

Retention of Anionic Pollutants by Overburden Material at Chromite Mines: An Experimental Investigation

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Abstract: The goethite-rich overburden material at chromite mines is an efficient sink for the chromate anion. Leaching experiments using a saline solution showed that the material at the Sukinda mine of Orissa had retained a higher amount of chromate compared with the material at the nearby Boula mine. This difference can be attributed to the mineralogy at the two sites. For example, the proportion of poorly crystalline goethite is higher in the Sukinda material compared with Boula. Experiments on further adsorption of arsenate and phosphate indicated that the Boula sample had higher uptake capacity for both anions. This is obviously because the Sukinda sample had initially adsorbed more chromate. These results can be useful in evaluating natural attenuation of fertilizer-derived pollutants in the agricultural land near chromite mines.

Key words: Chromite mines, laterite overburden, mineralogy, pollutant retention.

Introduction

In the natural system, the mobility of oxy-anions of trace elements is primarily controlled by adsorption-desorption reactions at the mineral-water interface (McBride, 1994). To cite a recent example, the on-going debate on arsenic contamination of ground water in the Ganges delta region is based on models which invoke interaction of dissolved arsenic species with iron oxide minerals in the aquifer (Acharyya et al., 2000; McArthur et al., 2001).

The ultra-mafic bed rocks at chromite mines commonly undergo extensive weathering under a tropical climate. The FeO component of primary minerals (e.g. chromite, olivine, serpentine) is oxidized by atmospheric oxygen and percolating ground water to a group of Hydrated Ferric Oxide (HFO) compounds in crystalline and amorphous state. They are represented by the general

formula $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ and are main constituents of the red coloured lateritic overburden in the chromite quarries.

Because of their fine-grained colloidal size, the HFO particles possess a pH-dependent surface charge. For example, at low pH values, a reaction of the type $\equiv\text{Fe}-\text{OH} + \text{H}^+ = [\text{Fe}(\text{OH})_2]^+$ gives a positive surface charge. On the other hand, at high pH values, the surface is negatively charged through a reaction such as $\equiv\text{Fe}-\text{OH} + \text{OH}^- = [\text{FeO}]^- + \text{H}_2\text{O}$. At a pH value in between these two extremes, known as the Zero Point of Charge (ZPC), the net surface charge is zero. The pH at ZPC of $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ compounds is in the range 6 to 9 (Drever, 1997). For individual minerals, different authors have cited a variety of values as shown in Table 1.

Therefore, at average groundwater pH around 7.0, most of the HFO minerals have positively charged surfaces and are capable of adsorbing oxyanions. It also follows that the anion uptake capacity will be high with a large proportion of goethite and amorphous $\text{Fe}(\text{OH})_3$ which have relatively high values of pH at ZPC. On the

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Table 1: pH values at Zero Point of charge for HFO minerals

<i>Minerals</i>	<i>pH at ZPC</i>	<i>Source</i>
Magnetite, Fe_3O_4	6.5	Drever (1997)
Hematite, Fe_2O_3	5 to 9 (commonly 6 to 7)	Drever (1997)
	7.1	Prasad (1994)
Goethite, FeO.OH or $\text{Fe}_2\text{O}_3.\text{H}_2\text{O}$	6 to 7	Drever (1997)
	7.3 to 7.8	Krauskopf and Bird (1995)
	9.5	Weerasooriya and Tobschall (2000)
Maghemite, $\gamma\text{-Fe}_2\text{O}_3$	6.7	Stumm and Morgan (1970)
Amorphous Fe(OH)_3	8.5	Stumm and Morgan (1970)

other hand, the capacity would be reduced in the presence of maghemite (which is believed to be the dehydration product of lepidocrocite $\gamma = \text{FeO.OH}$) or magnetite.

These predictions were confirmed during an earlier work by Raymahashay and Praharaj (1998) at the Sukinda chromite mine of Orissa. It was observed that up to 180 $\mu\text{g/L}$ of Cr(VI) was retained by the goethite-rich overburden material at this mine. In contrast, the amount retained was less for material which had higher amounts of maghemite. Likewise there is increase in the adsorption of phosphate and arsenate with more goethite content (Fontes and Weed, 1996; García-Sánchez et al., 1999).

In this work, overburden material from Sukinda as well as the nearby Boula mine (which has already retained chromate) was used in controlled laboratory experiments to study further uptake of phosphate and arsenate anions. The results are expected to be relevant to a situation where the chromate-saturated lateritic soil near a chromite mine is exposed to phosphate and arsenate pollution due to application of fertilizers as described by Campos (2002).

Materials and Methods

Description of Samples

The Sukinda laterite sample used in the experiments was from the collection of Raymahashay and Praharaj (1998). Similar samples were collected during this work from the Boula chromite mine situated 70 km away from Sukinda.

The samples were studied in hand specimen, under the binocular microscope and petrological microscope for broad mineralogy. The detailed mineralogy of samples was studied by X-ray diffraction both in bulk powders and oriented slides. The samples were scanned at 1.2° $2\theta/\text{min}$ under X-ray diffractometer Model ISO Debyelex 1001 and 2002, Rich-Seifert & Company. The XRD patterns of the samples and their description are given in Figure 1 and Table 2 respectively.

Chromate Desorption Experiment

In order to estimate the quantity of Cr(VI) held on the Sukinda samples, Raymahashay and Praharaj (1998) used a NaCl- NaHCO_3 leaching method. In this method, a saline solution of pH 8 and ionic strength 0.3 was prepared by dissolving 1.74 g of NaCl and 0.05 g of NaHCO_3 in 100 mL distilled water. They observed that 180 $\mu\text{g/L}$ Cr(VI) was released from an 1% suspension of the 63 μm to 74 μm size fraction kept in contact with the

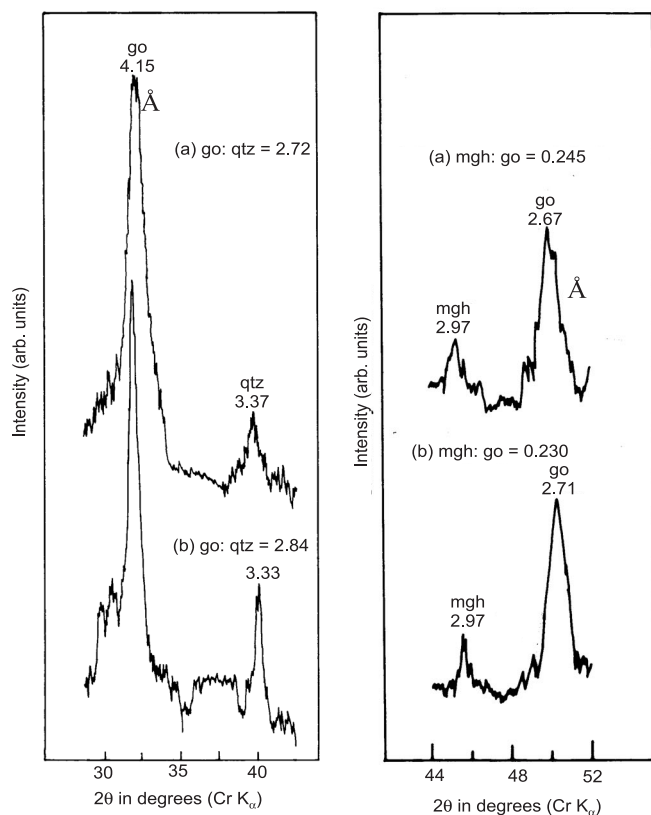


Figure 1: XRD patterns of (a) Sukinda and (b) Boula laterite samples. Peak area ratios indicate relative proportion of goethite (go), quartz (qtz) and maghemite (mgh).

Table 2: Description of soil samples

Properties	Boula Laterite	Sukinda Laterite
Colour	Reddish Brown	Reddish Brown
Depth below surface	5 m	42 m
Bed Rocks	Pyroxenite, Gabbroic- Anorthosite	Fresh Serpentinite
Mineralogy (X-ray)	Go>kao>qtz>mgh±ser	go>ser>mgh>chr
Crystallinity of go	Crystalline	less Crystalline
go : qtz	2.84	2.72
mgh : go	0.230	0.245

go = Goethite, kao = Kaolinite, qtz = Quartz, mgh = Maghemite, ser = Serpentine, chr = Chromite

saline solution for 24 hours. An identical procedure was adopted for the Boula samples used in the present experiment and the amount of Cr(VI) released was found to be 55 µg/L. The reason for this difference has been discussed later.

Arsenate and Phosphate Adsorption Experiment

Stock solutions of 100 mg/L arsenate and phosphate were prepared by dissolving 0.416 g of sodium arsenate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ and 0.143 g of potassium dihydrogen ortho-phosphate, KH_2PO_4 respectively in 1 L of distilled water. Initial pH was controlled by drop-wise addition of 0.1N HCl or 0.1N NaOH as required. Laterite samples, sieved between ASTM 230 and 200 mesh (63 and 74 µm) were used for the experiments. Arsenate and phosphate uptake was studied in 1% suspension of requisite concentration with occasional stirring for 24 hours. The solution was analyzed after centrifuging and filtering through Whatman 42 paper (2.5 µm). In order to confirm that the relatively coarse-grained material used in the experiments was effectively removed by this size of filter paper, comparison was made with filtration by Millipore (0.22 µm). As an example, in the run with Boula sample in 4 mg/L As(V) solution, removal was 79% for both filters. The arsenate remaining in solution was measured by SDDC (Silver Diethyl Dithio Carbamate) method having detection limit 1 µg/L (Standard Methods, 1985). Similarly, final phosphate was measured by colorimetric Stannous Chloride method (Standard Methods, 1985).

Results and Discussion

Removal of Arsenate

Batch experiments were carried out at various initial concentrations and at pH ranging between 3 and 11 for the removal of arsenate. Within this range arsenate occurs as the oxy-anions H_2AsO_4^- and HAsO_4^{2-} . Their distribution as a function of Eh and pH has been shown in Figure 2.

The data in Figure 3 shows that the removal decreases with increasing initial arsenate (As_i) concentration. Figure 3 also shows that Boula laterite removes more arsenate than Sukinda laterite. These results have been discussed later.

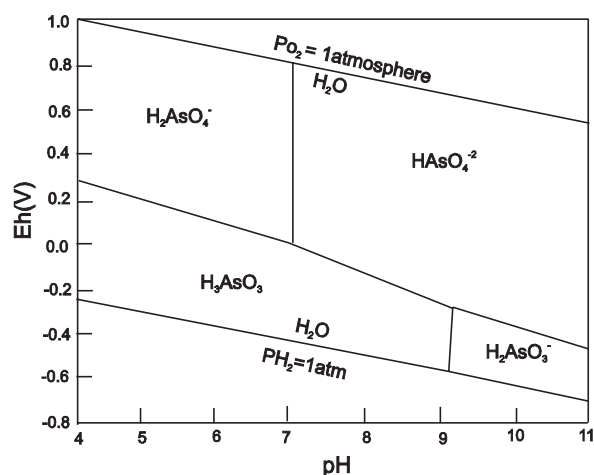


Figure 2: Distribution of Arsenic species with Eh and pH. Boundaries for equal activities of dissolved species.

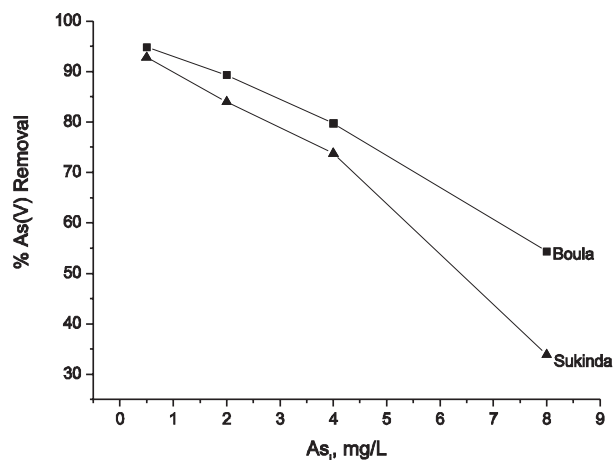


Figure 3: Comparison of As(V) removal by Boula and Sukinda Laterite.

Removal of Phosphate

Like arsenate, Figure 4 shows there is decrease of removal with increase in initial phosphate (P_i) concentration. Batch experiments were conducted at pH ranges between 2.5 and 10.5. Within this range phosphate occurs as $H_2PO_4^-$ and HPO_4^{2-} anions. Their distribution with pH is shown in Figure 5. Once again, Boula laterite removes more phosphate than Sukinda laterite (Figure 4).

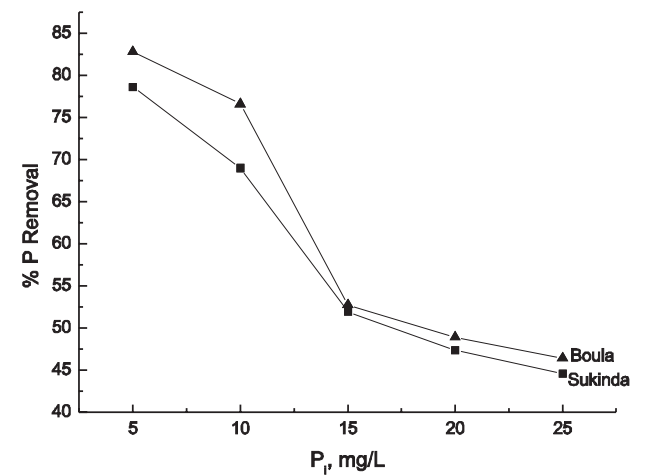


Figure 4: Comparison of Phosphate (P_i) removal by Boula and Sukinda Laterite.

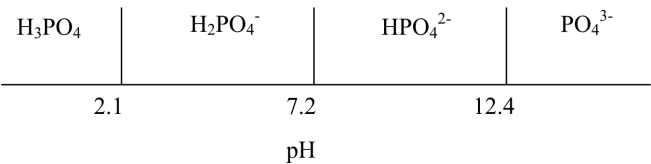


Figure 5: Distribution of Phosphate species with pH. Boundaries for equal concentration of dissolved species.

Discussion

The difference in arsenate and phosphate removal between Boula and Sukinda samples is apparently controlled by mineralogy. As listed in Table 2, the peak area ratio of goethite (4.16 Å) to quartz (3.35 Å) is 2.84 for Boula and 2.72 for Sukinda which indicates the presence of more goethite in Boula sample than that of Sukinda. The shape of the goethite peak is also sharper in the Boula laterite (Figure 1). Adopting the criteria commonly used for clay minerals, the peak width at half height is 0.4 units for Boula and 0.7 units for Sukinda. Similarly, peak height to half width (H/W) ratio is 26.25 for Boula and 15.28 for Sukinda. Therefore, it can be concluded that the Boula laterite has a higher proportion of more crystalline goethite. As the poorly crystalline

HFO substrate in the Sukinda sample would have a higher value of pH at ZPC and more surface area, it would have adsorbed more chromate in the beginning. Therefore, later arsenate and phosphate adsorption by this sample was less compared with the Boula samples. Beside this the presence of more goethite and kaolinite contributed towards more oxyanion uptake (Curi and Franzmeier, 1984; Lin and Puls, 2000; Edzwald et al., 1976). The influence of maghemite was different. Its pH at ZPC is lowest among the HFO minerals (Table 1). Therefore, a slightly higher proportion in the Sukinda sample (Figure 1) reduced the capacity to adsorb arsenate and phosphate anions.

Conclusions

The results of this experimental work on anion uptake by chromite mine overburden material can be interpreted in two stages. The first stage of uptake of chromate takes place at the mine itself. The material at Sukinda mine retained more Cr(VI) compared with the material at Boula mine. This is mainly because the goethite in Sukinda sample was less crystalline compared with the Boula sample. The second stage of uptake of arsenate or phosphate anion by the material which had already retained chromate was investigated in the laboratory. Here, the Sukinda sample which had adsorbed more chromate initially took up lesser amounts of either arsenate or phosphate. The presence of a slightly higher proportion of maghemite and less goethite in the Sukinda sample could have also contributed to less adsorption of these anions although the initial adsorption of chromate was not affected.

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