Review

Innovative methodologies for the utilisation of wastes from metallurgical and allied industries

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Abstract

This paper is an overview on the utilisation of solid wastes with focus on blast furnace slag, red mud and fly ash generated in large quantities from iron and steel industry; primary aluminium production and coal fired power plants, respectively. Innovative methodologies, based on the recent research by the authors, are highlighted and these include: (a) smelting reduction of red mud to produce pig iron and titania rich slag, (b) mechanical activation of the slag and fly ash to prepare improved blended cements in terms of higher usage of waste and enhanced cement properties, (c) synergistic usage of fly ash, blast furnace slag and iron ore tailings in the preparation of floor and wall tiles and (d) preparation of synthetic granite from fly ash as a value added product.

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Keywords: Waste management; Value added products; Recycling; Metal recovery; Utilisation of granulated blast furnace slag and fly ash; Mechanical activation

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### 1. Introduction

Metallurgical industries contribute significantly towards generation of solid wastes and creation of substantial environmental pollution. Typically, 300–400 kg of slag is produced in the production of 1 tonne pig iron (hot metal) by blast furnace route. Similarly, the red mud generated in alumina/aluminium production amounts to 1–1.5 times the alumina extracted by the Bayer process and about 4 times of aluminium produced by electrolytic smelting. Production of metals is highly energy intensive. The energy required includes significant amount of electrical energy. In countries such as India where bulk of the electrical energy is produced through coal-based thermal power plants, large quantities of fly ash is generated which represent additional solid waste generation associated with metal production. Over the last few decades, intensive Research and Development (R&D) efforts have been directed towards finding cost effective and compatible solutions for waste minimisation and utilisation (Johansson, 1992; Bandopadhyay et al., 2002). Some of the recent trends in solid waste management include newer or reengineered processes resulting in decreasing quantities of emissions, strategies to maximise current levels of waste utilisation and development of high value products (Johansson, 1992; Bandopadhyay et al., 1999, 2002; EPA Report on Environment, 2003; Kumar and Singh, 2004a; Kumar et al., 2005a). In addition, synergistic usage of solid wastes from different industries to produce value added product is also finding preference over use of a single waste (Das et al., 2003; Kumar and Singh, 2004a). Red mud and blast furnace slag are two of the major solid wastes generated by Indian metal industry and amounts to about 3 and 12 million tonnes per annum, respectively (Tamotia, 2003; LCA Report, 2003). Thermal power plants in India produce over 100 million tonnes of fly ash making the country as one of the largest producer of fly ash (Ashokan et al., 2005; Kumar et al., 2005a). This research article is an overview on the utilisation of solid wastes, especially red mud, blast furnace slag and fly ash, with emphasis on the recent innovations made by the authors. Specific innovations pertaining to utilisation of these wastes that are highlighted in the paper include smelting reduction process for metal recovery from red mud to minimise process by product and increased utilisation of granulated blast furnace slag (GBFS) and fly ash in blended cement making through mechanical activation. New
processes for fly ash-based value added products, for example wall tiles, incorporating wastes from other industries and synthetic granite as a substitute for the natural stone are also covered prominently.

2. Recent innovative developments

2.1. Recovery of metal values from red mud through the smelting reduction route

2.1.1. The red mud problem

Red mud or bauxite tailings produced during alkali leaching of bauxite by the Bayer process have continued to be one of the prime concerns of aluminium/alumina industry from the point of view of resource conservation and protection of the environment. For every tonne of alumina produced, 1–1.5 tonnes of red mud is generated as a waste. It is estimated that nearly 90 million tonnes of red mud is produced annually worldwide, and presently in India alone nearly 3 million tonnes red mud is generated (Kumar et al., 1998, 2005b). Most of the alumina plants dispose off red mud either in the nearby ponds or it is dumped at sea. The disposal costs as per regulations may add up to 5% of the alumina production cost. Red mud could contain as much as 63% Fe₂O₃, 43% Al₂O₃ and 24% TiO₂ depending upon chemical and mineralogical make up of bauxite and bauxite treatment technology (Kumar et al., 2002). While best available technologies (BAT) are in practice for red mud disposal, the utilization of red mud is of great significance from the point of view of resource conservation and sustainability of the aluminium industry (Kumar et al., 2005b).

2.1.2. Metallurgical utilisation of red mud—an overview

Over the years efforts have been made to develop processes for metallurgical as well as non-metallurgical applications of red mud (Fursman et al., 1970; Thakur and Das, 1994; Srikanth et al., 2000; Kumar et al., 2002). Till date, red mud has found limited commercial utilisation in road making, land reclamation and also used as a constituent in making Portland cement. Development of suitable metallurgical processes for metal recovery from red mud is important for bulk utilisation, value addition and moving towards zero waste.

Red mud may have 20–65% Fe₂O₃, 10–27% Al₂O₃, 5–25% TiO₂, 4–20% SiO₂ and 2–8% Na₂O depending on chemical and mineralogical make up of bauxite and bauxite treatment technology (Piga and Stoppa, 1993; Kumar et al., 1998, 2002). Since iron as oxides/oxyhydroxides is usually the largest component of red mud, iron recovery from red mud has attracted major attention (Kumar et al., 2002). Two main approaches which have been generally investigated to recover iron values are based on: (a) solid-state reduction of red mud followed by magnetic separation to recover iron and (b) smelting in a blast/electric/low shaft furnace (with or without pre-reduction) to produce pig iron. The former had limited success but the smelting technology appears to have been standardised on bench/pilot scale (Csikos et al., 1986; Piga and Stoppa, 1993; Prasad et al., 1985; Balazs and Jambo, 1987; Prasad, 1999; Kumar et al., 2002). Red mud cannot be considered as competitive raw material for iron and steel because the Fe₂O₃ content of the red mud is much lower than the iron ores used conventionally. Presence of other components and physical characteristics are the additional drawbacks of using red mud as raw material for ironmaking.
Based on these considerations, processes for the simultaneous recovery of all the major constituents have been developed (Kumar et al., 1998, 2002). Notable technologies developed at the laboratory as well as pilot plant scale include Complex Separation–Melting Process developed in Hungary, Smelting–Slag Disintegration Process (Yugoslavia) and Soda–Lime–Carbon Sinter Process of US Bureau of Mines (Fursman et al., 1970; Prasad et al., 1985; Porkolab et al., 1985; Piga and Stoppa, 1993; Thakur and Das, 1994; Balazs and Jambo, 1987; Wojcik, 1992). Ziegenbalg (1985) described an electrothermic process for red mud, which permits the recovery of soda and high quality pig iron. A number of studies have focussed on extraction of iron and titanium (as oxide) from red mud (Thakur and Das, 1994). Mixture of red mud and coke was smelted in an electric arc furnace at 1600–1700 °C to form an iron alloy with 90% recovery of iron. The slag was subsequently treated with sulphuric acid to recover the residual iron as Fe₂O₃ and Ti as TiO₂. Attempt has been made to smelt red mud mixed with limestone and coke in a blast furnace after prior sintering. The optimisation of process parameters during electro smelting of red mud for production of pig iron and a titania rich slag was also carried out. The titania was recovered from the slag by chlorination. A process for the production of sponge iron from red mud by reduction in a rotary kiln at 1050–1300 °C using hydrogen is also reported (Thakur and Das, 1994).

2.1.3. Smelting reduction of red mud

The recent trend in the development of cleaner processes for iron making is to reduce the number of steps involved in the conventional process. The newly emerging smelting reduction (SR) processes use non-coking coal as fuel and reductant and burden preparation steps such as sintering and coke making are not required. Hence, the environmental performance of a smelting reduction-based steel plant is expected to be significantly superior as compared to a blast furnace-based steel plant (Basu, 2002). Keeping this in mind, possible utilisation of red mud for the recovery of iron as cast iron and titania as synthetic rutile was explored (Srikanth et al., 2000). Laboratory scale reduction smelting experiments were carried out using mixtures of red mud from Alcan, UK and pig iron. The red mud used in the study contained 46% Fe₂O₃, 20% Al₂O₃ and 6% TiO₂. In a typical experiment red mud and pig iron (iron content: 91.6%) was smelted with graphite at 1600 °C to get the smelted iron. The compositions of the smelted alloy and slag are summarised in Table 1. The results indicate that about 95% of total iron bearing material smelted can

| Table 1 |
| Comparison of the metal and slag compositions obtained experimentally at 1600 °C after smelting |
| Species | Experimental results | Species | Experimental results |
| Iron | 94.08 | Al₂O₃ | 48.29 |
| Carbon | 5.04 | SiO₂ | 22.38 |
| Silicon | 0.28 | Na₂O | 8.28 |
| Titanium | 0.11 | TiO₂ | 11.50 |
| Sulphur | 0.29 | FeO | 7.92 |
| Phosphorous | 0.20 | Others (CaO, MgO) | 1.63 |
be recovered as hot metal and about 93% of titanium goes to the slag at a smelting temperature of 1600 °C. It may be noted that slag containing about 12% TiO₂ is too low for cost effective recovery of TiO₂ as synthetic rutile. However, red mud from India contain up to 25% TiO₂. Assuming a similar slag–metal distribution, this red mud will yield a slag of around 50% TiO₂, which is very attractive for the recovery of TiO₂. The investigations have shown that red mud and pig iron can be smelted together at 1600 °C for producing cast iron and a slag rich in TiO₂ for its subsequent purification and recovery. Based on these findings, the possible use of iron melting cupola for recycling of red mud merits attention.

2.2. High volume utilization of granulated blast furnace slag and fly ash in blended cements through mechanical activation

2.2.1. Resource conservation in cement manufacturing

Cement industry is material and energy intensive. Typically, 1–1.5 tonnes of limestone and 0.5 tonnes of coal are used per tonne of clinker produced. Specific energy consumption in cement manufacturing amounts to 4000 MJ/tonne of cement with nearly 80% contributions arising from thermal energy (mostly for clinker formation) and rest from electrical energy (major contribution arising from grinding). In addition, 0.8–1 tonne of CO₂ is generated per tonne of clinker formation. Replacement of clinker with industrial wastes, such as fly ash and granulated blast furnace slag is practised world over for resource conservation, reduce energy consumption and minimise CO₂ emission. This type of cement that uses fly ash and granulated blast furnace slag as partial replacement of clinker is known as blended cement. India is the second largest producer of the cement in the world. With its current level of production exceeding 110 million tonnes per annum, the country ranks only next to China. In India, blended cements containing 20–25% fly ash, and nearly 40% blast furnace slag are produced (Kumar et al., 2005c). The fly ash and the slag produced in the country amount to ~110 and 12–15 million tonnes, respectively. Ten to twelve percent fly ash and 40–50% slag are utilised in blended cement manufacturing and there is significant scope to increase the utilisation of these wastes in blended cement manufacturing. Recently, uses of large volume of slag and fly ash in blended cements have attracted intensive research attention (Dongxum et al., 2000; Olorunsogo, 1998).

2.2.2. Mechanical activation and blended cements

The higher usage in the blended cements is restricted by the low pozzolanic and/or latent hydraulic activity, consequently resulting in slow development of compressive strength as compared to ordinary Portland cement (OPC). Mechanical activation by high-energy milling is suggested to improve the reactivity of the blended cement constituents, namely the clinker, fly ash and the slag (Boldyrev, 1986; Juhasz and Opoczky, 1994; Boldyrev et al., 1996). Kumar et al. (2005a,d) has carried out a detailed study on the mechanically induced reactivity of blast furnace slag and fly ash. The formation of impervious surface film on slag surface that inhibits slag hydration is prevented due to increased reactivity through mechanical activation by attrition milling (Kumar et al., 2003, 2005d). Increased pozzolanic reactivity of fly ash through mechanical activation by attrition as well as vibratory milling results in a denser product (Kumar et al., 2005d,e). Increased reactivity of fly ash and slag by
mechanical activation has been exploited in the development of improved blended cements (Kumar et al., 2005d,e).

It was observed by the present authors that efficacy of mechanical activation is mill specific in the case of blast furnace slag. Up to 80% of clinker can be replaced by attrition milled slag with superior or similar compressive strength as observed for typical commercial cement (ICA) containing only about 35% slag (Kumar et al., 2004b). The effect of attrition milling was pronounced on early (1 and 3 days) strength development (Fig. 1). Similar results were not obtained for the ball milled or vibratory milled slag of similar fineness (Kumar et al., 2005d). Surface activation of slag in attrition mill (Kumar et al., 2005d) plays a decisive role in the strength development. Due to increased surface reactivity, the slag participated as major hydraulic phase in hydration reactions and formed the dense microstructure (Fig. 2) resulting in improved strength.

In the case of fly ash, both attrition and vibratory mills (Fig. 3) were found to be effective and allowed up to 65% replacement of clinker by the milled fly ash with strength comparable to commercial cement containing 20–25% fly ash (Kumar et al., 2005e). One of the important features of attrition and vibratory milled fly ash is that the coarser particles were reduced in size and small sized cenospheres (<1 \( \mu \)m) retains their original shape (Fig. 4). This is in sharp contrast to finely milled fly ash in a ball mill where most of the cenospheres are destroyed (Payá et al., 1996). The presence of cenospheres in the milled fly ash improves the flowability of cement without any increase in water demand. Increased water demand is an inhibiting factor in higher utilisation of fly ash. The beneficial effect of mechanically activated fly ash results due to increased reactivity and control over water demand attributed to the unique morphology of the milled fly ash. As a result, the hydrated cement has lower porosity and consequently improved strength.
2.2.3. **Alternate strategies in cement manufacturing using mechanical activation**

Alternate strategies need to be evolved based on the results obtained with mechanically activated slag and fly ash. Attrition milling may be carried out in wet condition and on-site milling and blending needs consideration. The current practice of fly ash containing blended cement production involves transport of fly ash from power plant to cement industry since the proportion of fly ash used is less than 25% of cement clinker. However, this may require...
raining for the cement containing 50% or more fly ash and their production in small scale units near coal fired thermal power plants may be a viable alternative in the future.

2.3. Synergistic usage of industrial wastes and value added ceramic products

2.3.1. Development of ceramic floor and wall tiles from industrial wastes

Synergistic usage from different industries is gaining increasing importance in solid waste management (Kumar and Singh, 2004a; Das et al., 2003). Innovative technology for ceramic floor and wall tiles has been developed based on fly ash from coal fired thermal plants, blast furnace slag from iron and steel industry and iron ore tailings from mines.

A typical tile body consists of SiO$_2$ and Al$_2$O$_3$ as major oxides and CaO, MgO, Na$_2$O and K$_2$O as minor compounds. For supplementing these compounds, the raw material is
selected from a group of plastic and non-plastic minerals. Clay minerals such as kaolinite, illite, montmorillonite, etc., belong to the first group and contribute to strength development of green tiles. The second group consists of feldspar, quartz, talc and wollastonite and is used as flux. Compounds like Fe₂O₃ and TiO₂ are kept to a minimum as they give colour to the tile body. However, uses of Fe₂O₃ rich material in ceramic tile body have been reported (Marghussian and Yekta, 1994). Fly ash, iron ore tailings and BF slag were used as a substitute for the natural raw material to supply SiO₂, Al₂O₃, Fe₂O₃ and CaO along with clay and feldspar (Table 2). Based on our earlier studies (Das et al., 2000), it is found that maximum 40% wastes can be accommodated in the tile body without any deterioration in properties. The properties of the tiles produced after firing at 1060–1200 °C in air for 30 min using different proportions of the wastes and other constituents are given in Table 3. Based on the water absorption studies (Fig. 5), it was found that the tiles containing fly ash, iron ore tailings and blast furnace slag in the ratio of 5:4.8:0.2 showed least water absorption (Kumar and Singh, 2004a). The tiles could be produced in glazed and unglazed

### Table 2

Chemical analysis of raw materials

<table>
<thead>
<tr>
<th>Constituents (wt.%)</th>
<th>Iron ore tailings</th>
<th>Fly ash</th>
<th>Blast furnace slag</th>
<th>Clay</th>
<th>Feldspar</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>51.12</td>
<td>61.8</td>
<td>33.1</td>
<td>52.5</td>
<td>65.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.22</td>
<td>27.9</td>
<td>21.6</td>
<td>26.3</td>
<td>19.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>44.36</td>
<td>2.6</td>
<td>0.87</td>
<td>1.9</td>
<td>0.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>–</td>
<td>1.0</td>
<td>–</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>CaO</td>
<td>0.22</td>
<td>1.7</td>
<td>33.0</td>
<td>3.6</td>
<td>0.2</td>
</tr>
<tr>
<td>MgO</td>
<td>–</td>
<td>0.3</td>
<td>8.85</td>
<td>–</td>
<td>0.0</td>
</tr>
<tr>
<td>Na₂O</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.2</td>
<td>4.3</td>
</tr>
<tr>
<td>K₂O</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.4</td>
<td>9.8</td>
</tr>
<tr>
<td>L.O.I.</td>
<td>2.95</td>
<td>2.0</td>
<td>–</td>
<td>14.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### Table 3

Properties of presently developed tile in comparison to EN specifications

<table>
<thead>
<tr>
<th>Properties</th>
<th>EN standard specification</th>
<th>NML developed tiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimension tolerance (%)</td>
<td>±0.5</td>
<td>As per specification</td>
</tr>
<tr>
<td>Thickness tolerance (%)</td>
<td>±0.5</td>
<td>As per specification</td>
</tr>
<tr>
<td>Straightness of sides (%)</td>
<td>±0.5</td>
<td>1% variation</td>
</tr>
<tr>
<td>Rectangularity (%)</td>
<td>±0.6</td>
<td>As per specification</td>
</tr>
<tr>
<td>Surface flatness (%)</td>
<td>±0.5</td>
<td>As per specification</td>
</tr>
<tr>
<td>Surface quality</td>
<td>95% free from visible defects</td>
<td>Needs some improvement</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>&lt;3</td>
<td>3–6</td>
</tr>
<tr>
<td>Group I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Group II</td>
<td>3–6</td>
<td>7–10</td>
</tr>
<tr>
<td>Group III</td>
<td>14–16</td>
<td>13–17</td>
</tr>
<tr>
<td>Scratch hardness (Moh’s)</td>
<td>Min. 5</td>
<td>Min. 6</td>
</tr>
<tr>
<td>Flexural strength (MPa) of 1150 °C fired tiles</td>
<td>–</td>
<td>&gt;25</td>
</tr>
<tr>
<td>Thermal shock resistance of 1150 °C fired tiles</td>
<td>To withstand min. 10 cycles</td>
<td>As per specification</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>Class AA</td>
<td>Confirms class AA</td>
</tr>
</tbody>
</table>
2.3.2. Synthetic granite tiles from fly ash

The synthetic granite tiles, also called as porcelainised stoneware tiles are low porosity, dense products with high technical performance (Barbieri et al., 1994; Manfredini et al., 1995; Dondi et al., 1995a), particularly with respect to abrasion and frost resistance, modulus of rupture and resistance to chemical attack. As in case of conventional tile body, it also consists of SiO$_2$, Al$_2$O$_3$, CaO, MgO, Na$_2$O, K$_2$O, and ZrO$_2$ but the SiO$_2$ and Al$_2$O$_3$ compounds are kept higher than the conventional tiles for vitrification. It is reported that additions of alumina to the feldspathic porcelain body could raise the flexural strength (Dondi et al., 1995b; Harada et al., 1996). Fly ash has been used as the main source of alumino-silicate compounds for the development of synthetic granite tiles (Kumar et al., 2001). Tiles having mechanical properties, e.g. strength, hardness, wear resistance, etc., comparable to natural granite could be produced through control of tiles microstructure. The microstructure comprising of needle shaped mullite reinforced with glassy phase is found to be responsible for the development of physico-mechanical properties (Fig. 6). The aesthetic features of natural granite, such as ‘salt and pepper effect’, ‘augun structure’, etc., can be produced in the synthetic granite through the use of appropriate colouring pigments. Water absorption and strength studies showed optimum combination of properties in the tiles containing 25% fly ash along with other silico-aluminate (Table 4).

Table 3 shows the properties of fired tiles. The European Nation (EN) standard specification is also included in the table for comparison. It is noteworthy that the tiles are superior in scratch hardness and strength and satisfies EN specification for all other properties.
Table 4
Properties of synthetic granite tiles

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water absorption (%)</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Bending strength (MPa)</td>
<td>38</td>
</tr>
<tr>
<td>Abrasion resistance (mm³)</td>
<td>&lt;150</td>
</tr>
<tr>
<td>Frost resistance</td>
<td>No defect</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (×10⁻⁶)</td>
<td>7</td>
</tr>
<tr>
<td>Chemical attack resistance</td>
<td>No variation</td>
</tr>
<tr>
<td>Thermal shock resistance</td>
<td>No alterations</td>
</tr>
<tr>
<td>Moh’s hardness</td>
<td>7</td>
</tr>
<tr>
<td>Spot resistance</td>
<td>No variation</td>
</tr>
</tbody>
</table>

3. Conclusions

The paper takes a critical look into innovative methodologies for the utilisation of metallurgical wastes. Issues concerning waste free metallurgy has been analysed. A few innovative methodologies developed by the present authors are discussed. These include recovery of metal values from red mud, high volume utilization of granulated blast furnace slag and fly ash in blended cements through mechanical activation, ceramic tiles from industrial wastes such as iron ore tailings, fly ash and blast furnace slag, and synthetic granite tiles from fly ash. The following conclusions can be drawn from the present study:

1. Iron can be recovered from red mud at a temperature of ~1600°C to produce hot metal containing about 5% carbon and 0.1% titanium. The results indicate the possibility of using a cupola in an iron foundry for recycling of red mud.
2. Mechanical activation improved the reactivity of blended cement constituents namely granulated blast furnace slag and fly ash. It is found that use of mechanically activated constituents allows up to 80% replacement of clinker by slag in Portland slag cement (PSC) and 65% by fly ash in Portland Pozzolanic cement (PPC), respectively. Use of mechanically activated constituents also results in early strength development.

3. Partial addition of iron ore tailing, fly ash and blast furnace slag in a suitable combination in ceramic tile body improved the scratch hardness (>6 on Moh’s scale) and flexural strength (>25 MPa) of ceramic tiles. Properties of these tiles conform to EN specifications.

4. The synthetic granite tiles developed using fly ash have very low porosity (<0.5%), high bending strength (38 MPa) and dense microstructure. Formation of mullite needles in the matrix contribute towards its excellent mechanical properties.

5. Gainful utilisation of the metallurgical wastes, reduction in CO₂ gas in case of blended cements, cost and energy savings are the salient features of these methodologies.

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References


