EFFECTIVE UTILISATION OF INDUSTRIAL WASTES

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1. INTRODUCTION

Environmental pollution is the major problem associated with rapid industrialisation, urbanisation and rise in living standards of people. For developing countries, industrialisation was a must and still this activity very much demands to build self reliant and in uplifting nation's economy. However, industrialisation on the other hand has also caused serious problems relating to environmental pollution. Therefore, wastes seem to be a by-product of growth. The country like India can ill afford to lose them as sheer waste. On the other hand, with increasing demand for raw materials for industrial production, the non-renewable resources are dwindling day-by-day. Therefore, efforts are to be made for controlling pollution arising out of the disposal of wastes by conversion of these unwanted wastes into utilisable raw materials for various beneficial uses. The problems relating to disposal of industrial solid waste are associated with lack of infrastructural facilities and negligence of industries to take proper safeguards.

The major generators of industrial solid wastes are the thermal power plants producing fly ash, the integrated Iron and Steel mills producing blast furnace slag and steel melting slag, non-ferrous industries like aluminum, zinc and copper producing red mud and tailings, sugar industries generating press mud, pulp and paper industries producing lime and fertilizer and allied industries producing gypsum. Waste management should include effective utilization of waste products produced by the industries for various applications.

2. FLY ASH

Thermal Power stations using pulverized coal or lignite as fuel generate large quantities of ash as a by-product. About 120 coals based thermal power stations in India are producing about 112 million tonne fly ash per year. With the increasing demand of power and coal being the major source of energy, more and more thermal power stations are expected to be commissioned/ augment their capacities in near future. Fly ash has been considered as a "Pollution Industrial Waste" till about a decade back and was being disposed off in ash ponds.

Indian coal has high ash content (35%- 45%) and low calorific value (3500 kcal/kg – 4000 kcal/kg) as a result of which huge quantity of fly ash is generated. It is expected to increase to about 200 MT per year by the year 2012. This would require about 4000 ha of land for the construction of ash ponds. Generally one acre of land is required per megawatt of power generation. Continuous studies have been carried out in India towards management of fly ash (FA), disposal and utilization. Out of total power generated of India, about 70% is produced by thermal power plants (TPPs). The Majority of thermal power plants 84% are run by coal; rest on gas (13%) and oil (3%). Thermal power plants uses 260 million tonnes (MT) of coal which is about 65% of annual coal produced in India The quality of flyash which depends on coal, coal particle fineness, percentage of ash in coal, combustion technique used, air/fuel ratio, burners used, and type of boiler.

The Indian Government has taken a target of 31.1 million housing complex as per 2001 Census out of which 24 million units are in rural area and 7.1 million units in urban areas, for that government targeted the year 2010. In 1998, National Housing and Habitat Policy has been announced by the govt which aims for providing "Houses for All" and facilitating the construction of 20 lakh additional housing units (13 lakh in rural areas and 7 lakh in urban areas) annually, with emphasis on extending benefits to the poor and the deprived. Apart from the above housing needs, nearly 1% of the housing stock in the country is destroyed every year due to natural hazards.

Large number of innovative alternate building materials and low cost construction techniques developed through intensive research efforts during last three to four decades satisfies functional as well as specification requirements of conventional materials/techniques and provide an avenue for bringing down the construction cost. Fly Ash, an industrial by-product from Thermal Power Plants (TPPs), with current annual generation of approximately 112 million tonnes and its proven suitability for variety of applications as admixture in cement/concrete/mortar, lime pozzolana mixture (bricks/blocks) etc. Cement and Concrete Industry accounts for 50% Fly Ash utilization, the total utilization of which at present stands at 30MT (28%). The other areas of application are Low lying area fill (17%), Roads & Embankments (15%), Dyke Raising (4%), Brick manufacturing (2%) and other new areas for safe disposal of fly ash is in paint industry, agriculture etc.

Table 1 Fly ash generation and utilization in different countries

Sl. No.	Country	Annual ash production, MT	Ash utilization %
1	India	112	38
2	China	100	45
3	USA	75	65
4	Germany	40	85
5	UK	15	50
6	Australia	10	85
7	Canada	6	75
8	France	3	85
9	Denmark	2	100
10	Italy	2	100
11	Netherland	2	100

Classes of Fly Ash

According to ASTM C-618 Fly ash is broadly classified into two major categories: Class F and Class C fly ash. The chief difference between these two classes is the amount of calcium, silica, alumina, and iron content. The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned (i.e., anthracite, bituminous, and lignite).

Class F fly ash

The burning of old anthracite and bituminous coal typically produces Class F fly ash which contains less than 10% lime (CaO). Possessing pozzolanic properties, the glassy silica and alumina of Class „F‟ Fly ash requires a cementing agent, such as Portland cement, quicklime, or hydrated lime, with the presence of water in order to react and produce cementitious compounds. Alternatively the addition of a chemical activator such as sodium silicate (water glass) to a Class „F" ash can lead to the formation of a geopolymer.

Class C Fly ash

Class C Fly ash produced from the burning of younger lignite or sub bituminous coal generally contains more than 20% lime (CaO). This type of ash does not require an activator and the contents of Alkali and sulfate (SO_4) are generally higher as compare to the Class F.

Eco-friendly building materials utilizing Fly ash

Cellular Light Weight Concrete (CLC) Blocks

These are substitute to bricks and conventional concrete blocks in building with density varying from 800 kg/m3 to 1800 kg/m3. The normal constituents of this Foaming Agent based technology from Germany are cement, Fly Ash (to the extent 1/4th to 1/3rd of total materials constituent), sand, water and foam (generated from biodegradable foaming agent). Using CLC walling & roofing panels can also be manufacture. Foaming agent and the Foam generator, if used for production of CLC with over 25% fly ash content invites concession on import duty by Govt. of India.

Development of Fly Ash Based Polymer Composites as Wood Substitute

Fly ash based composites have been developed using fly ash as filler and jute cloth as reinforcement. After treatment, the jute cloth is passed into the matrix for lamination. The laminates are cured at specific temperature and pressure. Number of laminates is used for required thickness. The technology on fly ash Polymer Composite using Jute cloth as reinforcement for wood substitute material can be applied in many applications like door shutters, partition panels, flooring tiles, wall panelling, ceiling, etc. With regard to wood substitute products, it may be noted that the developed components / materials are stronger, more durable, resistant to corrosion and above all cost effective as compared to the conventional material i.e. wood. This technology has been developed by Regional Research Laboratory, Bhopal in collaboration with Building Materials & Technology Promotion Council (BMTPC) and TIFAC. One commercial plant has also been set up based on this technology near Chennai.

Portland Pozzolana Cement

Up to 35% of suitable fly ash can directly be substituted for cement as blending material. Addition of fly ash significantly improves the quality & durability characteristics of resulting concrete. In India, present cement production per annum is comparable to the production of Fly Ash. Hence even without enhancing the production capacity of cement; availability of the cement (fly ash based PPC) can be significantly increased.

Anand Kumar studied the properties of concrete using various percentages of fly ash and GGBS. Fly ash was used from 50 to 70% and GGBS 5 to 30%. Superplastizer was used to achieve workability. With the study on the strength development on various high volume fly ash concrete (with at least 50 % fly ash as binder) mixes, the following conclusions were made. High volume fly ash concrete can be developed using GGBS upto 70% of fly ash as binder. It is possible to maintain a workability of minimum slump 100 mm using the available super plasticizer. The decrease in strength compared to control concrete with OPC as sole binder is around 20%. As the GGBS content increases the workability reduces at the same water containing and w/c. With a combination of 70% fly ash 10 % of GGBS and remaining quantity of binder compressive strength of 15MPa can be achieved. The cost of concrete may reduced upto 20% for high strength concrete, and about 45 % for lower strength concrete.

Ready mixed Fly Ash concrete

Though Ready Mix concrete is quite popular in developed countries but in India it consumes less than 5 percent of total cement consumption. Only recently its application has started growing at a fast rate. On an average 20% Fly ash (of cementitious material) in the country is being used which can easily go very high. In ready mix concrete various ingredients and quality parameters are strictly maintained/controlled which is not possible in the concrete produced at site and hence it can accommodate still higher quantity of fly ash.

Fly Ash- Sand-Lime-(Gypsum /Cement) Bricks /Blocks

Fly Ash can be used in the range of 40-70%. The other ingredients are lime, gypsum /cement, sand, stone dust/chips etc. Minimum compressive strength (28 days) of 70 kg/cm^2 can easily be achieved and this can go up to 250 Kg/cm^2 (in autoclaved type).

Sameer Mistry et al. studied the strength of Fly ash-lime-gypsum bricks. The bricks casted in pan mixer and brick making machine with some proportion of fly ash, lime and gypsum with quarry dust. The bricks were cured for 21 days. After curing the bricks were tested for water absorption test and compression test. We got water absorption = 15 % and compressive strength = 22.68 N/mm^2. Then we casted prisms with use of bricks and 1:6 mortars with 10 mm bed joints. The mortars were of two types:

- Cement: sand mortar and
- FaL-G : sand mortar

Such five samples were made and cured for 14 days and compression test were done. Based on the results for the experiments done on FaL-G brick prism masonry compressive strength measured at 14 days is 85.05 kg/cm2 for cement mortar (1:6) and 88.83kg/cm2 for fly ash mortar (1:6). As compare to conventional brick masonry prism compressive strength it is between 13.75 kg/cm2 to 121.80 kg/cm2 at 28 days strength. While FaL-G brick prism strength is 88.83kg/cm2 for cement mortar (1:6) and 85.05 kg/cm2 for fly ash mortar (1:6) just in 14 days. It can be increased up to 135 kg/cm2 to 145 kg/cm2 at 28 days. The results shows the FaL-G bricks are more safe, economical and having higher strength compare to conventional bricks. According to case study the fly ash bricks with conventional masonry work have 28% saving in cost with common red brick and conventional masonry work. The masonry work with new technology Rat-Trap bond in fly ash bricks have 33% saving in cost as compared to common bricks.

American civil engineer Henry Liu announced the invention of a new type of fly ash brick in 2007. Liu's brick is compressed at 4,000 psi and cured for 24 hours in a 150 °F (66 °C) steam bath, then toughened with an air entrainment agent, so that it lasts for more than 100 freeze-thaw cycles. Owing to the high concentration of calcium oxide in class C fly ash, the brick can be described as self-cementing. Since this method contains no clay and uses pressure instead of heat, it saves energy, reduces mercury pollution, and costs 20% less than traditional manufacturing techniques.[28][29] This type of brick is now manufactured under license in the USA.

There was a gradual increase in the use of fly ash in the manufacture of fly ash bricks or products from about 1.5 million tonne in 2002-2003 to 3.19 million tonne in 2006-2007 which need to be further encouraged for achieving the ultimate objective of conservation of top soil and minimise environmental pollution caused due to fly ash;

Fly ash aggregates

Pelletized or Expanded Slag is quickly cooled using water or steam to produce a lightweight aggregate that can be used for high fire-rated concrete masonry and lightweight fill applications over marginal soils. Due to its reduced weight, it is perfectly suited for aggregate in lightweight concrete masonry, lightweight ready-mix concrete and lightweight precast concrete.

Chang-Seon Shon presented comprehensive laboratory evaluation for developing synthetic aggregate using off-ASTM specification ash produced through a fluidized bed combustion (FBC) process. To determine optimum mix design which produces strong and durable synthetic aggregate, different combinations of water to fly ash ratio, various combination of fly ash (FAf) to stockpiled material (FAsp) ratio, curing temperature, and calcium chloride content were applied. Then, to evaluate the performance of synthetic aggregate for construction application, basic characteristics of synthetic aggregate such as density, specific gravity, absorption, gradation, strength, abrasion resistance, and soundness were carried out. The results indicate that 100% RH and 40 _C was determined to be the optimum curing conditions for both fly ash paste and FAf/FAsp mortar mixtures in terms of strength and minimal potential sulfate attack. The aggregate characterization results indicate that the produced synthetic aggregates met ASTM C 33/330 criteria for a concrete aggregate without inducing any soundness problems despite their relatively high water absorption. Therefore, the FBC ash and stockpiled ash can be used as primary resource materials for manufacturing synthetic light weight aggregate.

Based on the comprehensive laboratory evaluation to identify appropriate aging mechanisms and storage methods, an 80% fly ash and 20% stockpiled ash blend was selected as the optimum mixture proportion with 0.5 water to binder ratio to manufacture synthetic aggregate using off-ASTM specification fly ash. Furthermore, the optimum curing condition to minimize the potential of sulfate swelling was selected as 100% RH and 40ºC. The synthetic aggregates were produced through agglomeration and hardening process. Table 2 summaries all physical properties of manufactured FBC aggregate cured for 14 days. The bulk density was determined to be 79.9 lb/ft3, which meets the requirements of ASTM C 330 for coarse aggregate. The specific gravity was 1.74 which is somewhat lower than normal specific gravity of aggregate. As expected, this FBC aggregate has relatively high 24-h water absorption (20.1%) corresponding to low density. The combination of these properties would classify the manufactured synthetic FBC aggregates as lightweight aggregates.

Table 2 Physical properties of synthetic aggregate using off-ASTM specification ashes.

Aggregate property	Unit	Value	[a]ASTM criterion	
			C 33	C 330
Bulk density	kg/m3	1280		881
Specific gravity		1.74		
Absorption	%	20.1		
LA abrasion (Grade B)	% loss	19	50 (max)	50 (max)
Freeze and Thaw	% loss	20.5	-	
Sulfate resistance	% loss	10.85	18 (max)	

Strength	kPa	18,960		17,237

[a] Coarse aggregate

Fly Ash in Road Construction

Fly ash can be used for construction of road and embankment. This utilization has many advantages over conventional methods. Saves top soil which otherwise is conventionally used, avoids creation of low lying areas (by excavation of soil to be used for construction of embankments). Avoids recurring expenditure on excavation of soil from one place for construction and filling up of low lying areas thus created. Fly Ash may be used in road construction for:

i) Stabilizing and constructing sub-base or base.
ii) Upper layers of pavements.
iii) Filling purposes. Concrete with Fly Ash (10-20% by wt) is cost effective and improves performance of rigid pavement.
iv) Soil mixed with Fly Ash and lime increases California Bearing Ratio (CBR), increased (84.6%) on addition of only Fly Ash to soil. Addition of Fly Ash has not shown any adverse effects on the ground water quality in the vicinity of experimental plots.
v) National Highway Authority of India (NHAI) is currently using 60 lakh m3 of Fly Ash and proposed to use another 67 lakh m3 in future projects.

Roller compacted concrete

Another application of using fly ash is in roller compacted concrete dams. Many dams in the US have been constructed with high fly ash contents. Fly ash lowers the heat of hydration allowing thicker placements to occur. Data for these can be found at the US Bureau of Reclamation. This has also been demonstrated in the Ghatghar Dam Project in India.

Geopolymer concrete

Geopolymer is a hardened cementitious paste made from fly ash without Portland cement. It has greater compressive and tensile strengths, high strength gain rate, lower porosity and permeability, and greatly enhanced resistance to chemical attack compared with ordinary Portland cement (OPC) concrete. It combines waste products into a useful product, conserving landfill space and promoting sustainability, and compared with Portland cement, it features a 90% or greater reduction in carbon dioxide emission.

A solution of sodium hydroxide and potassium hydroxide (waste products from the chemical and petrochemical industries) must be prepared separately, then added to the liquid commercial sodium silicate; this solution may then be added to the powdered fly ash (waste product from coal and bio fuel combustion) in the same way as water is added for Portland cement.

The big difference between geopolymers and regular Portland cement is that their setting mechanism does not depend on HYDRATION, but rather in a POLYMERIZATION, which happens in a short period of time, while cement's hydration is mostly completed within one month, and fully completed only until one year. Geopolymer paste can be combined with the same aggregates used for Portland cement, for its use as mortar or concrete.

Among the many potential uses of geopolymer materials are heat insulation for re-entry for space crafts and the storage of corrosive substances, however possibly the most significant use is as a replacement for PORTLAND CEMENT as a cementitious binder in the construction industry.

Geopolymer's excellent mechanical and long term properties greatly exceed those of Portland cement and position geopolymer as an interesting new alternative to solve old civil engineering problems: how to obtain high early strength and durability.

Properties

- Compressive strength: 6,000 – 16,000 psi (depending on the fly ash used).
- Flexural strength: Approximately twice that of OPC.
- Chemical resistance: Two to Five times greater resistance to sulfuric acid attack compared with OPC; virtually immune to sulfate attack.
- Porosity/Permeability: Ten times lower than OPC utilized in typical structural applications.
- Strength gain: Full strength is gained within 1 to 3 days; 80% of ultimate strength is gained within a couple of hours.
- Setting time: 30 to 120 minutes
- Fire Resistance: Non-flammable non-combustible.
- Carbon dioxide emission: 10% or less compared with OPC (i.e., 90% CO 2 emission reduction).
- Alkalis are incorporated in the geopolymer paste, therefore will not react with aggregates
- Geopolymer does not have any phase that can lead to ettringite formation
- Geopolymer's structure will allow much less ion penetration (Chlorine and Carbonate ions).
- Small drying shrinkage due to the geopolymer's smaller capillaries and its overall higher density.

Embankment

Fly ash properties are somewhat unique as an engineering material. Unlike typical soils used for embankment construction, fly ash has a large uniformity coefficient consisting of clay-sized particles. Engineering properties that will affect fly ash use in embankments include grain size distribution, compaction characteristics, shear strength, compressibility, permeability, and frost susceptibility. Nearly all fly ash used in embankments are Class F fly ashes.

Asphalt concrete

Asphalt concrete is a composite material consisting of an asphalt binder and mineral aggregate. Both Class F and Class C fly ash can typically be used as a mineral filler to fill the voids and provide contact points between larger aggregate particles in asphalt concrete mixes. This application is used in conjunction or as a replacement for, other binders (such as Portland cement or hydrated lime). For use in asphalt pavement, the fly ash must meet mineral filler specifications outlined in ASTM D242. The hydrophobic nature of fly ash gives pavements better resistance to stripping. Fly ash has also been shown to increase the stiffness of the asphalt matrix, improving rutting resistance and increasing mix durability.

Use of Fly Ash in Agriculture

The large volume of fly ash occupies large area of land and possesses threat to environment. As such, there is an urgent and imperative need to adapt technologies for gainful utilization and safe management of fly ashes on sustainable basis. Agriculture and waste land management have emerged as prime bulk utilization areas for fly ash in the country. The field demonstration experiments carried out under varied agro-climatic conditions and soil types across the country by various R & D Institutes / Universities on the cultivation of different field crops (cereals, pulses, oil seeds, sugar cane, vegetables, etc.) and forestry species with different doses of fly ash and pond ash as soil modifier / source of economical plant nutrients with and without organic manure bio-fertilizer and chemical fertilizers in respect to crop yield, soil health, quality of crop produce, uptake of nutrients and toxic heavy metals, ground water quality etc. have revealed the following:

1. It improves permeability status of soil.
2. Improves fertility status of soil (soil health) / crop yield.
3. Improves soil texture.
4. Reduces bulk density of soil.
5. Improves water holding capacity / porosity.
6. Optimizes pH value.
7. Improves soil aeration.
8. Reduces crust formation.
9. Provides micro nutrients like Fe, Zn, Cu, Mo, B, Mn, etc.
10. Provides macro nutrients like K, P, Ca, Mg, S etc.
11. Works as a part substitute of gypsum for reclamation of saline alkali soil and lime For reclamation of acidic soils.
12. Ash ponds provides suitable conditions and essential nutrients for plant growth, Helps improve the economic condition of local inhabitants.
13. Crops grown on fly ash amended soil are safe for human consumption & Groundwater quality is not affected.

Keeping the above important findings in view, pond ash at a dose of 30-50 tonne per. Hectare on one time basis along with recommended dose of fertilizers / manures is recommended for its use agriculture/ forestry sector/wasteland management or cultivation of different cereals / pluses/ oil seeds / vegetables etc., the repeat application of which can be made after 4-5 years as it would have significant residual effect on the yield of succeeding crops over a period of 4-5 years. The abandoned ash ponds in the Vicinity of TPPs could also be safely reclaimed via suitable amendments for forestry/floriculture purposes.

Initiatives taken in the direction of creating Fly Ash grading facility at Thermal Power Plants.

As circular by CPWD, IS 456:2000 etc. specifies certain grade of fly ash (conforming to IS 3812) for cement/concrete applications which is not easily available at Thermal Power Plants. Even products like fly ash based bricks, blocks, tiles; pavers, etc. require fly ash of graded quality. Therefore, it was felt necessary to create some fly ash processing facility at TPP so that graded fly ash can be made available to end user. In this regard, letters have been issued to many Thermal Power Stations detailed presentation has been made to Central Electricity Authority and discussions are in progress with some of the TPPs.

Basu et al. discussed the adequacy of Indian Standards for High Volume Fly Ash Concrete (HVAC) and concluded that existing IS codes are suitable for characterisation of concrete ingredients for HVFAC. Major observations on IS 3812 (Part - I and II) : 2003 specifications for characterisation of fly ash are,

(a) The standard specifies suitable requirements for characterisation of fly ash. Requirement mentioned about average fineness is not necessary and may be deleted.

(b) Most important requirement for characterisation of fly ash is to restrain the LOI to 5 percent.
(ii) IS codes impose limitation of 35 percent on the maximum usage of fly ash in Portland pozzolana cement but there exists no limitation on the quantity of fly ash in concrete mix, if it is mixed separately in site batching.
(iii) HVFAC should be produced in mechanised batching plant or RMC plant under necessary quality control. Target strength for developing HVFAC or any concrete mix produced by mechanised mixer need not be fixed at characteristic strength plus 1.65 times standard deviation. A conservative estimate of target strength is 1.2 times the characteristic strength for mix not leaner than grade M30.
(iv) From the point of view of economy, HVFAC should be characterized for 56-day strength. However, the mix should have required strength for construction purpose after the minimum period required for curing, that is, 14 days.
(v) Neither IS code nor codes of any other country provides guidelines on mixing method of HVFAC. Published work on this subject suggests mixing method has influence on the performance of HVFAC and other types of concrete mixes.
(vi) HVFAC should be cured in two stages. Initial curing is dry curing for which no specification is available in any IS code. However, specification of IS 456 on wet curing is adequate.

Appreciating the overall concern for the environment and the need for the safe disposal and effective utilisation of fly ash, Department of Science & Technology (DST) as the nodal agency and Technology Information and Assessment Council (TIFAC) as the implementing agency commissioned a Flyash Mission in 1994. *Flyash Mission: a Technology Project in Mission Mode* (TPMM) is being implemented with participation of Ministry of Environment & Forest, Ministry of Power, Thermal Power Stations, R&D institutions and Industry. The focus is on demonstration of coal ash related technologies for developing confidence and thus ensuring large scale adoption.

The Ministry of Environment and Forests, Government of India, issued notification regarding the utilization of fly ash as per which every construction agency engaged in the construction of buildings within a radius of hundred kilometers (by road) from a coal or lignite based thermal power plant shall use only fly ash based products for construction, such as: cement/concrete, fly ash bricks or blocks or tiles or clay fly ash bricks, blocks or tiles or cement fly ash bricks or bricks or blocks or similar products or a combination or aggregate of them in every construction project.

"(1C) Minimum fly ash content for building materials or products to qualify as "fly ash based products" category shall be as given in the Table below:

Table 1

Sl.No.	Building Materials or Products	Minimum % of fly ash by weight
1	Fly ash bricks, blocks, tiles, etc. made with fly ash, lime, gypsum, sand, stone dust, cement, etc. (without clay).	50% of total raw material.
2	Paving blocks, paving tiles, checker tiles, mosaic tiles, roofing sheets, pre-cast elements, etc. wherein cement is used as binder.	Usage of PPC (fly ash) or 20% of OPC content.

3	Cement.	20% of total raw materials.
4	Clay based building materials such as bricks, blocks, tiles, etc.	25% of total raw materials.
5	Concrete, mortar and plaster.	Usage of PPC (fly ash) or 20% of total raw material.

3. GROUND GRANULATED BLASTFURNACE SLAG (GGBS)

GGBS (also known as GGBS or GGBFS) is manufactured from blast furnace slag, a by-product from the manufacture of iron. GGBS is obtained by quenching molten iron blast furnace slag immediately in water or stream, to produce a glassy granular product that is then dried and ground into a fine powder. It is an excellent binder to produce high performance cement and concrete.

The production technologies are mainly the following three: The traditional ball mill;
High Pressure Roller Press;
Vertical Roller Mill.

As compared to the traditional ball mill, the GGBS produced from the modern vertical mill has the following characteristics:

- High fineness, good particle size distribution, the GGBS activeness could be fully developed
- High activity index, small variation in the quality
- The product has low energy consumption, high production efficiency.

The difference in source materials: PFA is the finely divided mineral residue resulting from the combustion of powdered coal in electric generating plants, whereas GGBS is obtained by quenching molten iron blast furnace slag in water or stream, to produce a glassy granular product that is then dried and ground into a fine powder.The difference in chemical compositions:PFA usually contains very high SiO_2 and Al_2O_3, but very low in CaO (accounted for 1-5% only), whereas GGBS has very similar chemical compositions to Ordinary Portland Cement (OPC) such as 30-42% of CaO, 35-38% of SiO_2, 10-18% of Al_2O_3, 5-14% of MgO etc.The difference in hydration activity:PFA is not a hydraulic material, hydration will not take place on its own, and it will only harden with the use of activators (e.g. OPC). GGBS, in contrast, is a hydraulic material, which means that it will set and harden due to a chemical reaction with water. After hardening, it will retain some strength development and remain stable even under water. Concrete containing GGBS cement has a higher ultimate strength than concrete that uses 100% Portland cement.The difference in the permitted replacement ratio:The permitted replacement ratio of PFA in OPC is 20-40%, but it’s usually no more than 35% in concrete. On the other hand, the permitted replacement ratio of GGBS in OPC or concrete is 20-70%. It could even be replaced up to 85% in some of the European countries.The difference in usageTo ensure the strength of concrete meets the requirement, the amount of PFA used is usually more than the amount of OPC being replaced. GGBS, in contrast, is used in the equivalent amount to OPC being replaced, and yet the requirement on strength could still be met.

Replacement ratio of GGBS (Grade 95) in concrete

When GGBS is “single-blended”, the principle of equivalent amount replacement could be followed and the following methods can be used to determined the appropriate replacement ratio of GGBS:

- For on-the-ground concrete structures with higher early-age strength requirement, the replacement ratio would usually be 20 – 30%;
- For underground concrete structures with average strength requirement, the replacement ratio would usually be 30 – 50%;
- For mass concrete or concrete structures with strict temperature rise requirement, the replacement ratio would usually be 50 – 65%;
- For the specialty concrete structures with higher requirement on durability (e.g. corrosion resistance marine structures, sewerage treatment plants etc), the replacement ratio would usually be 50 – 70%;
- When GGBS is "double-blended" with PFA, due to the huge impact from the quality fluctuation in PFA, the user can follow the basic principles as stated above and determine the exact replacement ratio of each component through actual experiment.

GGBS Production in various countries

At the end of year 2005, GGBS producers using vertical mills were estimated to have increased to 20 over plants, the annual capacity increased to 12 million tons in China; It is forecasted that, in the coming 2 – 3 years, more than 85% of the large steel enterprises in China will build their own GGBS producing plants, either in the form of wholly-owned or joint-venture. By then, it is expected that around 25 million tons of high quality GGBS would be available in the market;

About 18 million tonnes of GGBS are currently used in Europe each year. GGBS represents about 10% of all cement supplied in Europe and is the second most-widely used type of cement. GGBS supplies 18% of the UK cement market. The same market share would represent about 700kt p.a. of GGBS usage in the Irish market. Currently only 50,000 tonnes of GGBS are used in Ireland each year due mainly to its lack of availability.

In the US, the government there gives "purchasing priority" in public procurement to GGBS on the grounds of its environmental benefits. This policy has resulted in a huge increase in the production, availability and use of GGBS in that country. If Ireland operated a similar policy, it is estimated that this alone could reduce CO_2 emissions by between 500,000 tonnes and 700,000 per annum, at no additional cost to industry or to the country.

In India, we produce about 7.8 million tons of blast furnace slag. All the blast furnace slags are granulated by quenching the molten slag by high power water jet, making 100% glassy slag granules of 0.4 mm size. The blast furnace slag is mainly used in India for manufacturing slag cement. In other countries GGBS is used more as an admixture than its use as slag cement. Now in India, since GGBS is available, its use as admixture should become more common. With growing popularity of Ready Mix Concrete (RMC), the use of GGBS for customer's specific requirement should also become popular.

Mix design characteristics of the High Slag Cement Concrete (with GGBS content more than 50%)?

Due to the fact that the fineness of GGBS is far higher than OPC (e.g. GGBS: 420-450m2/kg, OPC: 330-350m2/kg), as compared to the plain concrete, the High Slag Cement Concrete requires a water content increase of 5%; When the user design the mixture of the concrete, he as to fulfill the workability and strength requirement of the concrete by adjusting the amount of additives used, and should not increase the amount of water used as he wishes; Similar to the normal concrete, the mixture design of the High Slag Cement Concrete should go through the following steps by the relevant technical staffs: The preliminary concrete mix design involes trial mixing in the laboratory trial mixing on the site

Performance characteristics of the High Slag Cement Concrete

As compared to the plain concrete, High Slag Cement Concrete has the following basic characteristics: It prolongs the solidifying time, prolongs slump retention, which is particularly beneficial for construction work during summer; The binder has higher ohesiveness which does not segregate easily, its pumpability is good; It reduces the concrete bleeding, and beneficial in reducing the sedimentation craze.

Curing requirements for High Slag Cement Concrete?

High Slag Cement Concrete with higher than average replacement ratio (e.g. 30 – 40% and above) is particularly sensitive with the early curing conditions, and therefore strict requirements should be imposed, such as:

Early curing should be carried out before the concrete's final solidification (e.g. spray the curing compounds, use wet burlap or cotton mats etc);

Moisture-retaining curing for at least 7 days;

When the replacement ratio is above 50%, moisture-retaining curing period should be extended to at least 14 days.

I**mplications of steam curing to High Slag Cement Concrete**

Hydrothermal curing is particularly good for High Slag Cement Concrete. Steam curing with slightly higher temperature as compared to OPC cement can be adopted, in order to increase the steam curing strength of the High Slag Cement Concrete precast structures. However, since High Slag Cement Concrete has slower early-age strength development than OPC concrete and it is sensitive to the influence of temperature, the user has to appropriately adjust or delay the time for concrete pre-curing (especially for the production during winter season). This is to ensure that the concrete structures possess sufficient preliminary strength before putting into the autoclave, such that the best steam curing effect is attainable.

4. AIR COOLED BLAST FURNACE SLAG

Blast Furnace Slag is formed when iron ore or iron pellets, coke and a flux (either limestone or dolomite) are melted together in a blast furnace. When the metallurgical smelting process is complete, the lime in the flux has been chemically combined with the aluminates and silicates of the ore and coke ash to form a non-metallic product called blast furnace slag. During the period of cooling and hardening from its molten state, BF slag can be cooled in several ways to form any of several types of BF slag products.

Air-cooled Slag - Blast furnace slag is allowed to slowly cool by ambient air, is processed through a screening and crushing plant and is processed into many sizes for use primarily as a construction aggregate. Common uses are as aggregates in ready-mix concrete, precast concrete, hot mix asphalt aggregate, septic drain fields and pipe backfill.

Two key benefits associated with the use of ACBFS aggregate are resource conservation (reducing the need for natural aggregate) and the reduction or elimination of solid waste.

Chemical Composition

As a product of calcinated fluxstone and the alumina and silica phases present in iron ore, the four major oxide phases present in ACBFS are oxides of calcium (CaO), silica (SiO2), aluminum (Al2O3), and magnesium (MgO). These oxides account for approximately 95 percent of the composition of ACBFS, with the remaining 5 percent consisting of sulfur, manganese, iron, titanium, fluorine, sodium, and potassium (Hammerling 1999).

Physical Properties

The physical properties of ACBFS are largely controlled by how it cools and solidifies. Table 1 compares some of the typical ACBFS coarse aggregate properties with those associated with natural coarse aggregate. Some of the notable differences between the two different aggregate types include:

- Greater angularity of ACBFS, which can affect mix proportioning.
- Lower specific gravity of ACBFS, which can affect mix proportioning.
- Higher absorption of ACBFS, which can affect mix proportioning, workability, and early-age shrinkage.

In 2006, according to the USGS, air-cooled blast furnace slag sold or used in the U.S. was 7.3 million tonnes valued at $49 million, granulated blast furnace slag sold or used in the U.S. was 4.2 million tonnes valued at $318 million, and steel furnace slag sold or used in the U.S. was 8.7 million tonnes valued at $40 million. Air-cooled blast furnace slag sales in 2006 were for use in road bases and surfaces (41%), asphaltic concrete (13%), ready-mixed concrete (16%), and the balance for other uses. Granulated blast furnace slag sales in 2006 were for use in cementitious materials (94%), and the balance for other uses. Steel furnace slag sales in 2006 were for use in road bases and surfaces (51%), asphaltic concrete (12%), for fill (18%), and the balance for other uses.

About 35 million tones of steel and blast furnace slags are produced in the country during manufacture of iron and steel. It has been estimated that the quantity of slags will increase to about 60 million tones around 2000. The large quantity of slags generated in plants is dumped on land nearby, which not only results in wastages of land but also causes surface and ground water pollution.

5. GYPSUM FROM FERTILISER INDUSTRIES

Phosphogypsum is the waste generated by the phosphoric acid, ammonium phosphate and hydrofluoric acid manufacturing plants. There is an accumulation stock or more than 10 million tones of phosphogypsum at different at different plant sites. The fluoride content of gypsum generated is 0.7-1.5% which is the source of land and water pollution.

IIT Madras has recently constructed a two storeyed model building with Australian technology using gypsum reinforced with glass fibre. The housing technology costs Rs.1,250 per square feet compared to Rs. 1,500 for concrete structures. The model building is made of glass fibre reinforced gypsum (GFRG) panels. The panels are made of gypsum combined with additives and glass fibres. For construction ourposes, the panels are cut to desired sizes based on room dimensions, with openings made for doors and windows. The entire building uses prefabricated light weight GFRG panels including walls, floors, roofs, and staircases.

6. RED MUD

Red mud is a reddish-brown colored solid waste produced during the physical and chemical processing of bauxite. Bauxite is composed of aluminum hydroxide minerals, including primarily gibbsite [Al(OH)3], boehmite [γ-AlO(OH)] and diaspore [α-AlO(OH)], and other compounds, such as hematite [Fe2O3], goethite [FeO(OH)], quartz [SiO2], rutile/anatase [TiO2] and kaolinite [Al2Si2O5(OH)4] [1]. The red mud, according to the production process of the aluminum, can be divided into Bayer process red mud, sintering process red mud and combined process red mud. It was reported that 0.8~1.5 t of red mud is produced by each 1 t alumina produced. Globally, the total amount of red mud produced every year is between 60 and 120 million tons [2], about 30 million tons of which is produced in China. And the accumulated quantity can reach 200 million tons in China.

More than 4 million tons of red mud is generated annually in India only. Presently, it is stored or dumped on land, or in the oceans near alumina refineries. However, its high alkalinity is a potential pollution to threat water, land and air. While high costs are associated with the large area of land required for storage of the residue. India is amongst the major producers of alumina in the world. There are some differences in mineralogical composition between the residues from India and other countries due to the difference in the ore type in its production processes. Significant achievements in treatment and utilization of red mud have been obtained in India in the last decade. In this paper, the various proposals for the utilization of red mud generated in India are presented. Similarly, the drawbacks associated with these potential commercial applications of red mud are discussed.

As to the treatment of red mud, the first choice of most companies from all over the world would be stockpiling it in an open yard or marine dumping. Since there is a great deal of industrial alkali, fluoride and heavy metals and other potential pollutants in red mud, long-term stockpiling of red mud would not only occupy scarce land resources, but also easily lead to serious pollution of the surrounding soil, air and groundwater. On the other hand, treatment by marine dumping may destroy the ecological balance of the ocean. The dike breach at the red mud stockpiling yard at the Ajkai Timfoldgyar Zrt alumina plant in Hungary on October 4, 2010 released between 600,000 and 700,000 m^3 of caustic red mud suspension. This incident is unprecedented, given the scale of the release and the type of material involved [3]. And it is warning us to pay enough attention to the comprehensive treatment of the red mud.

The Basic Characteristics of Red Mud

Chemical and Mineral Composition

There are different aluminum production processes for different bauxites that subsequently produce different types of red mud. Red mud is mainly composed of coarse sand and fine particles of mud. Its composition, property and phase vary with the origin of the bauxite and the alumina production process, and will change over time when stocked. The amount of alkali in red mud fluid is about 2 to 3 g/L (calculated by Na_2O), which results in a pH value between 13 and 14. Tables 1 and 2 list the chemical and mineral compositions of three kinds of red mud that are produced by the Bayer process, sintering and Bayer-sintering process.

Table 1. The main chemical constituents of red mud (%) [4].

Chemical constituent	**Fe_2O_3**	**Al_2O_3**	**SiO_2**	**CaO**	**Na_2O**	**TiO_2**	**K_2O**	**MgO**	**Sc_2O_3**	**Nb_2O_5**	**TREO**	**Loss**
Bayer process	28.3	17.67	8.34	20.88	2.29	7.34	0.059	0.65	–	–	–	13.88
Combined process	10.97	7.68	22.67	40.78	2.93	3.26	0.38	1.77	–	–	–	11.77
Sintering process	6.66	9.18	18.1	38.09	4	6.72	–	–	0.02	0.0193	0.25	16.96

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Table 2. Mineral composition of red mud (%, ω) [5].

Mineral composition (chemical formula)

	Sintering process	Combined process	Bayer process
β-2CaO·SiO2	46	43	–
Sodium aluminosilicate (Na2O·Al2O3·1.7SiO2·nH2O)·NaX or Na2X	4	4	20
Anorthite 3CaO·Al2O3·3Si2O2 or 3CaO·Al2O3·xSiO2·(6-2x)H2O	5	2	20
Calcite CaCO3	14	10	19
Limonite Fe2O3·H2O	7	4	4
Boehmite Al2O3·H2O	–	1	21
Perovskite CaO·TiO2	4	12	15
4CaO·Al2O3·Fe2O3	6	12	–
Na2O·Al2O3·2SiO2	7	8	–
FeS2	1	–	–
Others	1	–	1
Total	95	96	100

It can be seen from Table 1 that the main chemical compositions of red mud are Fe2O3, Al2O3, SiO2, CaO, Na2O, TiO, K2O and MgO. Different kinds of red mud from the sintering process and combined process have similar composition characteristics. The contents of CaO and SiO2 in red mud from the sintering process and combined process are much higher than that from the Bayer process. But the contents of Fe2O3 in red mud from the sintering process and combined process are much lower than that from the Bayer process.

It can be seen from Table 2 that the main composition of the red mud from the sintering process is β-2CaO·SiO2, with the mass ratio being close to 50%, the same as the combined process. And the main mineral compositions of the red mud from the Bayer process are sodium aluminosilicate, aragonite, calcite boehmite and perovskite. However, major mineral compositions in Bayer process red mud include hematite (Fe2O3), nepernepheline (including natrodavyne, katoite *etc.*), gibbsite, quartz and other phases. This is consistent with the analysis of chemical compositions as stated above. It suggests some form of calcium silicate is the primary phase.

Physical Properties

Tian *et al.* [6] analyzed the mechanical property of red mud from the generation of red mud, pointing out that the properties of red mud vary significantly from different bauxites and different methods of generation. In general, red mud is a very fine material in terms of particle size distribution, having an average particle size <10 μm. Typical values would account for 90% of the volume below 75 μm. The specific surface area (BET) of red mud is as large as 64–187 m2·g−1, which indicates that red mud has a high degree of mineral particle dispersion. Red mud has a large water content, up to 700 to 1000 kg/m3, accounting for 79%–93% of the total weight. This water will be desorbed when the red mud gets shocked, which may lead to a decrease of mechanical properties of red mud. It has a porous structure with a void ratio of 2.5–3.0, a high compressibility (Eg = 28–40 MPa) and low shear strength (C = 9.6–74.3 kPa; φ = 13.5–21.0°). Despite red mud's properties of high porosity and water content, it will not shrink or expand after drying [5]. The sintering process creates relatively coarse particles (0.1–0.02 mm accounting for 65%), relatively good permeability (the osmotic coefficient is 10−4–10−5), relatively easy to dehydrate and for chemical cementation, a higher cementation strength (70–100 kPa). While Bayer process red mud possesses the characteristics of fine particles (0.01–0.005 mm accounting for 65%), poor permeability (the osmotic coefficient is 10^{-5}–10^{-6}), difficult to dehydrate under natural conditions, difficult to use for chemical cementation, with a low shear strength (40–50 kPa), *etc*. [6,7].

Comprehensive Utilization of Red Mud

The key to solving red mud stockpiling is to develop a comprehensive utilization technology that consumes red mud or converts it into a secondary resource. Since the 1950s, scientists have carried out research projects that explore disposal and utilization of red mud, according to the unique physical and chemical properties of red mud, which can be divided into three categories. First, recovery of the useful component metals in red mud. Second, reuse of red mud as raw materials, especially for cement production. Third, application of red mud for environmental protection, such as adsorption to purify water.

Recovery of Components in Red Mud

Red mud primarily contains elemental compositions such as Fe_2O_3, Al_2O_3, SiO_2, CaO, Na_2O and K_2O. Besides, it also contains other compositions, such as Li_2O, V_2O_5, TiO_2 and ZrO_2. For instance, the content of TiO in red mud produced in India can be as much as 24%. Because of the huge amount of red mud, value elements like Ga, Sc, Nb, Li, V, Rb, Ti and Zr are valuable and abundant secondary resources. Therefore, it is of great significance to recover metals, especially rare earth elements, from red mud.

Recovery of Divalent Metals in Red Mud

Due to the characteristics of a high iron content, extensive research into the recovery of iron from Bayer process red mud have been carried out by scientists all over the world. The recycling process of iron from red mud can be divided into roasting magnetic recovery, the reducing smelting method, the direct magnetic separation method and the leaching-extraction method, according to the different ways of iron separation. Researchers in Russia, Hungary, America and Japan have carried out iron production experiments from red mud. Researchers from the University of Central South have made steel directly with iron recovered from red mud [14]. The Chinese Metallurgical Research Institute has enhanced the iron recovery rate to 86% through making a sponge by red mud—magnetic separation technology. Sun *et al.* [15] researched magnetic separation of iron from Bayer red mud and determined the process parameters of the magnetic roasting-magnetic selecting method to recover concentrated iron ore.

In consideration of high content of aluminum and sodium in the red mud, only by recovering them can we make full use of these resources. Zhong *et al.* [16] recovered $A12O_3$ and Na_2O in red mud by the Sub-Molten Salt Method, with a one-way $A12O_3$ recovery rate of 88%. After dealuminization, the red mud undergoes a deep sodium removal treatment by NaOH solution, recycling Na_2O from red mud. Zheng *et al.* [17] discussed an aluminum and sodium recovery process of a soda lime method after adding silicon slag into red mud. Under the optimum conditions, the dissolution rates of aluminum and sodium is up to 95%, with red mud after the dissolution a Na_2O content of less than 1%, meeting the requirements for cement materials.

Recovery of Rare Earth Elements in Red Mud

Ochsenkühn-Petropulu *et al.* [18] compared metal leaching recovery under different concentrations of solvent and different leaching conditions. Their results showed that the leaching recovers scandium, yttrium, heavy rare earth elements, middle rare earth elements and light rare earth elements at the rates of 80%, 90%, 70%, 50% and 30% respectively. They also indicated that, under the leaching conditions, a concentration of 0.5 mol/L, a temperature of 25 °C, leaching time is 24 h and a solid-liquid ratio of 1:50, the leaching rate is as follow: nitric acid > hydrochloric acid > sulfuric acid. In another study of Ochsenkühn-Petropulu *et al.* [19], the ion exchange-solvent extraction method was used to extract scandium, yttrium and lanthanides. The process leaches the ions after mixing red mud and nitric acid (0.6 mol/L) in a liquid-solid ratio of 200:1 and stirring them for 1 hour at room temperature and at atmospheric pressure. The final leaching rates can be 50%–75%. Smirnov *et al.* [20] developed a new process for the recovery and gathering of scandium, uranium and thorium from red mud slurry by the resin adsorption—dissolving process, recovering scandium at a rate of 50%.

Xue *et al.* [21] recovered scandium from Bayer process red mud by the roasting-acid leaching method, with a scandium leaching rate of more than 80%. They calcined red mud to remove water and then leached Sc with sulfuric acid solution, leaving the impurities remaining in the residues. Zhang [22] recovered the metal ions Ti, Sc, Fe and Al by the double acid leaching method from Bayer process red mud. The first acid leaching of red mud is to recover Sc, Fe and Al from red mud by adding low concentrations of hydrochloric acid. The second acid leaching is to decompose the Ti-rich residues of the first leaching, add water, and recover Ti from the decomposed solution, with a rate of more than 98%. Wang [23] studied the extraction of Sc from red mud, and obtained a final product purity of 95% by using hydrochloric acid as leaching agent, with a liquid-solid ratio of 5:1, a reaction temperature of 60 °C and a reaction time of 1 h. Chen [24] studied the separation of vanadium by the method of precipitation from Bayer process sodium aluminates solution, with a total V2O5 recovery rate of 45%.

Resource Utilization of Red Mud

As to the resource utilization of red mud, alumina companies have been carrying out many technical researches on production of construction material, especially cement production and glass production, production of filling material for plastic, production of road base. And they have made some progress, especially in the production of cement using red mud.

Production of Construction Materials from Red Mud

Cement

Dicalcium silicate in red mud is also one of the main phases in cement clinker, and red mud can play the role of crystallization in the production of cement clinker. Fly ash is mainly composed of SiO2 and Al2O3, thus can be used to absorb the water contained in the red mud and improve the reactive silica content of the cement. Scientists conducted a series of studies into the production of cement using red mud, fly ash, lime and gypsum as raw materials. Use of red mud cement not only reduces the energy consumption of cement production, but also improves the early strength of cement and resistance to sulfate attack [25].

Ekrem Kalkan [26] studied using red mud as a cement stabilizer. In 1980, Barsherike [27] studied the possibility and rationality of producing cement with red mud as the raw material component of Portland cement, and successfully prepared cement complying with the relevant standards. Vangelatos [28] studied the preparation of ordinary Portland cement from red mud, lime and freestone, and the 28-day compressive strength of the cement strength can reach 63MPa. In China, research has been completed on the production of sulfo—aluminate cement from red mud in 1955 [29]. This kind of production process is simple and inexpensive. However, the performance of the cement, with the exceptions, which may be considerable, of some individual indicators such as soundness, is close to or greater than ordinary Portland cement. Pan *et al.* [30] studied slag and red mud activated by a composite solid alkaline activator, and developed alkali slag red mud cement which has the properties of greater early strength (the initial and final setting is separately 62 min and 95 min), high compressive strength (the 28-day compressive strength can be up to 125 MPa) and excellent resistance to corrosion, utilizing 30% of the red mud. Liang [31] and Zhong [32] prepared cement—red mud concrete using red mud. The compressive and flexural strength of this kind of concrete is close to or even higher than that of ordinary concrete, meeting the requirement of cement concrete used for pavement materials (the 28-day compressive strength is about 30–40 MPa; the 28-day flexural strength is about 4.5–5.5 MPa).

Brick

As an alternative to traditional raw materials used in brick production, red mud utilization can not only reduce the cost of raw materials, but also have great environmental significance. Xing [33], Yang [34], Zhang [35], Nevin [36] *et al.* separately reported the production of non-steam-cured and non-fired brick, fly ash brick, black pellet decorative brick and ceramic glazed tile. For instance, non-steam-cured and non-fired brick is developed by using industrial residues as raw materials, by adding cement and lime as binder and by pressing and natural curing technology. The Institute of Shandong Aluminum Company and the Institute of Chinese Great Wall Aluminum Company separately achieved the production process of non-steam-cured and non-fired brick using red mud and fly ash as raw materials. The active constituents, SiO2 and CaO, respectively accounting for 70% in sintering process red mud and 80% in fly ash, are, from the aspects of cost and performance, the ideal raw materials for the production of non-steam-cured and non-fired brick.

Glass

Yang *et al.* [37] conducted an experiment for red mud-fly ash glass, in which the maximum content of red mud and fly ash is collectively more than 90%. They acquired the optimum heat treatment process through investigation of crystallization and the factors influencing the crystal nucleation and growth. With red mud and chromium slag as the main materials, and quartz sand, fluorite, toner, manganese slag and other substances as the auxiliary materials, Liang *et al.* [38] successfully produced black glass decorative materials, which have good mechanical strength, chemical stability and optical properties.

Aerated Concrete Block

Aerated concrete is a new light porous building material that has great performances such as thermal insulation, fire resistance and seismic resistance, and is made from calcareous and siliceous materials. Red mud aerated concrete, developed by using cement (15%), lime (12%–15%), red mud (35%–40%) and silica sand (33%–35%), has the compressive strength and bulk density, complying with the lowest intensity level (MU7.5) of Chinese standards—about the strength of concrete block [39]. But, its production process is basically the same as that used to produce other aerated concrete. So, this process can reduce the costs of the production of aerated concrete by taking advantage of red mud. It is said that this process will become one of the new methods of red mud utilization.

Utilization of Red Mud As Filling Material

Road base Material

High-grade road base material using red mud from the sintering process is promising, that may lead to large-scale consumption of red mud. Qi [40] suggest using red mud as road material. Based on the work of Qi, a 15 m wide and 4 km long highway, using red mud as a base material, was constructed in Zibo, Shandong Province. A relevant department had tested the subgrade stability and the strength of road, and concluded that the red mud base road meets the level I standards of lime industrial waste stabilized soil and meets the strength requirements of the highway [41].

Mining

Yang *et al.* [42], from the Institute of Changsha Mining Research, have studied the properties, preparation and pump pressure transmission process of red mud paste binder backfill material. Based on this study, a new technology named "pumped red mud paste cemented filling mining" has been developed by the Institute of Changsha Mining Research, in cooperation with the Shandong Aluminum Company. They mixed red mud, fly ash, lime and water in a ratio of 2:1:0.5:2.43, and then pumped the mixture into the mine to prevent ground subsidence during bauxite mining. The tested 28-day strength can reach to 3.24 MPa. This technology is a new way not only for the use of red mud, but also for non-cement cemented filling, successfully resolving the problem of mining methods in the Hutian bauxite stope. Underground exploitation practice on the bauxite has proved that cemented filling technology is reliable and can effectively reduce the filling costs, increase the safety factor of the stope and increase the comprehensive benefits of mining [43].

Plastic

For PVC (polyvinyl chloride), red mud is not only a filler that has a reinforcing effect, but is also an efficient and cheap thermal stabilizer, providing the filled PVC products with an excellent anti-aging property. Its lifetime is 2 to 3 times that of ordinary PVC products. At the same time, the fluidity of red mud is better than other fillers, which makes it plastic with good processing properties. And the red mud PVC composite plastics have fire retardant property, and can be made into red mud plastic solar water heaters and plastic construction profiles [44].

Applying red mud as an environmental remediation material is a new hot point in terms of utilization. Due to the simple process, low cost, it is worth promoting its application in the field of environmental protection. However, there is a risk of introducing new contamination, and a difficulty of recycling it after the application. Therefore, more in-depth studies are needed and a comprehensive assessment of chemical and biological effects.

Sawant et al. studied studied the use of neutralized red mud in concrete. The decrease in initial setting time at 5% and 10% may be due to the light weight of neutralized red mud and finer particles of mud which fills the voids of the cement by which there may be increase in the density of the mix. Beyond 10% of neutralized red mud cement initial setting time increases may be due to reduction in the density of mix. The effect of replacement of cement by neutralized red mud has been studied on design mix concrete of grade M50. The water-cement ratio 0.36 is kept constant for different percentage replacement of cement by neutralized red mud. It is observed from the table no. 7 that the rate of gain in strength decreases with increases in neutralized red mud content at 7 days curing period compared to 7 days strength of pure cement concrete. For M 50 concrete mix the optimum replacement is 15 %. Referring to fig. no. 2 & 3 it is interesting to note that the particular variation in average compressive strength of cement concrete with different proportions of neutralized red mud in place of cement. It is observation that the average compressive strength decreases with increase in neutralized red mud content except for few percentage of replacement. It is observed from table no. 7, which shows that the average compressive strength values for M

50 grade concrete with constant water-cement ratio. The maximum compressive strength obtained is 60.238 N/mm2, for pure cement concrete i.e. for 0% of replacement and minimum of 47.407 N/mm2 with 25% of neutralized red mud at 28 days of curing period. For M50 grade concrete (0% replacement) the 28 days target strength is 58.25 N/mm2. So with reference to table no. we are able to partially replace cement by neutralized red mud up to 15 %. From economical point of view the conventional concrete costing around 13.7 % more than the costing of neutralized red mud concrete (15 % replacement) with the nominal decrease in the compressive strength of 2.97 % than the actual 28 days compressive strength of M 50 grade concrete.

Anuj Kumar et al. studied the use of red mud, a residue of Bayer's process synergistically with fly ash to develop geopolymer. An influence of 0–40% red mud addition on the reaction, structure and properties of fly ash geopolymer was studied using isothermal conduction calorimetry (ICC), Fourier transform infrared spectroscopy (FTIR), electron probe microanalysis (EPMA) and mechanical testing. An improvement in intensity of reaction was observed with the red mud addition at all replacement level but improvement in setting time and compressive strength was observed only in the samples containing 5–20% red mud. Structural characterization revealed that rate of reaction was dependent on the NaOH concentration but the development of mechanical properties were related to the compact microstructure which was developed due to the combined effect of NaOH concentration, solubility of silicates and the presence of iron oxides. Based on scientific understanding, paving blocks using 10% and 20% red mud was developed. These blocks were meeting IS 15658: 2006 standard and leaching of toxic metals were within permissible limits.

Table 1 Chemical composition and physical properties of fly ash and red mud.

Constituents	Fly ash	Red mud
Chemical analysis		
SiO2	60.48	29.2
Fe2O3	4.52	31.5
Al2O3	28.15	15.2
CaO	1.71	4.5
MgO	0.47	0.2
Na2O	0.14	3.1 (NaOH 2.2%)
K2O	1.41	–
LOI	1.59	10.2
Unidentified	1.53	6.1
Total	100.00	100.00
Physical properties		
Density (g/cm3)	1.89	2.88
Glass content	43	-

Fig.1 Paving blocks produced from fly ash red mud combination. (Anuj Kumar et al.)

Table 2 Properties of paving block and its compliance with IS specification.

Sl. No.	Property	IS 15658: 2006 specification	FARM10	FARM20
Obligatory requirement				
1	Visual Inspection	95% free from visual defect	95% free from visual defect	95% free from visual defect
2	Size tolerance (mm) (L+W)	±2	±1	±1
3	Water absorption (%)	7	6	7
4	Compressive strength (N/mm2)	30	>30	>30
Optional requirement				
5	Tensile splitting strength (MPa)	No spec.	>2.5	>2.1
6	Flexural strength (MPa)	3	>4.5	>3.2
7	Abrasion resistance (mm)	2	0.62	0.78

Perez-Villarejo studied the manufacture ceramic materials by adding the highly hazardous waste ‘‘red mud’’ to a ceramic matrix and neutralizing this waste in the matrix. The optimal proportion of mud to clay was found to be 50%. The samples manufactured were analyzed using XRD to determine the crystalline phases generated, and the microstructure was analyzed using a scanning electron microscope (SEM). Adding this industrial waste to the ceramic structure modifies and improves the physical and mechanical properties due to the great amount of vitreous phase that the waste produces.

Red Mud Plastic (RMP) Sheets

Red Mud Plastic (RMP) Sheets are fire resistant, generally conforming to BS 476:part 3:1975 and IS 1734: Part III:1973. The sheets can replace GI and AC sheets to a large extent for use particularly in Chemical and Food Processing Industries due to their excellent resistance to almost all organic solvents, for eg. Acid, Alkali and Salts.

The sheets are also ideal for use in hilly regions, very cold places as well as hot and humid zones due to their inherent property of ultra violet light and converting it into thermal energy, and functioning as heat isolation agents. Thus the place is kept warmer in winter and cooler in summer. M/s. Economical PEB Systems are manufacturing the roofing sheets at Chennai.

The product has been extensively tested at various recognised laboratories in India and abroad including Structural Engineering Research Center(CSIR), Central Building Research Institute(CBRI), Central Institute of Plastics Engineering and Technology(CIPET), Electrical Inspectorate of the Government of Kerala etc., and certified for all types of roofing applications in India. Following are the tests conducted on RMP sheets:

- External Fire Exposure Roof Test
- Test for Stability under different temperatures
- Static Bending Test
- Impact Test
- Tension Test
- Wind Load Test

Worldover roofings are going plastic, double quick. Not a bloated refrain as countries like U.S.A., Japan,Taiwan, Philippines and Thailand extensively use RMP for many of their roofing needs. The manifold advantages the RMP for many of their roofing needs. The manifold advantages that RMP offers is primarily responsible for this plastic switch, of which a few are spelt out here:

- 10% savings on total buildings costs
- Corrugation choices
- Waterproof
- More Safety
- Excellent Electrical Insulation
- SERC (Madras) Certified for adaptability to Indian conditions
- Economy on the number of laps used

The roofing sheets are available in brick red colour that lend distinct colours and strong shadow lines.

7. SILICA FUME

Silica fume, also referred to as microsilica or condensed silica fume, is used as an artificial pozzolanic admixture. It is a product resulting from reduction of high purity quartz with coal in an electric arc furnace in the manufacture of silicon or ferrosilicaon alloy. Silicon fume rises as an oxidized vapour. It cools, condenses and is collected in cloth bags. It is further

Fig.2 Red mud plastic sheets for roofing

processed to remove impurities and to control particle size. Condensed silica fume is essentially silicon dioxide (more than 90%) in noncrystalline form. It has spherical shape. It is essentially fine with particle size less than 1 micron and with an average diameter of about 0.1 micron, about 100 times smaller than average cement particles.Silica fume has specific surface area of about 20,000 m^2/kg, as against 200 to 300 m^2/kg that of cement

The use of silica fume in conjunction with superplasticizer has been the backbone of modern high performance concrete. The structures such as the Key Tower in Cleveland with a design strength of 85 MPa, and Wacker Tower in Chicago with specified concrete strength of 85 MPa, and two Union Square in Seatle with concrete that achieved 130 MPa strength – are testaments to the benefits of silica fume technology in concrete construction.

Silica fume has become one of the essential ingredients for making high strength and high performance concrete. Nuclear Power Corporation was the one of the first to use silica fume concrete in their Kaiga and Kota power projects. Steel Authority of India has facility to produce annually about 3,000 tons of silica fume at their Bhadravati Complex. The silica fume is marketed by Elkem Metallurgy Pvt. Ltd., Mumbai.

Microsilica is much more reactive than fly ash or any other natural pozzolona. The reactivity of a pozzolana can be quantified by measuring the amount of $Ca(OH)_2$ in the cement paste.

Water demand increases in proportion to the amount of microsilica added. The increase in water demand of concrete containing microsilica will be about 1% for every 1% of cement substituted. Therefore, 20 mm maximum size concrete containing 10% microsilica will have an increased water content of about 20 litres/m^3. Measures can be taken to avoid this increase by adjusting the aggregate grading and by using superplasticizers.

It is reported that concrete containing microsilica is vulnerable to plastic shrinkage cracking and therefore sheet or mat curing should be considered. Microsilica concrete produces more heat of heat of hydration at the initial stage of hydration. However the total generation of heat will be less than that of reference concrete.

By far, the most popular application of microsilica is in the 50:50 slurry form as it is easy to store and dispense. The slurry needs to be kept agitated for a few hours in a dayy to avoid gelling and sedimentation.

Curing is probably the most important aspect of microsilica concrete as the material undergoes virtually zero bleeding. If the rate of evaporation from the surface is faster than the rate of migration of water from interior to the surface, plastic shrinkage takes place. In the absence of bleeding and slow movement of water from interior to surface, early curing by means of membrane curing is essential.

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8. RICE HUSK ASH

Rice milling generates a by product know as husk . This surrounds the paddy grain. During milling of paddy about 78 % of weight is received as rice , broken rice and bran .Rest 22 % of the weight of paddy is received as husk . This husk is used as fuel in the rice mills to generate steam for the parboiling process . This husk contains about 75 % organic volatile matter and the balance 25 % of the weight of this husk is converted into ash during the firing process , is known as rice husk ash (RHA). This RHA in turn contains around 85 % - 90 % amorphous silica. So for every 1000 kgs of paddy milled , about 220 kgs (22 %) of husk is produced, and when this husk is burnt in the boilers , about 55 kgs (25 %) of RHA is generated.

India is a major rice producing country, and the husk generated during milling is mostly used as a fuel in the boilers for processing paddy, producing energy through direct combustion and / or by gasification. About 20 million tones of RHA is produced annually. This RHA is a great environment threat causing damage to the land and the surrounding area in which it is dumped. Lots of ways are being thought of for disposing them by making commercial use of this RHA.

When properly burnt, rice husk ash has high SiO_2 content and can be used as a concrete admixture. Rice husk ash exhibits high pozzolanic characteristics and contributes to high strength and high impermeability of concrete. Rice husk ash (RHA) essentially consists of amorphous silica (90% SiO_2), 5% carbon and 2% K_2O. The specific surface of RHA is between 40-100 m^2/g.

In U.S.A., highly pozzolanic RHA is patented under trade name *Agrosilica* and is marketed. It exhibits super pozzolanic property when used in small quantity i.e. 10% by weight of cement and it greatly enhances the workability and impermeability of concrete.

WASTE ROCK FROM GOLD MINING

Gold mining is estimated to create 18,000 kg of waste to yield enough gold for one 18-karat gold ring. When gold is mined from the ground, it typically is mixed with other rock that needs to be separated in order to process the gold. This excess rock is known as waste rock. Waste rock generally has no other use and is disposed of. Some mines treat waste rock with toxic substances, such as cyanide, to help separate it from the gold. Many countries have specific laws about how waste rock must be handled, to prevent contaminating water supplies, for example.

A total of 182,000 tons (165 million kg) of cyanide each year are estimated to be used by gold mines throughout the world. The waste generated from producing the gold needed for one 18-karat gold ring would weight about as much as 10 average-size cars. Waste rock dumped by the mining industry in the United States is estimated by the US Environmental Protection Agency to contain hundreds of millions of pounds of toxic substances, and some estimates are as high as hundreds of billions of pounds.

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