Extraction characteristics of alumina from Gujarat bauxites

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ALUMINIUM has been termed the versatile metal of the 20th century since it finds applications right from the kitchen to the spaceship. The growing popularity of this metal has been attributed to its outstanding physical and chemical properties, viz. lightness, high strength of its alloys, high electrical and thermal conductivity, good workability and the most important of all—its resistance to corrosion. Aluminium and its alloys find extensive applications in road transport, railways and aviation due to their good strength for relatively low weight. Aluminium also finds applications in chemical and food processing plants. Owing to its good electrical conductivity it finds use in electrical industries. Its strength, brightness, durability and capacity to take anodic coatings and colours are the most important properties for its use for architectural purposes.

There has been a significant growth of the Indian Aluminium industry in the last decade and the production has steadily increased from a mere 8,300 tonnes in 1958 to 96,500 tonnes in 1967 and to an estimated 1,19,000 tonnes by the end of 1968. The consumption has also been on the increase from 23,000 tonnes in 1956 to the present estimated value of 135,000 tonnes of aluminium. A target of 300,000 tonnes of installed capacity has been visualised by the end of 1970-71 and 450,000 tonnes by 1975-76.

The high cost of power, transport and the smaller capacity of the existing plants have all contributed to the comparatively high prices of aluminium in India. The economics of the Indian aluminium industry can be considerably improved if the above factors are borne in mind and emphasis laid on the setting up of economic sized units.

The National Metallurgical Laboratory since its inception has undertaken studies on the raw materials of the metallurgical industries and this report incorporates the results on the leaching characteristics of bauxite samples of Gujarat.

SYNOPSIS

The paper outlines the reserves, chemical and mineralogical make-up of Indian bauxites in general and Gujarat in particular. An outline of the Bayer’s process is given and the paper describes in detail the geology of Gujarat bauxites and the results of the extraction of alumina from eight bauxite samples with caustic soda. It has been found possible to extract 90-92% Al₂O₃ from most of the samples by digesting -10 mesh ore with caustic soda of concentration 200 gm/litre under boiling conditions at atmospheric pressure itself.

Gujarat bauxites and their geology

The bauxite deposits of Gujarat are located in Kaira, Kutch, Halar, Broach, Surat, Bhavnagar, Junagadh and Porbandur districts. The most important reserves are those of Halar, Kutch and Kaira deposits. The bauxites of Halar are of high grade, high in alumina and low in silica and iron. The Kaira bauxite deposits, located around Taibpur in Kapadranj taluk are high in TiO₂, lime and magnesia. The composition of Kaira bauxites varies from 45 to 58% Al₂O₃, 5 to 15% Fe₂O₃, 5% TiO₂, 1 to 3% CaO, 1-2% MgO and 2 to 12% SiO₂. The Surat bauxite deposits located in Tarakeshwar hill are small and of low grade suited for cement and abrasive industries. The Saurashtra and Kutch bauxites are of high grade containing 57% Al₂O₃ and above. The Kutch-Saurashtra bauxite deposits are localised mostly along a line joining Lamba and Ran in Halar district and a further extension of it in Kutch. The output from the Halar deposits exceed half the total bauxite production in India and most of it is exported.

The Saurashtra deposits1 characteristically lie upon or are part of gently undulating surfaces of erosion topographically, a flattish or gently undulating surface, in the latter case the crests typically display cappings of low grade to laterite bauxite. These bauxites are pocket deposits, whose bottoms are sheathed in aluminous clays (lithomargic) and are either white, grey or reddish in colour and compact or psilotic in appea-
Solubility of $\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O}$ in caustic

1. Panera Island (Gulf of Kutch) to Lamba in the Arabian sea.
2. Between Myani and Bakharla (Porbandur).
3. In Myari, Mangarol, Dolasa, Unajafarbad, Dongar, Mahura, Talaja, Ghoga and Bhavnagar vicinities.

At present large scale mining work is being carried out for the rich deposits in Jamnagar district, the deposits running to 14 miles long and one to three miles width. This strip covers the following regions:

(i) Nandana ($20^\circ8' : 69^\circ20'$)
(ii) Ran ($22^\circ10' : 69^\circ20'$)
(iii) Mevasa ($22^\circ13' : 69^\circ21'$)
(iv) Habardi ($22^\circ13' : 69^\circ25'$)
(v) Virpur ($22^\circ15' : 69^\circ21'$)

The high grade varieties of Saurashtra bauxite analyse minimum 58% $\text{Al}_2\text{O}_3$, 1.5 to 2.5% SiO$_2$, 2 to 3% TiO$_2$, 2 to 3% Fe$_2$O$_3$ and 31% L.O.I. whilst intermediate grades analyse 55 to 58% $\text{Al}_2\text{O}_3$, 2 to 3% SiO$_2$, 2 to 3% respectively of TiO$_2$ and Fe$_2$O$_3$ and about 2 to 2.5% CaO. The low grade ores analyse around 50 to 55% $\text{Al}_2\text{O}_3$, 4 to 20% Fe$_2$O$_3$.

Bayer's process and its chemistry

Numerous processes have been and are still being developed for the production of alumina from bauxites and other aluminous ores. The objective of these processes is essentially to economically produce alumina of high purity, suitable for its subsequent reduction to aluminium in the electrolytic cells. The various processes use alkalies or acids or salts to recover alumina. The choice of the individual process for a particular ore is, however, decided by the nature of the ore and the associated impurities. Most of these processes are not yet commercially well established and substantial quantities of $\text{Al}_2\text{O}_3$ are still produced only by Bayer's process.

The Bayer's process consists in digesting bauxite at 8 to 10 atmospheres with concentrated alkaline solution containing 350-400 g/l of caustic soda for 2 to 8 hours. The sodium aluminate solution so obtained is then diluted to 150 to 170 gms. NaOH per litre and the insoluble residue (red mud) separated by filtration. The red mud is washed free of alkali and the sodium aluminate solution cooled and treated with a seed charge to precipitate alumina trihydrate. The alumina trihydrate is then washed free of alkali and calcined to produce anhydrous alumina which is subsequently used in the reduction cells. The spent liquor is then concentrated and recycled to the digestion step after soda losses are made up.

Bauxites consist of a mixture of trihydrate and monohydrate which differ in their solubilities in caustic soda solutions. The solubilities of alumina trihydrate and monohydrate are shown in Figs. 1 and 2 and it is observed that monohydrate is much less soluble than the trihydrate. For a given weight ratio of alumina to caustic, the monohydrate requires both increased caustic concentration and temperature. The solubility of alumina hydrates is increased by either increase of temperature or concentration or both. Too low a caustic concentration results in decreased yield of alumina per unit volume processed which will ultimately make the process uneconomic. Increase in the caustic concentration increases the stability of sodium aluminate solution, which delays precipitation of alumina trihydrate and results in a fine grained alumina trihydrate with increased dust losses during calcination. The concentration of caustic solution in any alumina plant is evidently fixed by the nature of the bauxite.

Since the solubility of alumina is a function of both caustic concentration and temperature, it is possible to use a variety of combinations of both temperature and caustic concentration.
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Source of Bauxite</th>
<th>Chemical Analysis %</th>
<th>Petrography report</th>
<th>Mineralogical Analysis %</th>
<th>Plant method Gibbsite %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Naredi (23°11': 69°14') Abdasa taluk, Kutch district, Gujarat (0.7 million tons)</td>
<td>$Al_2O_3$: 54.10, $SiO_2$: 5.7, $Fe_2O_3$: 4.4, $TiO_2$: 4.3, CaO: 1.7, MgO: 0.28, L.O.I.: 29.28</td>
<td>Chieflly Chlorite Gibbsite was present as very fine microcrystalline aggregates occupying inside and around the cracks and cavities of the chlorite groundmass. Chlorite with appreciable amounts of gibbsite.</td>
<td>Gibbsite: 41.00, Boehmite: 8.5, Diaspore: 1.8, Kaolinite: 2.8,</td>
<td>50.2</td>
</tr>
<tr>
<td>B</td>
<td>Ran (20°11': 69°30') Kalyanpurmahal Jamnagar District (1.0 million tons)</td>
<td>$Al_2O_3$: 61.08, $SiO_2$: 1.3, $Fe_2O_3$: 1.8, $TiO_2$: 2.7, CaO: 0.32, MgO: 0.18, L.O.I.: 30.86</td>
<td>Do</td>
<td>Gibbsite: 50.11, Boehmite: 8.8, Diaspore: 1.09, Kaolinite: 1.8,</td>
<td>51.72</td>
</tr>
<tr>
<td>C</td>
<td>Location of mine not known supplier M/s Saurashtra Traders, Bankodi (whitish variety)</td>
<td>$Al_2O_3$: 57.62, $SiO_2$: 1.48, $Fe_2O_3$: 2.56, $TiO_2$: 3.26, CaO: 1.20, MgO: 1.23, L.O.I.: 32.65</td>
<td>Do</td>
<td>Clinohumite and Gibbsite: 51.2, Boehmite: 3.5, Diaspore: 1.5, Kaolinite: 1.00,</td>
<td>50.8</td>
</tr>
<tr>
<td>D</td>
<td>Do (Reddish variety)</td>
<td>$Al_2O_3$: 56.44, $SiO_2$: 1.28, $Fe_2O_3$: 5.00, $TiO_2$: 3.40, CaO: 0.46, MgO: 1.17, L.O.I.: 32.10</td>
<td>Do</td>
<td>Clinohumite with minor amounts of Gibbsite concentrated in the cracks and at grain boundaries of chlorite grains which were crypto-crystalline. Clinohumite, crypto-crystalline gibbsite was found to be present at the contact of chlorite grains. The presence of relict rutile was also observed though this was present in minor quantities when compared with iron oxide which was present as coating over alumina minerals.</td>
<td>48.0, Gibbsite: 5.3, Diaspore: 1.56, Kaolinite: 0.5,</td>
</tr>
<tr>
<td>E</td>
<td>Lamba Mines Kalyanpurmahal, Jamnagar District</td>
<td>$Al_2O_3$: 59.60, $SiO_2$: 1.64, $Fe_2O_3$: 6.04, $TiO_2$: 2.24, CaO: 0.64, MgO: 0.40, L.O.I.: 29.40</td>
<td>Do</td>
<td>Clinohumite with minor amounts of Gibbsite concentrated in the cracks and at grain boundaries of chlorite grains which were crypto-crystalline. Clinohumite, crypto-crystalline gibbsite was found to be present at the contact of chlorite grains. The presence of relict rutile was also observed though this was present in minor quantities when compared with iron oxide which was present as coating over alumina minerals.</td>
<td>55.0, Gibbsite: 3.2, Diaspore: 0.82, Kaolinite: 0.52,</td>
</tr>
<tr>
<td>F</td>
<td>Zanjaria mines</td>
<td>$Al_2O_3$: 58.0, $SiO_2$: 2.05, $Fe_2O_3$: 5.4, $TiO_2$: 3.0, CaO: 1.86, L.O.I.: 32.47</td>
<td>Chlorite with appreciable amounts of gibbsite</td>
<td>Gibbsite: 49.55, Boehmite: 3.85, Diaspore: 1.5, Kaolinite: 0.1</td>
<td>—</td>
</tr>
<tr>
<td>G</td>
<td>Mine not indicated Jamnagar District</td>
<td>$Al_2O_3$: 64.03, $SiO_2$: 1.16, $Fe_2O_3$: 2.3, $TiO_2$: 4.15, CaO: Trace, MgO: 0.65, L.O.I.: 27.25</td>
<td>Chieflly Chlorite Gibbsite was present as very fine microcrystalline aggregates occupying inside and around the cracks and cavities of the chlorite groundmass. Chlorite with appreciable amounts of gibbsite.</td>
<td>Gibbsite: 48.64, Boehmite: 5.7, Diaspore: 9.0, Kaolinite: 0.6,</td>
<td>49.0</td>
</tr>
<tr>
<td>H</td>
<td>Virpur Mines Halar District, Jamnagar</td>
<td>$Al_2O_3$: 55.38, $SiO_2$: 1.82, $Fe_2O_3$: 4.02, $TiO_2$: 3.2, CaO: 2.2, MgO: 1.66, L.O.I.: 31.92</td>
<td>Chieflly Chlorite Gibbsite was present as very fine microcrystalline aggregates occupying inside and around the cracks and cavities of the chlorite groundmass. Chlorite with appreciable amounts of gibbsite.</td>
<td>Gibbsite: 40.9, Boehmite: 9.75, Diaspore: 2.99, Kaolinite: 1.79,</td>
<td>50.49</td>
</tr>
</tbody>
</table>
The American plants use low caustic concentration and temperatures. In the European practice, the practical limit of caustic soda concentration is just below that concentration which when nearly saturated with alumina, would be sufficient to salt out some of the alumina and soda as a hydrated sodium aluminate. The caustic soda concentration and the temperature differ from plant to plant but it is a little less than the concentration which would salt out sodium aluminate at the lowest temperatures to which the liquors are subjected in certain parts of the plant.

The American practice is economical for trihydrate bauxites since it requires less evaporation and is more suited to continuous digestion.

Recent experiences in alumina plants have necessitated modifications to be incorporated in digestion of mixed trihydrate and monohydrate alumina bauxites. The adoption of American practice for bauxites containing both trihydrate and monohydrate alumina, results in the extraction of the former leaving the latter unaffected. This results not only in the low extraction but also additional difficulties and alumina losses since the undissolved alumina monohydrate results in a seeding effect on the saturated sodium aluminate solution thereby enhancing the alumina losses to the red mud.

A modified Bayer’s process known as the Sweetening Process was proposed for the treatment of a mixture of both monohydrate and trihydrate bauxite.

The essential reactions that take place in the Bayer process can be summarised as follows:
Studies on the nature of the sodium aluminate solutions have indicated that it contains NaAlO₂ in solution in the presence of excess alkali, which ionises into Na⁺ and AlO₂⁻. The AlO₂⁻ ions are extensively hydrated and these tend to decompose in dilute solutions to form aluminatrihydrate on the surface of the trihydrate seed.

Iron and titanium oxides remain unaffected in Bayer process and are discarded in the red mud. SiO₂ in the form of silicates reacts with alumina and soda to form an insoluble sodium aluminium silicate complex during digestion. The desilication compound is now believed to be of the composition 2Na₂O. 2Al₂O₃. 5SiO₂. 5H₂O which represents real losses of soda and alumina.

During calcination of the alumina trihydrate the gibbsite loses its water content and finally gets converted to α-Al₂O₃ which does not pick up moisture.

**Experimental:** Eight representative samples from different deposits were received and these samples were subjected to regular mineralogical and chemical analyses and tests to find their amenability to caustic soda digestion.

Besides the petrographic studies, the chemical methods developed by the Russians Maslenitski and Shmanenkov have been used for the quantitative estimation of the alumina minerals in all the eight bauxite samples which is further confirmed by the usual plant method of estimating gibbsite.

The samples were chemically analysed as per I.S.I. Specification I.S. 2000-1962 for all the constituents.

The leaching tests consisted in refluxing 25 grams of the bauxite sample of known particle size with a measured volume of caustic soda of known strength for a predetermined period under boiling conditions at atmospheric pressure. The solids and liquids are then separated and the residue washed under identical conditions. The filtrates and the residues were analysed for alumina immediately and the alumina recoveries computed. The various factors studied included the effect of particle size, concentration of alkali, molar ratio of alumina to caustic and rate of dissolution.

The results of the mineralogical and chemical analyses are indicated in Table I, whilst the results of the digestion tests are indicated in Figs. 3, 4 and 5.

**Discussions and conclusions**

A comprehensive survey has been made on the Gujarat Bauxites and their suitability to caustic soda digestion at the National Metallurgical Laboratory. It was observed that almost all the samples were mainly clauhitic with varying amounts of gibbsite and boehmite and minor amounts of diasporc and kaolinite. Only sample designated 'G' from Jamnagar was found to contain a high proportion of diasporc, whilst all the samples contained 1–2% Al₂O₃ as diasporc. The chemical method for the determination of the alumina minerals confirmed that most of the samples consisted of mainly gibbsite (>90%) with the exception of the sample designated 'G'. The petrographic studies revealed the main alumina mineral to be clauhite and since the chemical analysis of the alumina minerals revealed gibsite to be predominant, it is concluded that clauhite is soluble in the selective solvent used for gibsite estimation. All the samples contained mostly the amorphous clauhite with gibbsite present in the cavities and on the grain boundaries of clauhite.

All the samples were massive, earthy, less oolitic and varied from greyish white to reddish brown in colour. The alumina content varied from 54 to 64% while the SiO₂ varied from as low as 1% to about 5% maximum. The L.O.I. varied from 27–32% in most of the samples. The samples were tested for the extraction of alumina by caustic soda digestion at atmospheric pressure and it was observed that more than 90% of alumina could be dissolved in all the samples, excepting the sample 'G', on leaching 25 grams of ~10 mesh samples with caustic soda solution containing 200 gm, NaOH per litre, providing a molar ratio of Na₂O : Al₂O₃ as 2 : 1 for 30–60 minutes at the boiling point of the solution. The use of coarser size bauxite is advantageous since it

\[
\begin{align*}
\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 2\text{NaOH} & \rightarrow 2\text{NaAlO}_2 + 4\text{H}_2\text{O} \\
\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} & \rightarrow 2\text{NaAlO}_2 + 3\text{H}_2\text{O}
\end{align*}
\]
not only cuts down the grinding costs but also results in faster settling rates of the red mud and ease of operation.

From a comparative study of the effect of caustic concentration on the alumina extraction (Fig. 3) in the different samples, it is observed that most of the samples exhibit similar characteristics excepting the sample 'E' from Lamba Mines, Kalyanpurmahal, Jamnagar district, which indicated a recovery of 92% Al₂O₃ at as low a caustic concentration as 100 gm NaOH per litre. Sample 'E' from Zanjaria, Gujarat, recorded steady increase in the alumina extraction from 100 g/l to 200 g/l only. With the sample 'G' from Jamnagar the maximum yield of alumina was only about 76% even at a caustic concentration of 400 g/l.

Fig. 4 records the results obtained on the rate of dissolution of the contained alumina in the various samples. It is observed from Fig. 4, that the curves for different samples lie close to each other with the exception of sample 'G' in which only about 76% Al₂O₃ was dissolved. It is observed that more than two thirds of the alumina in all the bauxite samples is dissolved in the first few minutes. Initially since the caustic soda is nearly free, alumina rapidly dissolves and saturates the solution thereby decreasing the free caustic value of the solution. Further quantities of Al₂O₃ then slowly dissolve until the whole of available Al₂O₃ is dissolved.

Fig. 5 indicates the alumina recoveries at the vari-
ous molar ratios. The recovery curves for different bauxite samples lie close to each other after a molar ratio of 2:1 excepting the sample ‘G’.

The foregoing results of the tests with different bauxite samples from Gujarat clearly indicate the feasibility of alumina extraction by caustic soda digestion. At present, these high grade bauxites are exported which are capable of alumina extraction at atmospheric pressure itself, and the establishment of an aluminium industry in Gujarat is strongly advocated.

Acknowledgement

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References