Neutralization of bauxite residues by gas purging

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ABSTRACT

The utilization of industrial byproducts, IBPs, for creating huge infrastructure projects (viz., land reclamation, rehabilitation of low-lying areas, backfilling of mines and construction of embankments, etc.), is being hypothesized to address the issues related with the sustainability. One of such IBPs are the bauxite residues, BRs, which get generated at alumina refineries; either in the slurry form or cakes coming out of the filter press, has been stacked at industrial premises, in the form of heaps or dumps. Ideally, the BRs can be utilized for the above-mentioned projects, provided they are suitably ‘neutralized’ to bring down their pH. Though, at this stage, it appears to be a ‘distant dream’, successful demonstration of such a philosophy would be a game-changer for the alumina refineries and the infrastructure sector, in general. In lieu of this, different techniques for neutralizing the BRs by using various chemicals, (sea)water, and bacteria have been adopted in the past. However, another interesting strategy to neutralize the magnanimous quantity of BRs stacked could be through purging CO₂ that needs to be investigated in detail. With this in view, and to investigate the technical feasibility of CO₂ purging in the BRs in their semi-solid state, a setup NeGaPur (connoting to the Neutralization by Gas Purging) that simulates BRs-gas interaction in the laboratory conditions has been adopted and its details are presented in this paper.

Keywords: Bauxite residues, carbon-dioxide, gas purging, NeGaPur, neutralization, electrical conductivity.

1 INTRODUCTION

The modern-day industrial economy demands implementation of sustainable practices such as 4R’s of waste management (recover, reduce, recycle and reuse), zero waste discharge, waste to energy, valorisation of waste materials, etc. for their long-term existence. Among this, the management of industrial byproducts, IBPs, has become a big challenge, if not a menace, due to an exponential growth rate of its generation, scarcity of land for disposal/storage, minor utilization potential and the reluctance towards to the contamination potential of the IBPs. One such IBPs is the bauxite residues, BRs, which are generated at alumina refineries; either in the slurry form or filter pressed cake by following the Bayer’s process of alumina extraction. Approximately, each ton of alumina production leads to the generation of nearly 1.0-1.6 Ton of the BRs. With the present generation rate of alumina, the global annual production of BRs has crossed 120 Million Tons (Santini et al., 2015). It is worth noticing that not only the quantity but also the unwanted characteristics such as extremely high alkalinity and tendency to pollute the nearby surroundings due to the fine-particulate nature, adds salt to the miseries in the degradation of the ecosystem.

Conventional practice is to discharge the slurry of the BRs in the lagoons and recovering/decanting the caustic. However, this practice might become a potential source of contamination of the ecosystem, due to spillage of the BRs and leachate migration into the surroundings (Kuntikana and Singh, 2017). This situation has been instrumental in alumina refineries changing the practice related to the disposal and storage of the BRs. Hence, the recent trend is to employ filter press to squeeze the caustic from the BRs and dispose it in a semi-solid form (viz., cakes with moisture content ≈17 to 21%). Although this exercise overcomes the ill effects of slurry disposal of BRs, the stack of these cakes becomes quite vulnerable to the (i) rainwater induced sludge of high alkalinity and (ii) uncontrolled release of fugitive dust that remains airborne, thereby polluting the native environment. Apart from these issues, due to extremely limited utilization of the BRs, in the cement plants, the management of these stacks and their rehabilitation becomes a daunting task.

One of the ways to come out of this situation would be to neutralize BRs, by resorting to various techniques that are well accepted but not practiced yet, to overcome the issues related with the higher alkalinity through the process of neutralization. In this context, organic and inorganic acids, synthetic solutions, chemicals, (sea)water, and bioremediation have been researched by earlier researchers (Jayanthi and Singh, 2016; Rai et al., 2012). However, these technologies do not appear to be
feasible for the heaps of BRs due to various impediments or lack of initiatives (Kuntikana and Singh, 2017).

However, it should be realized that the neutralized BRs would become the manmade resource (read soils), which can be employed for infrastructure development, soil rejuvenation, mine backfilling, etc.

With this in view, preliminary investigations were conducted on the reconstituted sample of BRs and subsequently purging CO₂ into it, as discussed in the following.

2 MATERIALS USED IN THE STUDY

The BRs used in the current study were characterized to obtain their physical, chemical and mineralogical properties. The specific gravity, G, of the BRs, obtained using an Ultra-Pycnometer (Quantachrome, USA) is observed to be ranged from 3.16-3.3 (ASTM D 5550-14, 2014). The sample of BRs contains 85% of particles finer than 0.1 mm sieve size. The specific surface area (SSA) of BRs determined by BET technique with a gas-porometer (NOVA1200e) was found to be 12.2 m²/g (ASTM C1069 − 09, 2014). The chemical composition of the BRs determined by using the X-ray fluorescence (XRF) technique showed the presence of silica, alumina, and oxides of iron, titanium and calcium in major proportions (as listed in Table 1).

Table 1. The chemical composition and leaching characteristics of the BRs considered in the study

| Chemical composition | Leaching characteristics |
|----------------------|--------------------------|
| Metal Oxide          | % by weight              |
| Fe₂O₃                | 40.20                    |
| Al₂O₃                | 18.84                    |
| TiO₂                 | 11.05                    |
| SiO₂                 | 10.64                    |
| Na₂O                 | 4.79                     |
| CaO                  | 2.42                     |
| V₂O₅                 | 0.29                     |
| P₂O₅                 | 0.27                     |
| K₂O                  | *                        |
| MgO                  | *                        |
| LOI                  | 11.5                     |

| Element | Concentration (in mg/L) |
|---------|-------------------------|
| As      | 0.061                   |
| Ba      | 0.006                   |
| Ca      | 0.730                   |
| Co      | *                       |
| Cr      | 6.660                   |
| Cu      | *                       |
| Fe      | 2.590                   |
| K       | 4.400                   |
| Mg      | 0.160                   |
| Mo      | 0.189                   |
| Na      | 514.0                   |
| P       | 0.452                   |
| Pb      | *                       |
| Sc      | 0.001                   |
| Si      | 4.150                   |
| Sr      | 0.001                   |
| Ti      | 0.350                   |
| V       | 0.432                   |
| Zr      | 0.024                   |

The leaching characteristics of BRs have been established in DI water as per USEPA-1311, (1992). The filtrate was collected and its pH and electrical conductivity, EC, was measured. Further to get the leachable ion concentration the filtrate was acidified by adding 250 μl of 1M HNO₃ solution to 10 ml of the filtrate. Subsequently, the prepared solution was analysed by employing the ICP-AES. It can be noticed that the major mineral phases present in the BRs are anatase, hematite, sodalite, goethite, gibbsite and rutile, as depicted in Figure 1.

![Figure 1. The XRD pattern for the BRs considered in the study](image)

3 EXPERIMENTAL INVESTIGATIONS

3.1 Test setup

Fig. 2 depicts the device that has been developed for conducting the proposed study. This device, designated as NeGaPur, consists of six basic units: (a) the plunger, (b) the specimen cell, (c) the base plate, (d), the jacket, (e) the connecting plate and (f) the top plate, respectively. The sample has been filled in the specimen holder which has been provided with stainless steel electrodes to capture the state of material intermittently and in a non-destructive manner.

![Figure 2. Details of the device NeGaPur (Applied for Indian Patent)](image)

Subsequently, various point-electrodes were inserted in the specimen and the background electrical conductivity BRs, σ, across them was recorded, with the help of an impedance analyzer (make Novocontrol Technologies, Germany), which works in the frequency range 3 μHz to 40 MHz, AC, with a root mean square voltage, Vrms, of 1.414 V.

3.2 Sample cell calibration

Initially, the impedance analyzer has been calibrated by using standard resistors and capacitors at 25±1°C.
Furthermore, the calibration of the impedance cell, IC, was performed with deionized water, DI water, following the methodology proposed by earlier researchers (Susha Lekshmi et al. 2016). It has been observed that corresponding to a tip-to-tip distance of electrodes equal to 48 mm, the effective diameter of the electrode turns out to be 13 mm and the corresponding impedance spectra have been recorded.

3.3 Sample preparation

The BRs from the alumina refinery, M/S HINDALCO Ltd., Belgaum, India, were used in this study. The lumps of the BRs were broken and air-dried. Subsequently, the processed BRs are packed in unit B, which is positioned on unit C, from the base with a porous disc kept in between. The desired dry-density of the fill has been attained in 3 layers of equal thickness, each layer is tamped with the help of a mallet, which weights 138 g, to achieve the desired density of 1.5 g/cm³. Along the height of unit B, eight pairs of 2 mm diameter stainless-steel point electrodes pairs, numbered from bottom to top as A-A, B-B, C-C... to H-H, have been inserted.

3.4 Methodology

Initial attempts were made to purge CO₂ gas in the BRs, by connecting the gas cylinder to the port I₁ and maintaining the gas pressure equal to 98.0 kPa, and closing I₁, O₂ and O₁ (refer Fig. 2). The exposure time, t exp, of the BRs to these gases has been varied from 0 to 12 days and the electrical conductivity of the solids, σ, corresponding to various electrode pairs was recorded. It is worth mentioning here that CO₂ reacts with the hygroscopic moisture on the surface of the BRs. As a result of this interaction, the electrochemical properties of the specimen change, as per Equations (1) and (2).

\[
\text{OH}^{−} (\text{aq.}) + \text{CO}_2 \rightarrow \text{HCO}_3^{−} (\text{aq.}) \quad (1) \\
\text{OH}^{−} (\text{aq.}) + \text{HCO}_3^{−} (\text{aq.}) \rightarrow \text{CO}_3^{2−} (\text{aq.}) + \text{H}_2\text{O} \quad (2)
\]

The alkaline BRs host ‘net surface +ve charge’ due to the presence of Na⁺, which after coming in contact with carbonate/bicarbonate ions, formed due to the reactions defined by Equations (1) and (2), would result in the formation of MgCO₃, NaHCO₃, and CaCO₃ as the end products. This ultimately results in the neutralization of the BRs.

4 RESULTS AND DISCUSSION

For the sake of brevity, the variation of σ with respect to the frequency, ω, of AC is presented for different durations, t, of CO₂ purging for the electrode pair AA (refer Figure 3). It can be noted from the figure that after initial increment in σ, with ω, it becomes a constant for ω>10⁵ Hz. Subsequently, the DC conductivity, σdc, of the sample, was determined by following the methodology proposed by Shah and Singh (2004), and the results are listed in Table 2.

![Fig. 3 The results obtained from impedance spectroscopy for electrode pair AA, for different interaction time t (in days).](image)

It can be inferred from the data presented in Table 2 that a drastic reduction in σdc occurs near the inlet point (electrode pair A-A) and for t = 12, the sample attains a practically constant σdc. Furthermore, the sample from the unit B was scraped, layer-by-layer with the help of a spatula, and the representative specimens of the neutralized bauxite residues, NBRs, corresponding to each pair of electrodes were collected and transferred into glass beakers. Later, these specimens were mixed with the deionized water to create a solution of liquid to solid ratio equal to 10 and their pH and electrical conductivity, EC, were recorded by employing a water quality analyzer and the results are presented in Table 3. A similar procedure was adopted for the specimens of BRs, as well, to establish a comparison of the effectiveness of the gas purging for their neutralization. A drop in the value of electrical conductivity, EC, of the leachate for NBRs indicates the effectiveness of the neutralization of BRs by CO₂ purging by employing the setup NeGaPur.

| Electrode Pair | σdc (×10⁻⁸ S/cm) corresponding to different interaction time t (in days) |
|---------------|---------------------------------------------------------------------|
|               | 0          | 1         | 2         | 3         | 4         | 5         | 7         | 9         | 12        |
| AA            | 117.7      | 8.692     | 5.808     | 4.492     | 4.086     | 5.316     | 2.657     | 2.357     | 2.641     |
| BB            | 125.3      | 9.609     | 6.373     | 4.629     | 4.310     | 5.599     | 3.472     | 2.352     | 2.356     |
| CC            | 76.35      | 14.42     | 8.863     | 6.583     | 5.338     | 5.975     | 3.946     | 3.068     | 3.103     |
| DD            | 77.22      | 15.12     | 9.693     | 6.917     | 5.585     | 6.255     | 4.003     | 3.874     | 3.047     |
| EE            | 73.21      | 21.60     | 13.97     | 9.982     | 7.300     | 7.016     | 5.280     | 3.984     | 3.466     |
| FF            | 80.91      | 25.27     | 15.74     | 10.83     | 7.753     | 7.208     | 5.331     | 4.665     | 3.220     |
| GG            | 135.9      | 37.68     | 24.92     | 17.57     | 11.34     | 8.678     | 6.931     | 4.848     | 3.663     |
| HH            | 209.6      | 44.48     | 28.18     | 18.40     | 11.36     | 8.607     | 7.225     | 5.098     | 3.448     |
Furthermore, the specimens of BRs and NBRs were analyzed for thermogravimetric and differential thermal analyses and the results are presented in Figure 4.

The broad peak ‘a’ corresponds to the dissociation of NaHCO₃ into Na₂CO₃ which usually starts dissociating at T>50 °C. This peak is less prominent in the BRs as compared to the NBRs that were collected from different electrodes. The peak ‘b’ is a compound peak of the dehydroxylation reaction of gibbsite phases to the boehmite phase and the goethite phase decomposition. In addition, the decomposition of the MgCO₃ also happens to start around 350 °C. The peak ‘d’ corresponds to the dissociation of Mg(OH)₂ which starts at 450 °C. Since the BRs contain traces of Mg(OH)₂, there is no significant change in this peak. The peak ‘d’ for 550<T<700 °C corresponds to the decomposition of CaCO₃ and NaCO₃. The peak ‘d’ becomes more prominent in the case of NBRs and a right-hand shift in its dissociation temperature indicates a reduction in alkalinity.

### 5. CONCLUSIONS

This study has successfully demonstrated the neutralization of BRs in their semi-solid form by CO₂ purging and employing the setup NeGaPur, under laboratory conditions. Efforts should be made to quantify the parameters that could be plugged into suitably developed mathematical models, which in turn could be employed for planning the pilot and field-scale neutralization of the BRs.

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