bauxsol™)	[115]	Phosphate removal	Water and waste water treatment	Laboratory	Cost-effective adsorbent
3	Red mud and fly ash	[110]	Absorption of heavy metals	Mine tailing dam	Laboratory	Neutralization
4	Neutralized red mud,seawater and Bauxsol™	[116]		Water treatment	Laboratory	Porous Pellets
5	Seawater neutralise red mud (Bauxsol™)	[111]	Arsenate removal	Water treatment	Laboratory	Adsorbent
6	Bauxsol™ and biosolids	[117]	Biomass production	Mine soil	Laboratory	Soil amendment
7	Mixture of Bauxsol™, sand and burnt lime	[118]	Metal salt removal	Water treatment	Laboratory	Adsorbent
8	Activated red mud	[107, 109, 119, 119]	Sorption of phosphate	Waste water treatment	Laboratory	Adsorbent
9	Red mud	[120, 121]	Heavy metal removal	Water removal	Laboratory	adsorbent
10	Red mud bauxite	[104–106, 122]		Acidic mine tailings	Laboratory	Neutralization

mud. The findings of the works reported by researchers[126–133] are summarized as: specific gravity (2.64–3.95), maximum dry density (1.42-1.53 g/cc), optimum moisture content (18-33.5%), liquid limit (25–66%), plastic limit (27–40%), plasticity index (4–32%), permeability (10^{-4}–10^{-8} cm/s), coefficient of consolidation (0.26–0.39 cm^2/sec), classification (ML), cohesion (0.1-0.2 kg/cm^2), angle of internal friction (26–28°), unconfined compressive strength (0.41–1.75 kg/cm^2), and California bearing ratio (4.2-7.8). From the above findings, it appears that red mud contains mostly fine particles. It has low permeability, and high specific gravity, and density compared to soil. These basic properties support that red mud can be used as a geotechnical material such as in filling for embankment and as pavement material.

1.4.3.1 Production of Construction and Building Materials

Construction and building materials play an important role in the development of any infrastructure projects. It also consumes a significant volume of building materials such as brick and paving block. For their resourceful use, researchers have used various types of cementing materials, such as traditional (lime and cement) and non - traditional (geopolymer and biopolymer) additives to stabilize red mud.

Traditional Additives: Lime and Cement

Brick and Paving Block

Several investigators have been trying to develop bricks and paving blocks of red mud, in conjunction with fly ash, silica fume, stone dust and lime, cement,gypsum, clay or other industrial residues [134–138]. Initially, **Dass and Malhotra (1990)** [139] prepared unfired red-lime brick and reported strong compressive strength (3.75 MN/m^2) and 4.22 MN/m^2 with 5 percent and 8 percent lime after 28 days of healing respectively. They recommended that the brick can be used for low-cost shelters. Further, **Zhongli (1993)** [140], **Jianshu (2007)** [141],**Yang and Xiao (2009)** [142],**Guitang (2009)** [143], **Yuezhu (2009)** [144], **Minglei et al. (2012)** [145],**Fanmao (2013)** [146] have separately reported the production of non steam-cured and non-fired red mud brick using powdered coal ash, lime powder and gypsum and claimed good strength and endurance of the prepared bricks.

Binding Materials

Gordon et al. (1996) [147] investigated Jamaican red mud incorporating hydrated lime, condensed silica fume, and limestone as a binder in construction material. They also reported that the prepared red mud composite shows good compressive strength 15 to 18 MPa and 18 to 22 MPa after 28 and 122 days respectively. Further,a special cement was prepared with red mud-lime, fly ash-red mud-lime-gypsum and reported equivalent strength of special cement (28 days) and normal Portland cement. [22, 23]. **Tsakiridis et al. (2004)** and **Vangelatos et al. (2009)** [24, 148] has also examined the feasibility of the red mud as a raw material for the production of Portland cement clinker and found that small amount (3–5%) of red mud residue is beneficial to improve the compressive strength of ordinary Portland cement.

Miscellaneous Application

Young (1996) [149] claimed stabilization of red mud and their procedure using phosphoric acid for ceramic products. The stabilization process comprises of mixing of red mud with water (about 45%) and stirring at 70–80°C then put 1 to 3% by weight phosphoric acid to make mixture pH 7-9 then molding and curing to finally get a ceramic product based on stabilized red mud. **Kalkan (2006)** [21] has also prepared compacted clay liners with red mud and cement mix and reported high compressive strength, decreased the hydraulic conductivity and swelling with respect to natural clay samples. Further, he recommended the cement – red mud mix could be successfully used in Geo technical applications as clay liners. **Sabat and Mohanta (2006)** [150] have studied the effects of lime and fly ash on red mud's engineering properties and reported that red mud could be adopted as a mix optimal for civil engineering application with 15% fly ash and 8% lime. **Jian et al. (2007)**

[151] has prepared base material and their procedure for pavement from sintered red mud. The optimal mix contains red mud 75–85%, fly ash 10–5% and lime 17–15%. The construction method which primarily consists of sequentially (a) red mud layer is formed by evenly spreading the red mud and then rolling the roller, (2) paving fly ash, lime, and an outer additive layer of the red mud and then, using stabilized soil mixing machine and then mixing the mixture two times, and (3) watering, rolling, shaping, rolling and then the base layer is formed and the surface of the layer should be covered with grass plastic film to maintain the mixture moisture content of about 45 to 48%. Further, **Das, Rout, and Sahoo (2013)** [152] conducted a laboratory test and numerical study for the feasibility of red mud as an embankment material and reported that it meets the criteria and has the potential to be considered as an embankment material. **Jupei et al. (2013)** [153] prepared road material (base layer, cement stabilized gravel layer and surface layer) produced by using Bayer process red mud. Base layer is prepared using 4–25% low-temperature ceramic curing agent, 45–96% red mud and 0–30% aggregate whereas cement stabilized gravel layer having 8–20% low-temperature ceramic curing agent, 10–20% red mud and 60–82% aggregate and the road base layer is manufactured by 10–30% low-temperature ceramic curing agent, 2–10% red mud and 60-88% aggregate. They also suggested the beneficial effects of red mud that great amount of natural resources and the cost of road engineering could be saved during the roadway building process. Similarly, **Deelwal, Dharavath, and Kulshreshtha (2014), Kushwaha and Kishan (2016)** [129, 154] have investigated the effect of lime and gypsum on engineering properties of red mud and reported that the 7 days cured red mud with 12% lime and 1% gypsum can be chosen as the optimum dosage and can be used as sub grade material for road construction. **Kishan, Kushwaha, and Dindorkar (2018)** [155] explored the potential of Red mud– fly ash-gypsum mix for leaching problems. They reported that stabilization with proper proportioning of red mud with fly (0%– 25%)

ash and gypsum (0%– 0.75%) can immobilize the metal concentration and reduced the permeability of the mix.

Non-traditional Additives

1.4.3.2 Geopolymer

As discussed earlier in Sec.1.3.3, geopolymers are inorganic polymers produced by the chemical reaction of aluminosilicate oxides (Si_2O_5, Al_2O_2) with alkali poly silicates. In the geopolymerization process, Si/Al ratios, solid-to-liquid ratio and quantity of the alkali solution, temperature, curing conditions and additives are key factors affecting the geopolymer's performance [156]. Generally, materials containing silica (Si_2O_5) and alumina (Al_2O_2) are a possible source for geopolymer production [18, 157]. Different industrial byproducts such as pozzolana, natural aluminosilicate minerals, metakaolin, fly ash, granulated blast furnace slag, fly ash and kaolinite mixture, fly ash-metakaolin mixture, red mud-metakaolin mixture and red mud-fly ash mixture were studied as geopolymer synthesis raw materials[158–164]. **Dimas et al. (2009)**[165] studied the effect of solid-to-liquid ratio, $NaOH$, silica concentrations, and metakaolin on the properties of red mud geopolymer materials and suggested that these polymer composite material has good compressive strength, low water absorption and excellent fire resistance. **Kumar and Kumar (2013)** [166] developed environmentally safe paving blocks using red mud and fly ash using geopolymer technology and recommended that red mud and fly ash geopolymer paving blocks meet the criteria of the Indian standard " IS 15658: 2006". **He et al. (2013)** [167] investigated the potential of red mud and rice husk ash geopolymer as construction materials. They reported high compressive strengths ($20.5 MPa$) and they recommended that red mud may be viewed as alternatives in the industrial sectors of construction and building materials. Further, **Hajjaji et al. (2013)** [168] designed composite material with metakaolin, iron oxide,red mud and activated by sodium silicate and $NaOH$ and reported good mechanical properties of composite matrix with curing time. They also recommended red mud as suitable material for geopolymer production when it mixed in reasonable ratios (red mud 25 % and 75 % metakaolin). **Zhang et al. (2014)** [169] also investigated the influence of various factors such as curing temperature, curing time and aluminosilicate materials (fly ash) on mechanical properties and microstructural red mud (RM) geopolymer. Further, they suggested that the composite materials can a greener alternative for ordinary Portland cement in various engineering applications. Further, **Hairi et al. (2015)** [170] prepared geopolymers with red mud and silica fume and reported very high compressive strengths (44–58 MPa) with an optimal SiO_2/Al_2O_3 ratio of about 3. Whereas, **Kaya and Soyer (2016)** [171] also investigated the mechanical properties of red mud–metakaolin (40:60) geopolymers and found compressive strength values between 14.2 to 10.6 MPa. Later on, **Zhang et al. (2016)** [172] studied the long term durability and leaching behavior (heavy metal) of red mud- fly ash (class F) geopolymers and found that Strength (UCS), Young's modulus (E) and flexural strength of the composite specimens decreased by 30%, 70% and 45% after 120 days after soaking in the H_2SO_4. Further, the concentration of heavy metals in red mud-fly ash (class F) geopolymers specimens found much lower than the respective contamination limits in soils set by the united state environmental protection act (US EPA) standard. They also recommended that geopolymer technology can not only be uses as an economical and greener alternative to ordinary Portland cement, but also utilize (recycle and reuse) these waste into significant quantities.

1.4.3.3 Biopolymer Stabilized Red Mud

Panda and Das (2015, 2017) [173, 174] studied morphological, physical and geotechnical properties of neutralized red mud using biopolymers (xanthan gum and guar gum) and found a noticeable change in the behavior such as improvement in unconfined compressive strength, split tensile strength, increase in optimum moisture content and decrease in maximum dry density with increase in the amount of xanthan gum (up to 1%) then decreases due to change in the structure of red mud. **Alam, Das, and Das (2018)** [175] studied the dispersive and sedimentation characteristics of red mud. Further they recommended that small amount (0.5%) of biopolymers such as guar gum (GG) and xanthan gum (XG) was very effective in controlling the dispersiveness of red mud. Recently, **Reddy, Rao, and Reddy (2018)** [176] also investigated the potential of environmental friendly biopolymers (guar gum, xanthan gum) to mitigate the dispersive characteristics of red mud waste. They found that guar gum was more effective than xanthan gum in controlling the dispersive characteristics of red mud. However, both the biopolymers having potential in mitigating the dispersive behavior of red mud waste.

1.4.4 Application of Design of Experiment

It can be noted from the previous section that most researchers have adopted a conventional method for planning and conducting experiments to determine the desired properties of the stabilized red mud. In addition, author could not find any work on stabilized red mud using a different approach to optimize the experiment number. Very limited works have been reported by the researchers on the application of experiment design to study the influence of different factors on soil engineering properties or industrial waste. However, it has been successfully applied in other areas. For example, researchers have used design of experiment to optimize the dose of sewage sludge [177]. Some researchers have successfully applied DOE for the Optimization of chemical oxygen demand, and suspended solids in waste water treatment [178, 179]. The details of works reported by various researchers are briefly summarized in Table 1.6.

Although, it can be done using a conventional approach but sometimes conducting experiments and data collection are extensive and time-consuming. In general, one variable at a time ($OVAT$) is used in the conventional experimental approach, that results in large number of experiments that is time consuming and expensive. Sometimes it is very difficult or impossible to vary all the variables at the same time to optimize the result. In such a situation, experiment design can be tried as an alternative approach which overcomes the deficiencies of the conventional experimental method [189]. Design of experiment is simply statistical technique that defines optimal relations between independent variables and response to develop an efficient model. The fundamental advantage of experiment design is the simultaneous influence of all independent variables on the response in a set of designed experiments. However, in conventional approach, the entire independent variables are kept constant while varying single variable at a time to see its effect on the response. Design of experiment (DOE) is now gaining popularity among researchers and has become notably useful alternative tool due to its capability that presents reasonably alternative solutions for the decision support of engineering problems. The basics of experiment design are well discussed in various reference books and magazines and are therefore not included in this thesis [190–194]. In addition, the basic methodology for ready reference is briefly discussed in Chapter 2.

TABLE 1.6: Studies on application of design of experiment in engineering problems

Sr. No	Materials	Ref.	Methods	Parameter studied	Goal
1	wastewater sludge ash	[177]	Factorial experimental approach	California bearing ratio	Optimize dose of sewage sludge ash for highway materials
2	Sand	[180]	Response Surface Methodology	Unconfined compressive strength	Optimum amounts of Polypropylene Fiber and Sewage Sludge Ash
3	Expasive soil	[181]	Response surface methodology	Durability (freeze-thaw)	Optimize amount of lime, rice husk ash and fiber
4	Concrete	[182]	Response surface methodology	Characteristic length , splitting tensile strength and flexural strength	Cement, silicious sand, limestone
5	Biodiesel Wastewater	[178, 179]	Response surface methodology	Electrocoagulation process	Optimization of chemical oxygen demand, and suspended solids
6	Concrete	[183]	Response surface methodology	Strength and Permeability	Fly ash and metakaolin
7	Metal cutting wastewater	[184]	Response surface methodology	Chemical oxygen demand , total organic carbon , and turbidity, and operating cost	pH, Current density, and Operating time
8	Azo dye reactive black	[185]	Response surface methodology	Dye decolourization	Optimization of dose of dye , enzyme , redox mediator, concentrations
9	Embankment	[186]	Full quadratic response surface model	Frictional angle stochastic properties	Soil proprties
10	Surfactin production	[187]	Multi-stage Monte-Carlo optimization, Full quadratic response surface model	pH, temperature, rates of agitation and aeration	Fermentation process
11	Review	[188]	Response surface methodology , artificial neural networks	Misclenious	Biosorption processes

1.4.5 Application of Artificial Neural Network

Recently, due to their high ability to address the extensive variety of problems , artificial neural network is being more and more used in civil engineering [195–199]. Artificial neural network (ANN) is a soft computing technique inspired by our biological nervous system. In the ANN model, a computer program is framed to replicate to process the information in a manner that the human brain performs, which improves its skill in identifying the pattern/relations among the input and output parameters. In this model, relationships are established between the dependent and independent variables by examining the patterns inherent within the data set. However, the development of predictive models based on a statistical technique from restricted data base is very challenging and difficult because it makes use of a possibility distribution feature as there are inherent uncertainties in the data set. For that reason, artificial neural network has been used extensively to solve complicated problems in the areas of geotechnical engineering.

Several researchers have applied soft computing techniques to predict the geotechnical behavior such as unconfined compressive strength [200, 201], maximum dry density, optimum moisture content, shear strength and permeability [202–206], swelling pressure[207], settlement of footings [208]. However, the main constraints with the artificial intelligence based model are that it requires sufficient numbers of data set for good neural network training. It will not work if the data set available for training is insufficient. There is still no unique formula or thumb rule available in the literature regarding the number of data sets needed for training the neural networks, and it solely depends upon the nature of problem and quality data set. The number of data in the optimization problem remains an important problem in the application of artificial intelligence. Sometimes, such a large number of experiments for the time-bound important projects can not be carried out. To overcome this limitation, experiment design is used to plan the experiment and the *DOE* data set is used as training and test data sets in artificial intelligence techniques to observe how these techniques work with limited numbers but properly optimized data sets[209].

From the literature survey, it is found that there are several studies reported on metal extraction / recovery, water and waste water treatments, treatment of acidic mine drainage, removal of acidic gases from waste streams, adsorption, removal of trace metals, nutrient supplement and water holding capacity of soils. Furthermore, few attempts have also been made by researchers and reported in the literature on the development of construction and building materials such as bricks and paving blocks using various industrial residues . Additionally, it is observed that there is a paucity of information in the literature about the influence of various factors (dose and types of cementing agent, dry unit weight, molding moisture content, number of wetting-drying cycles, curing time and curing conditions) that affect the mechanical properties of stabilized red mud. Furthermore, it also appears that no predictive equations are available on the stabilized red mud which could be used as a ready reference for practicing engineers. Also, the researchers haven't tried for the optimization of variables which affects the mechanical properties of stabilized red mud. Furthermore, the author could not find any work on the application of machine learning for the design and development of a predictive model based on different designed approach data sets and hence could be a new research area.

1.5 Motivation and Objectives of Research

From the available literature, it appears that the various researchers have reported several works for the use of such by-product (red mud). However, some of the areas discussed earlier have not been explored much. The present work is therefore an attempt to bridge the gap in previous studies on red mud. The objectives of the present works are as follows:

- To explore the different approach to study the parameters affecting the strength and durability of red mud.
- To develop semi-empirical equations for the prediction of strength and durability characteristics of stabilized red mud for the range of the studies.
- To examine the performance of the different approaches (conventional and experimental designed (DOE)) used for the assessment of mechanical properties of the stabilized red mud.
- To explore the potential of using stabilized red mud for different civil engineering applications.
- To study the effectiveness of the artificial neural network model based on database obtained from different approach for prediction of the mechanical properties of stabilized red mud.

1.6 Organization of the Thesis

The present thesis is made up of six chapters based on the study of red mud and lime.

Chapter 1 addresses the production of different industrial wastes from various sources and how they effect our environment and Eco-system. It discusses the origin, generation and basic characteristics of bauxite ore and their by-product (red mud or bauxite residue). It also discusses the difficulties and problems, that led into the direction of its utilization as a resource for various engineering applications.

The existing literature exploring the problems in the utilization of red mud and establishing the level of knowledge as a foundation for the current research are also reviewed.

Chapter 2 outlines the details of materials (raw materials as well as additive) and methodologies (statistical and numerical techniques) used in the present study. A brief description on sample preparation and testing procedure for various laboratory tests carried out as per relevant standards/code of practices have also been included.

Chapter 3 discusses the influence of various parameters on the strength and durability characteristics of stabilized red mud using two different approach (conventional and design of experiment). Further, the performance of the different methods are analysed and discussed in detail. It also demonstrates application of design of experiment (DOE), an alternative approach to optimize the number of experiments and their performance analysis with the conventional approach. Further, it presents a predictive model (empirical correlation) as a ready reference for the range of study. Finally, cross-correlation study to see the relative contribution of individual parameters on the response and different performance indices is also incorporated at the end of this chapter.

Chapter 4 pertains to the application of artificial neural network in predicting the strength of stabilized red mud using conventional and DOE designed data sets. The results so obtained are compared with measured data set using various approaches to analyse the performance of different predictive models. Finally, a predictive equation based on artificial neural network is also suggested that can be used to predict the strength characteristics of stabilized red mud for the range of studies.

Chapter 5 discusses the potential of using stabilized red mud mix in civil engineering application (pavement layers and unfired bricks).

Finally, **Chapter 6** presents a generalized conclusions made from the entire work. It also indicates the possible scope of work for future study.