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Effective Remediation of Groundwater Fluoride with Inexpensively Processed Indian Bauxite

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ABSTRACT

India represents one-third of the world's fluorosis burden and is the fifth global producer of bauxite ore, which has previously been identified as a potential resource for remediating fluoride-contaminated groundwater in impoverished communities. Here, we use thermal activation and/or groundwater acidification to enhance fluoride adsorption by Indian bauxite obtained from Visakhapatnam, an area proximate to endemic fluorosis regions. We compare combinatorial water treatment and bauxite-processing scenarios through batch adsorption experiments, material characterization, and detailed cost analyses. Heating Indian bauxite above 300°C increases available surface area by 15x (to ~170 m²/g) through gibbsite dehydroxylation and reduces the bauxite dose for remediating 10 ppm F⁻ to 1.5 ppm F⁻ by ~93% to 21 g/L. Additionally, lowering groundwater pH to 6.0 with HCl or CO₂ further reduces the average

required bauxite doses by 43-73% for ores heated at 100°C (~77 g/L) and 300°C (~12 g/L). Product water in most examined treatment scenarios complies with EPA standards for drinking water (e.g., As, Cd, Pb, etc.) but potential leaching of Al, Mn, and Cr is of concern for some scenarios. Among the defluoridation options explored here, bauxite heated at 300°C in acidified groundwater has the lowest direct costs (\$6.86 per person per year) and material-intensity.

1. INTRODUCTION

Chronic ingestion of groundwater containing excess naturally occurring fluoride leads to skeletal fluorosis, a debilitating health condition that disproportionately affects² children by damaging their developing bones and joints¹ through the deposition and accumulation of fluoride. Skeletal fluorosis is endemic in 25 countries worldwide, but it is predominantly reported in resource-constrained rural regions of India, China, and the East African Rift Valley³, where populations must rely heavily on contaminated groundwater as their primary drinking water source^{2,4}. Despite almost a century of reported causative understanding for endemic fluorosis⁵⁻⁸, an appropriate technology to address this global health crisis has not yet been implemented at scale in such isolated regions. Numerous materials (e.g. bio-sorbents, bone char, synthetic hydroxyapatite, activated alumina, etc.) have been tested and proposed as adsorbents for fluoride removal⁹⁻¹⁶. However, neither natural nor lab-derived technologies have successfully scaled up in rural, resource-constrained regions due to various barriers including sourcing and cost of materials, processing methods, complexity of operation and maintenance, labor intensity, and social acceptability.

Bauxite, a globally abundant ore of aluminum, is a viable, effective, and low-cost fluoride adsorbent alternative. Earlier researchers have reported the fluoride-affinity of bauxite ores from specific sources¹⁷⁻³¹ and red mud (alumina refineries' residue)^{32,33}, but most of them

did not explore the specific dose needed to remediate contaminated groundwater to the World Health Organization's Maximum Contaminant Limit (WHO-MCL= 1.5 ppm F⁻). In a recent study, our team established that bauxite ores from different parts of the world differ significantly in their fluoride adsorption efficiency³⁴. We determined that in comparison to bauxite from sites in Ghana, Guinea, and U.S., an Indian-sourced bauxite had the poorest fluoride removal performance because it contained the trace mineral calcium carbonate (CaCO₃), which upon dissolution increased solution pH well above the optimal pH (of 5.0- 6.0) for fluoride removal.

India represents one-third of the global fluorosis burden (66 million people)^{2,35}. Excess fluoride contamination of groundwater occurs in approximately 70% of India's states³⁶. However, India is also the fifth major global producer of bauxite³⁷, so there exists a promising opportunity to better utilize the abundant bauxite available throughout India for affordable defluoridation. Indian bauxite, if successfully modified through a low-energy, low-cost processing method, could be a practical, locally available, and inexpensive route to alleviate a significant source of chronic human suffering for millions of people. To further advance relevant knowledge and overcome the challenges with using Indian bauxite presented in our previous study³⁴, here we report novel findings to enhance the fluoride removal performance of Indian bauxite through mild thermal treatment at 300°C. We also investigate the feasibility and impact of acidifying fluoride-contaminated groundwater using mineral acids (e.g., HCl) or carbon dioxide gas (CO₂).

The primary objectives of this paper are to 1) report the impact of heating and chemical transformation of bauxite on fluoride removal at molecular scale and explain its practical significance, 2) discuss the effects of groundwater acidification on fluoride removal, and 3) evaluate cost tradeoffs of the various combinatorial treatment scenarios to determine the

feasibility of using Indian bauxite as an effective groundwater defluoridation method in low-income regions.

2. MATERIALS AND METHODS

2.1. Preparation of Bauxite Samples. The bauxite used in this study was collected from a mine in Visakhapatnam, Andhra Pradesh, India. For brevity, we hereafter refer to this bauxite in this paper as “Indian Bauxite” while recognizing that diverse bauxite ores (with differing physical and chemical compositions) could exist within India. This bauxite was dried overnight ($T=100^{\circ}\text{C}$) to remove moisture prior to milling 15 g for 15 minutes in an agate milling jar of a shaker ball mill (SPEX8000) to generate micron-sized powders, as confirmed by dynamic light scattering (Malvern Zetasizer Nano ZSP). The powdered Indian bauxite was then heated in a muffle furnace (Fisher Scientific, Isotemp) for 4h at the desired temperatures (100°C , 200°C , 300°C , and 400°C) for heat activation studies, based on previously documented methods^{27,29,38}. Scanning electron microscopy (SEM) images of some thermally activated bauxite samples are shown in the Supporting Information (Section 1, Fig. S1).

2.2. Materials Characterization. Percent mass loss and chemical composition of effluent gases from heating the bauxite samples were measured using Thermogravimetric Analysis and Mass Spectrometry (TA Instruments Q5000IR TGA, with attached Pfeiffer Vacuum Thermostar MS). Procedures to determine bulk crystalline mineral composition from X-ray diffraction (XRD) patterns and specific surface area (SSA) using multipoint Brunauer-Emmett-Teller (BET) measurements have been described in our previous publication³⁴ and are detailed in Section 2 of the SI. Our previous publication also reports additional material characterization details for the raw Indian bauxite ore used here, including point of zero charge, elemental composition, and adsorption isotherms and envelopes.

93 **2.3. Batch Adsorption Studies.** Standard batch adsorption experiments were designed to
94 determine the respective effects of reaction time, bauxite activation temperature, groundwater
95 acidification method, and bauxite dose (g/L) on fluoride removal in a synthetic Sri Lankan
96 groundwater matrix. Table 1 shows the groundwater recipe, which was selected to overlap with
97 our previous work³⁴ and was prepared using stock solutions of 100 mM CaCl₂, 100 mM MgCl₂,
98 200 mM NaHCO₃, 100 mM Na₂SO₄, 10 mM SiO₂ (Na₂SiO₃•5H₂O), and 10 mM NaNO₃. Initial
99 fluoride concentrations of all lab-synthesized groundwater were set to 10 ± 0.5 mg F⁻/L using a
100 stock solution of 100 mg/L NaF and sample fluoride concentrations were measured as outlined in
101 our previous work³⁴.

Table 1. Chemical composition of the synthetic Sri Lankan groundwater matrix used in this study, borrowed from the British Geologic Survey¹². Aside from alkalinity (which is reported in mM as HCO₃⁻), all component values are reported as gravimetric target concentrations in ppm (mg/L)

Component	Sri Lankan Groundwater (mg/L)
F	10.0
Ca	173.0
Mg	179.0
HCO ₃ ⁻	516.0
SO ₄ ²⁻	15.5
Si	45.0
NO ₃ ⁻ as N	9.0
Alkalinity (mM as HCO ₃ ⁻)	8.5

102 To determine the effect of reaction time on fluoride removal, kinetics experiments were
103 conducted for 2 h and samples were taken at 5,10, 20, 40, 60, 90, and 120 min. All subsequent

batch adsorption studies were conducted for a shorter reaction time (20 min) because subsequent fluoride removal was marginal and shorter reaction times reduce field operational costs, making the overall process more attractive for real-world application.

In each acidification experiment, 20 mL of Sri Lankan groundwater matrix was acidified using either 1.1M Hydrochloric acid (HCl) or pressurized CO₂. The desired solution pH for these experiments was selected based on previous studies^{25,34,29}, which experimentally verified pH 6.0 $\pm$ 0.1 as an optimal pH for fluoride adsorption with bauxite ore. To determine differences in fluoride removal based on groundwater acidification timing, we examined the following two cases where (1) the acidification source was gradually added in small quantities over the study duration to maintain solution pH at 6.0 $\pm$ 0.1, and (2) the total measured volumes of HCl and CO₂ required in case (1) were added initially at once in bulk, so that the desired pH was reached by the experiment end. In total, per liter of water, addition of approximately 211 - 401 mg HCl or bubbling of 22.5 - 34.7 g CO₂ maintained the solution pH 6.0. Theoretical calculations in Section 6 of the SI indicate that much lower quantities of CO₂ (about 35-53x less) actually need to be dissolved in the water to reach a solution pH of 6.0. Fluoride measurements taken at regular time intervals for 1 hour of settling after these 20-minute batch adsorption experiments demonstrated no fluoride desorption. Even in cases where groundwater was acidified with CO₂ and the solution pH rose slightly during the settling period due to CO₂ evolution, adsorbed fluoride did not return to the groundwater matrix. To determine the influence of drastic solution pH changes in case (2) on the potential leaching of harmful trace contaminants from the dispersive bauxite adsorbent, we used an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Agilent Technologies 7000 series) to measure drinking water contaminants regulated by the US Environmental Protection Agency's enforceable Maximum Contaminant Limits (EPA-MCL)

for primary contaminants (e.g., Ag, As, Cd, Cr, Pb, Se) and by non-mandatory Secondary Maximum Contaminant Limits (SMCL) for secondary contaminants (e.g., Al, Cu, Fe, Mn, Zn) in the product water³⁹.

Six combinatorial treatment scenarios using bauxite heated at 100°C and 300°C, with and without groundwater acidification using HCl or CO₂, were compared in terms of fluoride removal performance by calculating the optimal solid: liquid ratio (referred to henceforth as “minimum required dose”) to remediate 10 mg F⁻/L down to the WHO-MCL (1.5 mg F⁻/L) using a method described in our previous publication³⁴ (SI Section 3, Fig. S2).

2.4. Estimation of Combinatorial Treatment Costs. For each treatment scenario described above, we estimated annual per-capita costs of remediating fluoride-contaminated groundwater using conservative assumptions about material and electricity costs, supply chain logistics, and bauxite processing and water treatment plant design.

As schematically shown in the SI Figure S3, our model assumes that raw bauxite is first transported from a mine to a central processing plant (CPP) located 500 km away, the average estimated distance between bauxite-producing mines and Indian districts with endemic skeletal fluorosis⁴⁰ (Section 4). The CPP in our analysis was designed to have appropriate infrastructure to process (e.g., crush, mill, and heat-treat) enough raw bauxite for 500 villages of 1,000 people each. We assumed each village would have a separate community-scale water treatment plant (WTP) and that the villages were located approximately 25 km from the CPP. The average village population was chosen based on a previous publication⁴¹ and the population density for the circular area covered by the CPP was calculated (~300 people/km²) using Indian Census data⁴² for the three most heavily affected states with endemic fluorosis (i.e., Gujarat, Rajasthan, and Madhya Pradesh).

Fig. 1a shows a map of Indian districts with reported endemic fluorosis, excess groundwater fluoride contamination, and bauxite mine locations. The example in Fig. 1b demonstrates the feasibility of the assumptions used in our general cost model by showing that the bauxite used in this study (from Visakhapatnam) could realistically be transported to a CPP in Nalgonda District (a fluorosis affected region located approximately 500km away). Additional details on generation of Fig.1 and population density calculations are in the SI (Section 4).

Fig. 1. Map of **A)** districts in India with endemic fluorosis (red), excess groundwater fluoride (orange), and bauxite mines locations (black dots), and **B)** A realistic example of the relative locations of a bauxite mine in Visakhapatnam, a central processing plant (CPP, shown as a yellow star) in Nalgonda District, and water treatment plants (WTP, shown as yellow triangles) to demonstrate the feasibility of the assumptions used in our cost model. This figure was generated from data presented in Section 4 of the SI using R visualization packages.

The WTP shown in Fig. 2 was designed to operate at a minimum capacity of 5000 L water/day to meet the daily need for the village, assuming a per capita use of 5 L/person. We selected this value as a field-relevant compromise between the anecdotal reports of daily per

capita water purchase value in rural regions (2 L/person) from small commercial water providers in India (e.g., WaterLife, and WaterHealth (India)) and the WHO’s recommendation for daily per capita drinking and cooking water needs (7.5 L/person)⁴³. We assumed that a realistic field pilot WTP relying on bauxite-based defluoridation would require a mixing tank (for addition and mixing of treated bauxite and acid/CO₂ to fluoride-contaminated groundwater), a presedimentation basin (for initial clarification), alum addition prior to running water through a tube settler and micron filter (to reduce water turbidity to < 1 NTU), and a holding tank (for storing treated water) (Fig. 2).

Fig. 2. Schematic representation of treatment processes at a village-scale community water treatment plant. Bauxite is injected and mixed into pumped groundwater for 20 minutes after which it enters a presedimentation basin. The supernatant water is then dosed with 30 mg/L alum and run through a tube settler and final micron filter for additional particle removal to ensure WHO turbidity standards are met (< 1 NTU). Treated water is stored in a holding tank, which can be connected to automated dispensing machines or kiosks for sale of water. The acid flask and CO₂ cylinder icons were sourced from The Noun Project and respectively created by Gabor Fulop and Arosh Khan.

Machinery was assumed to have a lifetime of 10 years, a conservative estimate that also accounts for the possibility of premature obsolescence due to up-scaling and growth. For each piece of equipment, cost estimates were solicited for products currently available in (or for delivery to) India (Section 5, SI). Additionally, we made the conservative assumption that physical assets had no resale value at the end of their lifetimes. The costs of specific portions of the WTP, namely the pumps, tube settlers, and power supply, were obtained from actual

fabrication cost estimates of a 10,000 L/day field implementation of an electrochemical arsenic remediation technology in operation since April 2016 in West Bengal, India⁴⁴. This large pilot demonstration plant is a scaled up implementation of a 600L prototype, whose cost estimates are reported by our group in an earlier publication⁴⁵. Since that field trial involved daily processing twice the amount of water as ours (10,000L versus 5,000L), we are comfortable with these estimates being especially conservative.

For cost estimation, we chose current market prices of tanks (3), pumps (5), and consumables (e.g. bauxite, alum, acid, and CO₂), and reasonable values for shipping costs, which are outlined in a spreadsheet found in Section 5 of the SI. We estimated electricity costs based on machinery power rating; the number of hours of use based on laboratory tests; and an assumed electricity tariff of \$0.07/kWh. The WTP was assumed to be able to operate up to 16 hours per day. Additional cost estimation details related to the mining, transportation, central processing plant, and water treatment plant (e.g. equipment model numbers, commercial supplier companies, lifetime, duration, and usage assumptions, etc.) are provided in the SI (Section 5).

Since the primary purpose of the cost estimate is to compare processing options, the analysis ignores the time value of money and uncertainties around the exchange rate between dollars and Indian rupees. All estimates are given in recent (2017) USD assuming an exchange rate of 67 rupees to the dollar. Our estimates include core technology costs and exclude costs of land, operator salaries, building infrastructure, quality control, public education, marketing, and outreach to target populations. We have excluded these latter costs as they contain greater uncertainty and since they are common to all treatment options, they do not contribute to differentiating between the different treatment options.

3. RESULTS AND DISCUSSION

3.1. Characterization of thermally activated bauxite. Fig. 3a shows the percent mass loss from the Indian bauxite ore during heating, as determined by TGA-MS. The majority of the mass loss (~15% due to dehydroxylation) occurred at temperatures between 250°C and 300°C, and the compound given off was confirmed via mass spectrometry to be water. Fig. 3b shows the XRD patterns of Indian bauxite heated at four temperatures (100°C, 200°C, 300°C, and 400°C). The main crystalline Al phase was gibbsite, and additional crystalline Fe oxide phases (goethite and hematite) and Ti oxide phase (anatase) were detected. The diffraction patterns for crystalline gibbsite in bauxite samples heated at 100°C and 200°C were indistinguishable (100°C peaks have been truncated in Fig. 3b for convenient display) and these same major peaks were absent when the bauxite was heated at 300°C or 400°C. The iron and titanium oxide phases present in bauxite did not show the same structural deformations or changes in crystallinity at 300°C or 400°C. Fig. 3c presents surface area and particle size measurements of the heated Indian bauxite. The particle size remained constant across samples heated between 100°C and 400°C but the surface area increased dramatically (> 15X) from approximately 11 m²/g at 100°C to 170 m²/g at 300°C.

Taken together, the results in Fig. 3 show that the major impacts of heating Indian bauxite occur between 200°C and 300°C, indicated by the decrease in crystallinity and increase in surface area due to loss of structural waters of hydration. Other studies have observed a similar structural deformation of crystalline gibbsite minerals present in bauxite when heated between 200°C and 300°C, as it transforms to the more amorphous boehmite phase through partial dehydroxylation (e.g., loss of two waters of hydration)^{24,29,46,47}.

Fig. 3. Characterization of thermally-activated Indian bauxite in terms of **A)** Mass loss measured using Thermogravimetric Analysis and Mass Spectrometry (TGA-MS), **B)** Mineralogy as determined by X-ray diffraction patterns, and **C)** Particle size and specific surface area measurements. In panel **C**, we present averages from duplicate experiments and errors are the largest of the range from duplicate tests and measurement errors associated with the analytical equipment used (e.g., DLS, Tristar II 3020).

3.2. Effect of thermal activation of bauxite on fluoride removal.

Bauxite samples heated at temperatures greater than 200°C showed substantial improvement in fluoride removal performance in batch adsorption studies using finely powdered bauxite as single-use dispersive media (Fig. 4). Consistent with the similar XRD peaks and surface area measurements presented in Fig. 3b & 3c, fluoride removal performance of bauxite samples heated at $T \leq 200^\circ\text{C}$ or $T \geq 300^\circ\text{C}$ were comparable. Fig. 4 also demonstrates that fluoride adsorption using bauxite was rapid; within 20 minutes the system was close to equilibration (fluoride concentrations did not vary greatly between 20 min. and 2 hr.), a finding confirmed in our prior study³⁴. This initial rapid uptake is likely due to surface adsorption and the flattening of the curve after 20 minutes represents diffusion of fluoride into interior pores of micron-sized bauxite particles. Researchers studying other aluminum-based adsorbents used for fluoride removal have reported similar kinetic trends^{48–50}.

Fig. 4. Fluoride concentration as a function of contact time for thermally activated Indian Bauxite (raw dose 10 g/L) in alkaline synthetic Sri Lankan groundwater (initial pH 8.7). We present averages and error bars as the largest of the range from duplicate batch adsorption tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe).

3.3. Effect of groundwater acidification on defluoridation and leaching of metals. Fig. 5

shows the improvement in fluoride removal performance as a result of lowering the alkaline initial pH of Sri Lankan groundwater (pH ~ 8.7) down to 6.0 ± 0.1 through addition of HCl or bubbling of CO₂ gas. In all the experiments summarized in Fig 5, a dose of 10 g/L (= 0.169 g/20 mL) of raw bauxite (with or without heating) was added to synthetic Sri Lankan groundwater containing an initial fluoride concentration of 10 mg F⁻/L. Regardless of the source of acidification, the improvement in fluoride removal due to groundwater acidification appears to be consistent. Furthermore, regardless of whether the acid source was added continually over the experimental duration or whether it was added in bulk initially did not make a difference in the overall percent fluoride removal. At a dose of 10 g/L, bauxite heated to 300°C and added to acidified water is nearing the WHO-MCL for fluoride, but a much larger dose of 100°C bauxite is required to remediate an initial concentration of 10 mg F⁻/L. Our ICP-MS data indicate the product water for all the treatment scenarios in Fig. 5 is compliant with EPA guidelines for drinking water for a majority of the primary and secondary contaminants. In all scenarios, the aqueous concentrations of Ag, As, Cd, Cu, Fe, Ni, Pb, Se, and Zn were below 25% of the EPA-MCL.

Groundwater Acidification Method

Fig. 5. Effect of various groundwater acidification methods on fluoride removal (initial concentration 10 mg F⁻/L). Batch adsorption experiments were conducted for 20 minutes in synthetic Sri Lankan groundwater using Indian bauxite (raw dose 10 g/L) heated at 100 °C or 300 °C. Solution pH was maintained at 6.0 ± 0.5 through either continuous or bulk initial addition of acid (1.1 M HCl) or CO₂ (rate 0.25 L/min). We present averages and error bars as the larger of the range from duplicate batch adsorption tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe).

248 Table 2 highlights three elements of concern (e.g., Cr, Mn, and Al) that approached or
249 exceeded the EPA limit in the product water for some of the scenarios outlined in Fig. 5. Our
250 data indicate that Cr dissolution was more prominent in treatment scenarios using 300°C bauxite,
251 perhaps due to a temperature-dependent increase in oxidation rate of insoluble Cr (III) to its
252 more soluble Cr (VI) form. Although the Cr concentrations in our product water were below
253 75% of the current national EPA-MCL (100 ppb total Cr), the primary drinking water standard
254 for Cr (VI) is being revisited by the US-EPA and has recently been lowered in particular states
255 (e.g., CA, where the EPA-MCL for total Cr is 50 ppb).

In scenarios where 300°C bauxite was added to acidified groundwater, Mn concentrations tended to be higher. The Mn concentration exceeded the SMCL (50 ppb Mn) for one particular scenario where 300°C bauxite was used in groundwater acidified through bulk acid addition. It was also observed that for all treatment scenarios where 100°C bauxite was added to acidified groundwater, the concentration of Al in the product water exceeded the SMCL (200 ppb Al). One explanation for why Al dissolution is less prominent in 300°C bauxite is that bauxite dehydroxylates to boehmite in that temperature range and boehmite is generally less soluble than gibbsite, as reported by other theoretical studies^{51,52}.

Table 2. Concentrations (in ppb) of metals of concern in product water of batch experiments outlined in Fig. 5 measured using ICP-MS. We present averages and error bars as the range from duplicate batch adsorption tests.

EPA Standards (MCL in ppb)	100° C					300° C				
	No pH Adjustment	Continuous Addition		Bulk Addition		No pH Adjustment	Continuous Addition		Bulk Addition	
		Acid	CO ₂	Acid	CO ₂		Acid	CO ₂	Acid	CO ₂
Cr 100	0.7 ± 0.2	0.9 ± 0.2	0.8 ± 0.0	1.3 ± 0.2	1.0 ± 0.3	64.4 ± 3.4	53.8 ± 0.5	64.2 ± 1.5	48.7 ± 0.4	60.1 ± 1.4
Mn 50	1.6 ± 0.5	21.1 ± 1.5	25.3 ± 1.4	36.5 ± 8.7	23.3 ± 3.9	2.4 ± 0.8	45.9 ± 1.2	41.3 ± 1.7	56.6 ± 2.4	44.9 ± 3.3
Al 200	49.1 ± 4.2	252.8 ± 6.5	261.3 ± 38.6	619.4 ± 37.0	373.1 ± 18.6	65.4 ± 3.0	45.8 ± 2.1	100.6 ± 1.3	58.5 ± 11.2	102.9 ± 10.6

Ratio of Measured Concentration to MCL			
< 25%	25-74%	75-99%	≥ 100%

3.4. Comparing combinatorial treatment scenarios. Fig. 6 presents the minimum bauxite doses required to remediate 10 mg F/L down to the WHO-MCL in synthetic Sri Lankan groundwater. For the baseline (no acidification) scenario, the minimum required dose for 100°C bauxite (~287 g/L) is impractically large, approximately 13.5 times larger than for 300°C bauxite (~21 g/L). Groundwater acidification by acid or CO₂ reduces the required doses, but not in the same proportion: the resulting average minimum required dose for 100°C bauxite (~77 g/L) is approximately 6.4x larger than for 300°C bauxite (~12 g/L). As a result, based on doses alone,

271 the most practically feasible options for defluoridation with manageable material handling and
272 disposal requirements appear to be any of the scenarios using bauxite heat-activated ($T=300^{\circ}\text{C}$).

Fig. 6. Comparison of minimum required doses for various combinatorial treatment scenarios. Batch experiments run for 20 minutes in Sri Lanka groundwater. In certain scenarios, groundwater pH was maintained at 6.0 ± 0.5 through addition of acid (1.1 M HCl) or CO₂ (rate 0.25 L/min). We present averages and error bars as the larger of the range from duplicate batch adsorption tests and measurement errors associated with the analytical equipment used (e.g., fluoride probe).

273 In addition, Table 3 presents the total cost for treating water for each of the possible
274 processing methods. This analysis takes into account the capital and operational costs of the
275 entire bauxite processing and water treatment process. Numbers are reported in USD per person
276 per year and where multiple cost estimates were obtained, the median value is reported
277 plus/minus the low-end range. The results indicate that the total cost of the unheated bauxite is
278 up to an order of magnitude higher than for the heated bauxite. This implies that the additional
279 cost of purchasing and operating an oven is offset by the substantially higher material and

transportation costs associated with using the much larger required doses of raw unheated bauxite. The general trends were as expected; the raw material and transportation costs were significantly higher for the processes requiring additional bauxite. On the other hand, the cost of the CPP step was lower for the unheated bauxite since no oven would be required. The costs at the WTP were highly dependent on the costs of hydrochloric acid and CO₂ for the cases where they are used.

Table 3. Treatment costs (in \$ per person per year) of combinatorial treatment scenarios including heating Indian bauxite and acidifying groundwater using acid or CO₂. Costs for the baseline treatment scenario (no heating or groundwater acidification) are not reported because the minimum required dose (Fig. 6) is unrealistically high for field operation. The values and errors presented in this table reflect the median cost estimate $\pm$ the low-end range based on three cost estimates obtained from quotes given by the manufacturing companies of the machinery and items (exceptions were instances where machinery was custom designed and estimated for this process). This reporting method avoids presenting potentially unrealistic extreme low and high cost estimates. Additional details can be found in Section 5 of the SI.

Groundwater Acidification Method	Heating Temperature (°C)	Mining & Transport Costs	CPP Costs	WTP Costs	Total Costs
None	100	-	-	-	-
	300	7.22	0.059 $\pm$ 1.6E-04	1.60 $\pm$ 1.02E-02	8.88 $\pm$ 1.04E-02
Acid	100	25.8	0.018 $\pm$ 3.6E-04	4.72 $\pm$ 5.04E-01	30.6 $\pm$ 5.04E-01
	300	3.56	0.059 $\pm$ 1.6E-04	3.24 $\pm$ 2.69E-01	6.86 $\pm$ 2.70E-01
CO ₂	100	26.7	0.022 $\pm$ 3.6E-04	31.4 $\pm$ 17.7E+00	58.1 $\pm$ 17.7E+00
	300	4.61	0.059 $\pm$ 1.6E-04	21.9 $\pm$ 10.5E+00	26.5 $\pm$ 10.5E+00

We found that using 300°C heat-treated bauxite in groundwater acidified with hydrochloric acid (“300-acid”) was the cheapest option at \$6.86 per person per year. This option benefits from significantly reduced raw material and transportation costs relative to the other options, though it makes the WTP process more expensive due to the cost of the acid. The second cheapest option was using heated bauxite without the additional groundwater acidification step (“300-only”); the total cost of this process was \$8.88 per person per year. The other three options (300-CO₂, 100-acid, and 100-CO₂) were significantly more expensive than

the cheapest option. However, the empirically calculated mass of CO₂ used in this cost estimate is likely much higher than the actual amount of CO₂ that would be needed, in practice, to adjust the groundwater pH to 6.0. Additional discussions on the differences in empirical and theoretical estimations of CO₂ requirements are in Section 6 of the SI (Fig. S4).

Within the range considered here, our estimates suggest that the most field-relevant and favorable processing option is likely to be to use 300°C heat-treated bauxite without groundwater acidification because this treatment scenario balances the benefits of lower bauxite doses (Fig. 6) with increased logistical simplicity. Moreover, pH reduction using mineral acids and the Cr/Mn/Al data reported in Table 2 requires additional safety constraints, the costs of which are not included in this cost analysis but would certainly increase labor and operational costs. Therefore, heating without any acidification appears for now to be the most optimal and practical treatment scenario to follow in field operation. It is worth noting that low-end ranges reported in Table 3 are lower than median total cost estimates, and the overall conclusion of the analysis remains unchanged. We therefore believe that uncertainty in the costs that were included is not a major source of error.

In future work, it will be desirable to measure the total dissolved solids (TDS) in product water for certain groundwater acidification scenarios where addition of HCl could increase the TDS and adversely affect treated water taste. Additional research is needed to compare the fluoride removal efficiency and energy requirements of the current batch reactor configuration to regenerative filter columns using coarsely milled bauxite particles. To assess feasibility for large-scale field application of the proposed defluoridation process, it would also be valuable to study solids removal and handling and disposal of spent bauxite sludge. Potential applications include incorporation of bauxite waste into construction materials (e.g., cement, bricks) or resource

recovery of Al for use in the metal manufacturing industry. Otherwise, proper disposal costs of used bauxite should also be taken into account in future cost models.

ASSOCIATED CONTENT

Supporting Information. Details of methodology including electrolyte and sample preparation and characterization, calculations for minimum required dose, and information on map generation and cost estimation process are all provided in the SI, in addition to supporting tables and figures referenced in the text. The SI is available free of charge on the ACS Publications website.

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Notes. The authors declare no competing financial interest.

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