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Bio-chemical leaching of kaolinite-hematite-boehmite type bauxite ore

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Low grade bauxites of Severo-Onezhsky and Sredne-Timansky deposits of Russia have been evaluated for their amenability towards bioleaching. Two microbial isolates of *Bacillus* genera have been isolated in Zak medium and enriched to conduct leaching experiments of bauxites. The bacteria are chosen due their specific ability to secrete exo-polysaachrides (EPS), which is believed to be very beneficial in dissolution-cum-flocculation of aluminosilicates. The microbes have been able to leach nearly 50% alumina and nearly 10-35% SiO_2 and Fe_2O_3. Chemical leaching experiments with citric and oxalic acids on bauxite leaching result in a maximum extraction of aluminum to be nearly 39% at elevated concentrations of leaching agents and 2-8 hours residence time.

Keywords: Bioleaching, Bauxite, Microbial EPS, Specificity, Alumina

Extraction of aluminum from raw bauxite involves considerable costs with much intense processing. The conventional processing methods sometimes are unable to utilize a wide variety of feed, especially those rich in gangue content, thus raising an imperative need to improve traditional methods. The mined bauxite ore needs to be separated from its undesirable mineral components, where in preferential dissolution can be carried by microbes in a process called biobeneficiation (removal of silica, calcium and iron being major impurities). Use of microorganisms to bring out microbially-induced flotation or flocculation of the desirable mineral constituents could prove to be a novel alternative to existing physico-chemical methods in bauxite processing[1,2]. In recent years, attention has been drawn to extract aluminum[3]. Resolution of this most difficult problem opens new paths by development of conceptually new technologies for its production. The major gangue minerals present in bauxite are silica in the form of quartz and aluminosilicate with alumina in the form of clay, such as kaolinite. Bioleaching techniques utilizing different organic acids are often considered used to remove iron from bauxite and its residues[4,5]. These techniques are extremely safe.

This work considers the feasibility of leaching of bauxites by microorganisms isolated from the natural microflora of deposits and organic acids, wherein the efficiency of bioleaching is compared with that of organic acids. We aim to project the unpublished facts to attempt aluminum leaching, with co-extraction/removal of silica and iron.

Experimental Section

Bacteria and raw material

Bacteria were obtained by selection of active mixed cultures from the microflora of Severo-Onezhsky and Sredne-Timansky deposits, Russia. In terms of dominant minerals, the bauxites used in the work belong to kaolinite-hematite-boehmite type with high silica content. Principal alumina-containing mineral is Boehmite (45%), along with hydrargillite, diaspore and alumogel in close association. The bauxite contains elevated quantity of silica/quartz (10-16% SiO_2) and iron (10-26% Fe_2O_3). In bauxite specimens from Severo-Onezhsky deposit, aluminum (Al_2O_3) content was 52.5%, against 43-46% in Sredne-Timansky deposit.

For this purpose, the as-collected lumps of bauxite were placed in a nutrient medium to grow microorganisms in a batch mode. A series of reinoculations resulted in consortia of microorganisms used as the primary inoculum for leaching experiments. The nutrient medium (Zak medium) in following composition (g/L): $(NH_4)_2SO_4$ – 0.1,

$MgSO_4 \cdot 7H_2O$ – 0.15; NaCl – 0.15; $MnSO_4$ – 0.05; Ca_2PO_4 – 1.5; Starch – 20, was used to maintain microorganism growth. Zak medium is recommended to extract silicate and phosphate-mobilizing microorganisms[6]. The composition of the medium was modified in some stages, specifically, with respect to a source of nitrogen as $(NH_4)_2SO_4$ (0.1 g/L). Microbial growth was compared in presence of varying solid ratio of bauxite ore (in the range of 50-250 g/L), for its adaptability.

Experimental procedure

Experiments were carried out in two stages. In the first stage, feasibility of leaching aluminum, iron, silica and potassium from Severo-Onezhsky and Sredne-Timansky deposits by bacteria were conducted on an orbital shaker at the initial *p*H of 6.9, at 22-26°C and solid-liquid ratio of 1:20 and 1:4. On completion of one cycle, the residue was re-processed with microorganisms periodically replacing a part of the liquid phase. Leaching was also carried out by organic acids (citric and oxalic acids as products of microbial metabolism) at 75-80°C and periodic shaking for 4 h, unless stated otherwise. Bauxite leaching was monitored with periodic measurements of *p*H of the media, analysis of aluminum. In the liquid medium, the dissolved orthosilicate species were evaluated by colorimetric method[7]. In an acid medium with molybdate, the dissolved orthosilicate species yield yellow-coloured compounds. Concentration of aluminium, silica and iron in the liquid phase was evaluated with AAS/ICP.

Results and Discussion

Microbial growth-cum-tolerance development

Extremophiles capable of solubilising aluminum and silica/quartz minerals were mixed in the pulp containing specimens of bauxite samples in Zak medium with additional source of nitrogen as ammonium sulfate. As a result of a series of reinoculations and recultivations of grown microorganisms, a mixed culture with more efficient growth on this media was selected. The aboriginal microorganisms produced in this manner were used as starters to leach the tested bauxites. These species were then added to the pulps with modified Zak medium (with nitrogen source) and bauxite specimens, to evaluate the bacterial adaptation. Microscopic studies of specimens showed the consortia had a high diversity of mobile species, single and generating micro-aggregates (Fig. 1a). Growth of bacteria resulted in decrease in *p*H to 5.5 in pulp from bacterial standard growth *p*H of 7.0. It was also seen that the bacteria belong to spore-producing species with high muco-polysaccharide/ EPS secreting ability (as evident from plates). However, the medium became viscous and *p*H was noted to be nearly 8 in nearly 7 days. This implies to the ability of organism to create conditions to adapt and grow proficiently. Microscopic data and change in viscosity of culture provided grounds to assume about the aggregation in cells and microscopic characteristics were similar to ***Bacillus muciliganosus***. This species have been reported by various authors for their ability to dissolve silica[7-9]. But repeated culturing and purification with sequencing revealed the microbe to be ***Bacillus aryabhattai*** (100% similarity to strain B8W22(T)-EF114313. These microbes had ability to secrete EPS when fed to starch. EPS seen were light coloured halos around the bacteria (Fig. 1b).

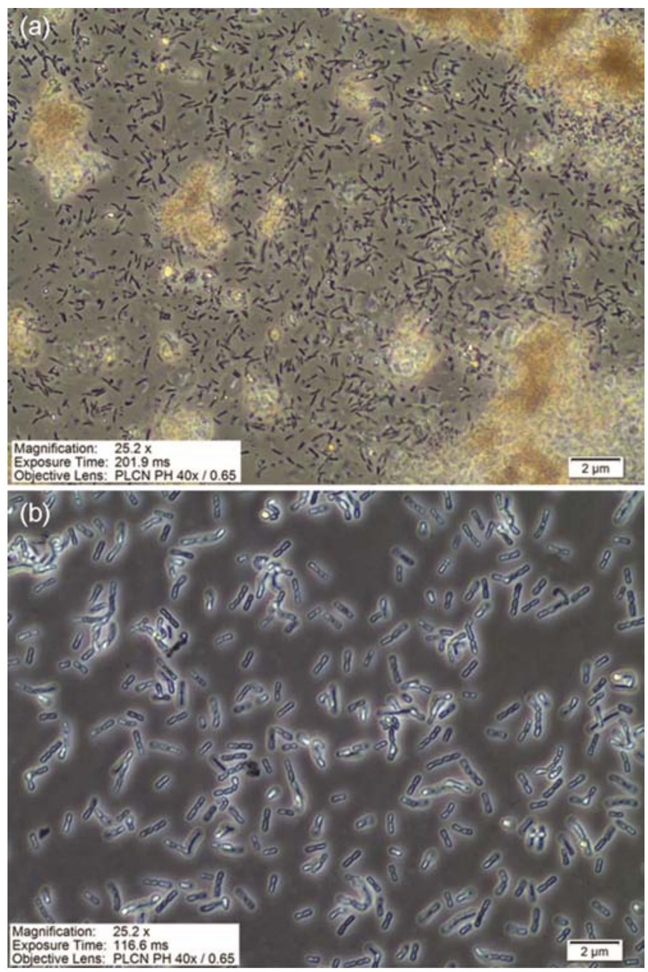

Fig. 1 — Microbial isolates from (a) Severo-Onezhsky, (b) Sredene-Timansky deposit.

Leaching experiments with bacteria

The bacterial species of *Bacillus* genera were directly placed for experiments on lab scale with the bauxites from Severo-Onezhsky and Sredne-Timansky deposits as given in Table 1. Comparison of experiments 1-4 shows that bacterial processing of bauxite specimens both from Severo-Onezhsky and Sredne-Timansky deposits leached aluminum, silica/quartz, iron. Leaching was maximum when bauxite from Severo-Onezhsky deposit was processed with partial replacement of liquid phase for fresh nutrient medium. The number of partial replacements was kept minimum to 2 per cycle (unless stated otherwise) during each experiment, but it yielded better leaching[10]. The measured concentration of Al, Si, Fe were normalized with respect to their concentrations in initial ore specimens, to plot a dispersion analysis showing the efficiency of bacterial leaching of bauxites and medium replacement. Dispersion analysis was carried by comparing the leached content of Al, Si, Fe against the feed content, and was found statistically valid mass balance with probability 0.99.

In the next series of bauxite leaching experiments, the number of media replacements were kept above 3 (5 times more than in experiments 2 and 3 as in Table 1), giving a daily replacement ratio of 80% in liquid phase. From Table 2, it was seen that bacterial processing considerably reduced aluminum oxide and silica/quartz content in the bauxite specimen from Severo-Onezhsky deposit. At the same time, concentration of iron oxide in the leached bauxite somewhat increased. Assuming the iron from Severo-Onezhsky deposit not being leached, its content increased due to selective dissolution and lower loss of initial solid mass. Aluminum and silica/quartz extraction were evaluated with this assumption. The extraction of Al/Si turned out to be more than 22% of the initial value (Table 2). Obviously, silica/quartz is actually leached, but substantially less than by bacterial leaching of the bauxite specimen from Severo-Onezhsky deposit. In general, the assumptions made decrease in calculated estimates of aluminum and silica/quartz leaching.

However, bioleaching of bauxite specimen from Sredne-Timansky deposit decreased concentration of aluminum and iron with no leaching of silica. Such calculation for the bauxite specimen from Sredne-Timansky deposit assuming no silica/quartz leaching shows that aluminum and iron were leached (Table 2). The results were confirmed with the XRD patterns as in Fig. 2, which shows the diffraction patterns of initial and post-leach material for Sredne-Timansky deposit. The most marked changes were expressed with increase in boehmite content and decrease in relative ratios of quartz and gypsum (Figs 2a and 2b).

Leaching experiments with organic acids

Bacterial leaching of bauxites in former case is largely accounted for the effect of organic acids produced by cells[11]. Efficiency of this mechanism is proved by experiments of leaching bauxites with citric and oxalic acids performed by 2 × 2 factorial pattern analysis. Acid concentration was set at 6 g/L (basic level), 4 and 8 g/L with variability interval 2 g/L (in coded variables their values were 0, -1 and +1). Results are presented in Table 3.

Table 1 — Bauxite leaching by aboriginal microorganisms

Experiment	Deposit	Experimental conditions	Al_2O_3	SiO_2	Fe_2O_3
	Severo-Onezhsky	Initial composition of ore	52.5	15.9	10.90
1		S:L = 1:4, w/o medium	51.7	16.4	10.38
2		S:L = 1:4, with medium	51.4	16.2	10.34
3		S:L = 1:20, with medium	49.9	15.6	9.0
4	Sredne-Timansky	Initial composition of ore	46.4	9.9	26.05
		S:L =1:20, w/o medium	43.2	9.8	22.13

Table 2 — Bauxite leaching in higher liquid phase (media) replacement mode

Experiment	Ore	Content of elements in leached bauxites, %			Loss of solid mass, %	Extraction, %		
		Al_2O_3	SiO_2	Fe_2O_3		Al_2O_3	SiO_2	Fe_2O_3
1	Severo-Onezhsky	42.5	13.1	11.5	5.22	22.53	22.4	0
2	Sredne-Timansky	39.9	11.4	16.9	8.77	8.77	0	35.12

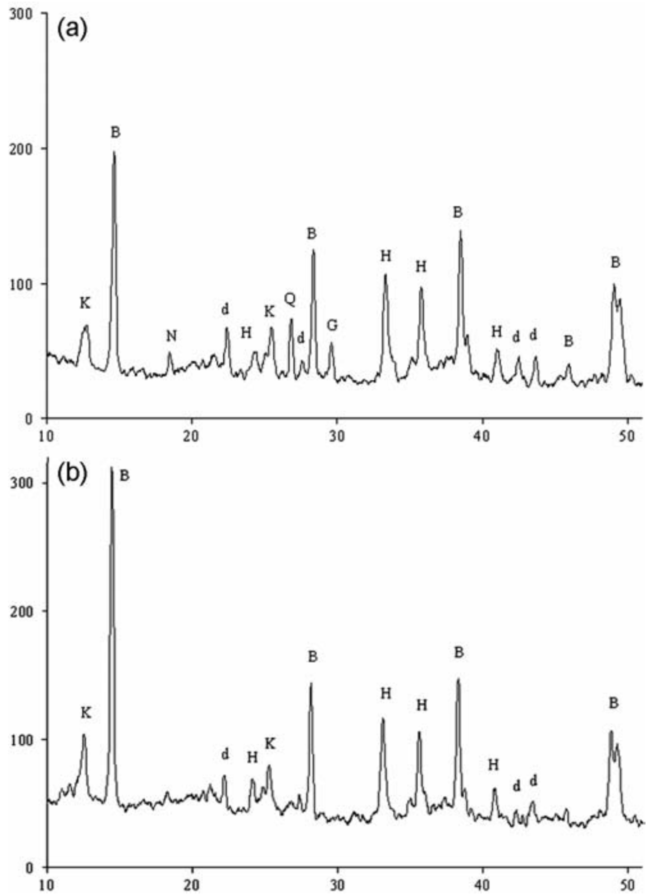

Fig. 2 — X-ray diffraction analysis of bauxite samples of Sredne-Timansky deposits, (a) initial and (b) leach residue [B - boehmite (ASM 21-1307), d – diasporite (ASM 5-355), H –hematite (ASM 33-664), K – kaolinite-serpentinite (ASM 34-163)]

They were used to calculate regression equation (Eq.1) of general form.

$$Y_i= b_0 + b_1X_1 + b_2X_2 +b_{12}X_1X_2 \quad \ldots(1)$$

where, regression coefficients b_1 and b_2 are the quantitative estimate of the effect of citric and oxalic acids, respectively.

Specific form of equations (2-4) for the loss of mass of bauxite specimens processed (Y_{mass}), leaching of (Y_{Fe}) and (Y_{Al}) into liquid phase is calculated based on data in Table 3, as

$$Y_{mass}= 28.56 + 0.19X_1 + 2.7X_2 \quad \ldots(2)$$

$$Y_{Fe} = 40.52 – 3.65X_1 + 17.36X_2 – 6.35X_1X_2 \quad \ldots(3)$$

$$Y_{Al} = 18.48 – 2.48X_1 – 1.55X_2 + 3.96X_1X_2 \quad \ldots(4)$$

From comparison of zero regression coefficients and results of leaching at acid concentrations equal to basic level (6 g/L), it was sent that leaching of

Table 3 — Results of bauxite leaching by organic acids

Experiment	Citric acid, g (X_1)	Oxalic acid, g (X_2)	Loss of mass, %	Leaching, %	
				Fe_2O_3	Al_2O_3
1	4	4	25.74	20.67	26.47
2	8	8	31.52	47.67	18.42
3	4	8	31.00	68.10	15.45
4	8	4	25.98	25.64	13.59
5	6	6	29.52	44.79	32.60

aluminum into solution nonlinearly depends on concentrations of leaching agents[10]. This means that aluminum yield into the liquid phase depends on the ratio of both organic acids, which as an essential content of bacterial EPS. In addition to the estimated effect of citric and oxalic acids on bauxite leaching[11,12], it was found that as the bioleaching proceeded from 2 to 8 h, the efficiency grows linearly achieving a maximum extraction (39%) of aluminum at elevated concentrations of leaching agents. The comparison in the efficacy of bioleaching experiments on bauxites against commercial organic acids does not mean that their action is identical to that of bacterial culture. This follows from their noted physiological specificities and non-unique leaching of silica/quartz from bauxites of Severo-Onezhsky and Srende-Timansky deposits. Concentration of organic acids in bacterial cultures is considerably lower than set values in the experiments, still giving a comparable metal extraction thus citing possibilities to use bacterial culture, the role of EPS, which aids in selective dissolution and flocculation. Primarily this is true for increasing extraction of aluminum into liquid phase. Leaching of iron, silica/quartz and calcium can be essential to enrich the aluminum ores, thereby targeting the unutilized bauxite reserves, with more scale-up experiments planned.

Conclusion

- Low grade bauxites of Severo-Onezhsky and Sredne-Timansky deposits are amenable to microbial leaching.
- Two microbial isolates of *Bacillus* genera have been isolated in Zak medium and identified to be with high EPS secreting ability.
- The microbes have been able to leach nearly 50% alumina and also able to tackle SiO_2 and Fe_2O_3 to good levels (10-35%), outweighing the

reported results with citric and oxalic acids giving 39% dissolution in same duration.

- This work infers the role of EPS and cellular organic acids in bioleaching sets to preferentially dissolve metal from such raw materials.

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