



## Organo-Complexing Leaching of Iron from Indegeneous Bauxite

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Extraction of iron from bauxite ore was employed by phase extraction. Steps involved the formation and dispersion of the iron complex in aqueous phase and then extracting the iron complex by addition of organic solvent. Iron was complexed with oxalic acid and citric acid and the complex was extracted by adding ethyl acetate, chloroform and benzene as organic solvents. Chloroform gives 33 % of iron and 8.5 % extraction of aluminium with oxalic acid and 37 % extraction of iron and 10.2 % extraction of aluminium with citric acid (complexing agent). Benzene provides 30 % extraction of iron and 10 % extraction of aluminium with oxalic acid and 35 % extraction of iron along with 10.3 % that of aluminium with citric acid. Ethyl acetate gives different results of extraction by the phase separation method. Using oxalic acid, only 3.4 % extraction of iron and 9.29 % extraction of aluminium results, while 4.34 % iron extraction with citric acid were observed under the same conditions. The extraction of aluminium was zero, which is the requirement of the process. Comparison of extraction shows that chloroform and benzene give almost similar extraction results for aluminium and iron with citric acid and oxalic acid. Ethyl acetate give comparatively lesser extraction with both acid complexes but it gives direction towards removal of iron without removing useful aluminium from the ore sample.

**Key Words:** Complex formation, Phase extraction, Chloroform, Benzene and ethyl acetate.

### INTRODUCTION

Bauxite varies greatly in physical appearance, depending on its composition and impurities. It ranges in colour from yellowish white to gray or from pink to dark red or even brown if high in iron oxides. Not all bauxites are economical for aluminium production, but the ores with an aluminium oxide content of 30 % or more are considered practical. Only those ores are considered economical which contain significant concentrations of alumina *e.g.*, gibbsite and boehmite which contain 65 and 85 % alumina.

After getting the alumina from the ground ore, it is then ready to be processed. The first step of processing is the process of refining it; refining bauxite to obtain alumina and smelting alumina to produce aluminium. Bauxite contains a number of impurities, including iron oxide, silica and titania. If these impurities are not removed during refining, they will form alloy with and contaminate the metal during the smelting process. The ore, therefore, must be treated to eliminate these impurities. Purified alumina usually contains 0.5-1.0 % water, 0.3-0.5 % soda and less than 0.1 % other oxides. There are a number of alkaline, acid and thermal methods of refining bauxite, clay or other ores to obtain alumina. Bauxite ore having

higher Al<sub>2</sub>O<sub>3</sub> contents can be imported instead of aluminium hydroxide if some viable procedure for the removal of iron from bauxite/ bauxitic alum is adopted.

Houben<sup>1</sup> worked on the removal of iron encrustations to improve the performance of wells and drains. Meng *et al.*<sup>2</sup> worked to investigate the redox transformations of arsenic and iron in water treatment sludge during aging and to evaluate the impact of those transformations on the leachability of arsenic determined with the US EPA toxicity characteristic leaching procedure (TCLP). Nakajima and Sakaguchi<sup>3</sup> worked on aspects of iron adsorption by immobilized persimmon tannin using both formaldehyde and potassium peroxodisulfate. Maranon *et al.*<sup>4</sup> worked on two anionic ion-exchange resins, Lewatit MP-500 and Lewatit M-504, to remove iron and zinc from acid pickling baths employed in the galvanizing process. Sogaard and Medenwaldt<sup>5</sup> worked on a comparison of iron precipitation in the sand filters of a new freshwater plant with the abiotic precipitation of iron in the sand filters of a traditional fresh water plant.

Nishihama *et al.*<sup>6</sup> worked on the mechanisms of the photoreductive stripping of iron(III) in the liquid-liquid extraction process by employing (2-ethylhexyl) phosphonic acid mono (2-ethylhexyl) ester (EHPNA) and *bis*(2-ethylhexyl)-

phosphoric acid (D<sub>2</sub>EHPA) as extractants, *n*-dodecane and kerosene as diluents and a xenon lamp as the light source. Roden and Urrutia<sup>7</sup> worked on semi-continuous cultures to assess the effect of aqueous Fe(II) removal on the dissimilatory reduction of crystalline Fe(III) oxides by *Shewanella* alga strain BrY. Ali *et al.*<sup>8</sup> worked on iron removal from commercial brine fluids using the basic iron removal procedures that are available and practical for rig-site applications. Ercag and Apak<sup>9</sup> presented a combined process involving smelting and hydro-metallurgy for the total recovery of valuable substances from bauxite wastes of alumina manufacture. Davis<sup>10</sup> worked on the control of iron and manganese found in natural water by removal and by chemical sequestering. Iron and manganese can cause fouling problems. Hurst and Knocke<sup>11</sup> investigated the effects of alkaline conditions and the presence or absence of dissolved oxygen on the ability of Fe(II) to reduce ClO<sup>2-</sup> ion to Cl<sup>-</sup> ion.

Veglio *et al.*<sup>12</sup> worked on iron removal from yellowish kaolin supplied by ECC International (Europe) Ltd., using mainly oxalic acid and ascorbic acid in sulfuric acid solutions. Rasmussen and Halkjaer<sup>13</sup> studied to find methods for quantifying Fe(II), Fe(III) and total iron content in activated sludge. The study was also designed to evaluate the significance of Fe(III) as an electron acceptor during anaerobic conditions.

## EXPERIMENTAL

**Iron determination:** To 1 mL of digested ore sample, added 9 mL of distilled water. Added 2 drops of 1 % aqueous solution of KMnO<sub>4</sub>, 1 mL 25 % KCNS solution and 0.6 mL 4 N HNO<sub>3</sub>. The absorbance for developed colour was noted under UV/VIS double beam spectrophotometer at 480 nm. Iron was determined by using following regression equation obtained from the standard curve:

$$A = 0.1254c - 0.0383$$

where; A = absorbance, c = concentration in ppm and the value of R<sup>2</sup> is:

$$R^2 = 0.9979$$

**Aluminium determination:** To 1 mL of digested ore sample, add 9 mL of distilled water. Then added 0.4 mL of 0.1 % eriochrome cyanine R dye and allowed to stand for 5 min after mixing. The absorbance of developed colour complex was noted under UV/VIS spectrophotometer at 580 nm. Aluminium was determined by using the regression equation obtained from aluminium standard curve:

$$A = 1.0984c + 0.0286$$

and the value of R<sup>2</sup> is:

$$R^2 = 0.9717$$

**Solvent extraction:** Different organic solvents like ethyl acetate, benzene and chloroform were used for this purpose. To the 50 mL of digested ore sample, added equivalent weight of oxalic acid and citric acid (1 g) separately. Refluxed the flasks for 0.5 h at 60-80 °C and after cooling, added 50 mL of organic solvent. Mixed well the flask contents by shaking and allowed to stand over night. The layers were separated by separating funnel and developed the colours for aluminium and iron by their respective colour development techniques. The absorbance was noted under UV/VIS spectrophotometer at 520 and 480 nm for aluminium and iron, respectively.

## RESULTS AND DISCUSSION

### Solvent extraction with chloroform

**Using oxalic acid:** To the 50 mL of digested ore sample, added equivalent weight of oxalic acid (1.0 g). Refluxed the flask for 25-30 min at 60-80 °C. Cooled the flask and added 50 mL of chloroform. Mixed well the flask contents by shaking and left it over night. Separated the two layers using separating funnel. Developed the colours for Al<sup>3+</sup> and Fe<sup>3+</sup> separately by previous technique using aqueous layer. Noted the absorbance under UV/VIS spectrophotometer.

**Using citric acid:** To the 50 mL of digested ore sample, added equivalent weight of citric acid (1.0 g). Refluxed the flask for 25-30 min at 60-80 °C. Cooled the flask and added 50 mL of chloroform. Mixed well the flask contents by shaking and left it over night. Separated the two layers using separating funnel. Developed the colours for Al<sup>3+</sup> and Fe<sup>3+</sup> separately by previous technique using aqueous layer. Noted the absorbance under UV/VIS spectrophotometer.

### Solvent extraction with benzene

**Using oxalic acid:** A flask, containing 50 mL of digested ore sample and 1.0 g oxalic acid, was prepared using the same method as was used while using chloroform. After cooling the flask contents, added 50 mL of benzene and applied the same procedure mentioned above. Developed the colours for Al<sup>3+</sup> and Fe<sup>3+</sup> and noted the absorbance.

**Using citric acid:** The same procedure was adopted while using citric acid in benzene. The difference was, 1.0 g citric acid was used in place of oxalic acid and colours for Al<sup>3+</sup> and Fe<sup>3+</sup> complexes were developed and their respective absorbance was noted under UV/VIS spectrophotometer.

**Solvent extraction with ethyl acetate:** Similar procedure was adopted for oxalic acid and citric acid as was done earlier but the organic solvent used was ethyl acetate. The comparison of the three solvents was made in the form of column chart.

**Using citric acid:** When the ore is complexed with citric acid and determined for iron and aluminium extractions. The extraction of aluminium is 10 % with chloroform, 10.70 % with benzene and no aluminium is extracted with ethyl acetate. Results of aluminium extraction have been plotted in the Fig. 1.

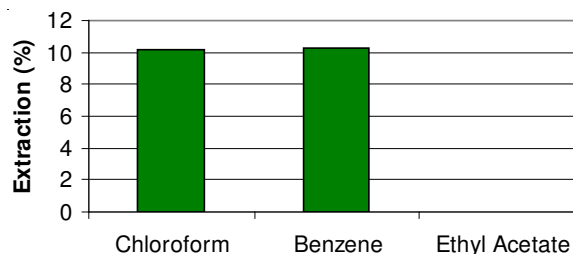


Fig. 1. Comparison of extraction of aluminium with citric acid

At the same time, citric acid provides satisfactory results for extraction of iron. With chloroform 37 % iron is extracted, 35 % of iron is extracted with benzene and 4-5 % of iron is extracted when ethyl acetate is used as solvent. Although iron leached with ethyl acetate is lesser than other solvents, yet the aluminium extraction is almost zero. This is unique example among most of the organic and inorganic acids employed,

where aluminium extraction is zero. Following Fig. 2 gives comparison of iron extraction with various solvents when citric acid was used as complexing agent.

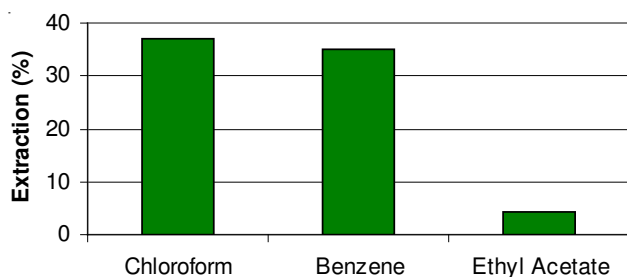


Fig. 2. Iron extraction with various solvents using citric acid as complexing agent

**Using oxalic acid:** Finely ground ore was complexed with oxalic acid. After leaching time at required temperature, the complex was extracted from the solution with various organic solvents. Extraction of iron with oxalic acid has been compared in the Fig. 3. From graph, it is obvious that 33 % iron is extracted with chloroform, 31 % with benzene and 3 % with ethyl acetate. Oxalic acid gives satisfactory extraction of iron with chloroform and benzene but only 3 % with ethyl acetate.

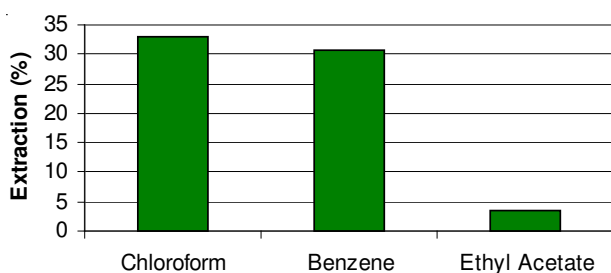


Fig. 3. Iron extraction with various solvents when oxalic acid was used as complexing agent

Aluminium extraction with various solvents was also compared in order to get optimized process for iron extraction without leaching of aluminium (Fig. 4). Oxalic acid offers 9 % aluminium extraction with chloroform, 10 % extraction with benzene and 9.5 % with ethyl acetate. Hence oxalic acid gives relatively higher extraction of aluminium with benzene and ethyl acetate, only chloroform gives lesser extraction of aluminium, 9 %, which is still high enough from the process development point of view.

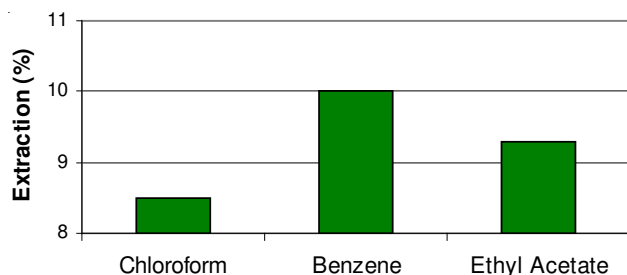


Fig. 4. Extraction of aluminium with various solvents using oxalic acid as complexing agent

## Conclusion

Extraction of iron from bauxite ore to make it economically useful is possible by organic and inorganic means. Leaching of iron with organic solvents after complex formation with citric acid and oxalic acid was employed in this work. Comparison of different organic acids such as citric acid and oxalic acid showed good results of extraction. Oxalic acid gives 34 % extraction of iron and 6-7 % that of aluminium, using bauxite ore. The results are almost same for citric acid *i.e.*, 34-35 % for iron and 5-6 % for aluminium. Extraction with citric acid and oxalic acid was enhanced by organic solvents like chloroform, benzene and ethyl acetate. Chloroform gives 33 % of iron extraction and 8.5 % extraction of aluminium with oxalic acid and 37 % extraction of iron along with 10.2 % extraction of aluminium with citric acid. Benzene provides 30 % extraction of iron and 10.02 % extraction of aluminium with oxalic acid and 35 % extraction of iron and 10.31 % of aluminium with citric acid. Ethyl acetate gives very poor extraction iron by this method. Only 3.4 % extraction of iron and 9.2 % extraction of aluminium with oxalic acid and 4.34 % extraction of iron with citric acid were observed. Ethyl acetate gave almost zero extraction of aluminium with citric acid.

Comparison of extraction shows that chloroform and benzene give almost similar extraction results for aluminium and iron with citric and oxalic acids. Ethyl acetate gave lower extractions for iron *i.e.*, 4-5 % only. But, the results are striking due to zero aluminium extraction under the same environment that can be improved by modifying the process.

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## REFERENCES

1. G.-J. Houben, *Ground Water*, **42**, 78 (2004).
2. X. Meng and G.-P. Korfiatis and C. Jing, *Environ. Sci. Technol.*, **35**, 3476 (2001).
3. A. Nakajima and T. Sakaguchi, *J. Chem. Technol. Biotechnol.*, **75**, 977 (2000).
4. E. Maranon, Y. Fernandez and F.-J. Suarez, *Ind. Eng. Chem. Res.*, **39**, 3370 (2000).
5. E.-G. Sogaard, R. Medenwaldt, P. Abraham and V. Joanna, *Water Res.*, **34**, 2675 (2000).
6. S. Nishihama, T. Hirai and I. Komasa, *Ind. Eng. Chem. Res.*, **38**, 4850 (1999).
7. E.-E. Roden and M.-M. Urrutia, *Environ. Sci. Technol.*, **33**, 1847 (1999).
8. S.-A. Ali, D.-C. Shelby and W.-E. Foxenberg, *Petrol. Eng. Int.*, **72**, 35 (1999).
9. E. Ercag and R. Apak, *J. Chem. Technol. Biotechnol.*, **70**, 241 (1997).
10. J. Davis, *Plant Eng.*, **51**, 80 (1997).
11. G.-H. Hurst and W.-R. Knocke, *Am. Water Works Assoc. J.*, **89**, 98 (1997).
12. F. Veglio, B. Passariello and L. Toro, *Ind. Eng. Chem. Res.*, **35**, 1680 (1996).
13. H. Rasmussen and P.-H. Nielsen, *Water Res.*, **30**, 551 (1996).