

Technical Note

Effect of Cu(II) doping on physical properties of synthetic goethite
and their reactivity in $\text{SO}_2\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ medium

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ABSTRACT

Pure and copper-doped goethite samples were prepared by precipitation/co-precipitation method. The XRD patterns of both un-doped and Cu(II)-doped samples showed goethite as the only crystalline phase with slight shift in d-values for doped samples. Based on the weight loss measurements in the temperature region of 120-400°C, % age goethite in those samples was estimated and it was found that % age goethite was nearly 100% for the samples containing nil or up to 0.4% Cu and decreased to 90 and 65 % with the increase in % age of copper to 1.15 and 2.7% respectively. Surface area of samples increased from 47.9m²/g to 105m²/g by increasing the % age of doped copper from nil to 2.7%. The dissolution of these samples in $\text{H}_2\text{SO}_4\text{-SO}_2\text{-H}_2\text{O}$ media showed interesting trends. The dissolution of iron was found to be complex due to difference in (a) goethite content of doped samples (b) nature of goethite due to Cu(II) ion incorporation and (c) surface area of various samples. At lower concentrations of Cu(II), ratio of % dissolution of Fe to Cu was nearly one indicating uniform distribution of Cu in iron matrix. In case of samples containing 2.7% Cu, ratio of % dissolution of Fe to Cu increased to ~2 indicating preference of Cu incorporation in iron oxide other than goethite. © 2005 SDU. All rights reserved.

Keywords: Copper; Iron; Goethite; Reduction; Precipitation

1. INTRODUCTION

Goethite is one of the most common iron oxides associated with many metal values found in metal rich oxidic ores such as manganese nodules and nickel laterites (Fuerstenau and Han, 1977; Fuerstenau and Han, 1983; Das *et al.*, 1997). The general properties of goethite matrix are significantly affected due to the presence of other metal ions in its matrix. In nature the formation of goethite from iron hydroxide gels depends on various cations (Cornell *et al.*, 1989). Both the morphology and chemical properties of those substituted goethites are somewhat different for different cations present in the structure. Fe^{2+} is well known for promotion of ferrihydrite aging to goethite (Baes and Mesmer, 1976). The various metal ions may be either incorporated in place of central Fe^{3+} ion in the octahedra or associated by occlusion in defects of the crystal symmetry (Giovanoli and Cornell, 1987). Depending on the crystallinity of goethite, the extraction of Ni and Co varied from nickel laterites with sulphuric acid at moderate to elevated temperatures (Das *et al.*, 1995; Das *et al.*, 1997). The leaching conditions required for Ni recovery from nickel laterite containing goethite in amorphous form required comparatively milder conditions as compared to the ones containing crystalline goethite. In an earlier work typical samples of Cu(II), Ni(II) and Co(II) doped goethite were prepared to study their conversion to magnetite under ammoniacal conditions (Mohapatra *et al.*, 2002). The present work has been taken up with a view to prepare a series of Cu(II) doped goethite samples and study the effect of copper doping in goethite matrix on properties such as phase formation, surface area, iron content and compare the dissolution behavior of doped goethite samples with un-doped goethite in $\text{SO}_2\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ medium.

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2. EXPERIMENTAL

Goethite samples, named as G, CuG1, CuG2 and CuG3 were prepared without and with doping of Cu(II) by precipitation/co-precipitation method using 1M ferric nitrate, 10M sodium hydroxide, and 0.08M copper sulphate solutions following the procedure described elsewhere (Schwertmann and Cornell, 1991, Mohapatra *et al.*, 2002). The concentration of copper during co-precipitation was varied between 100 and 500mg/liter while keeping the Fe(III) concentration constant. The prepared products were dried at 100°C for 24h. Known amounts of the Cu(II)-doped goethite samples were digested in hydrochloric acid and the solutions obtained thereof were analysed volumetrically for total iron using the standard procedure (Vogel, 1991). The concentration of metal ion was estimated by Atomic Absorption Spectrophotometer (AAS). The XRD patterns of various samples were obtained using a Phillips Powder Diffractometer model PW 3710 using a Ni-filtered Co target at a scanning rate of 2°/min. Surface area measurements were carried out using QUANTSORB 1750 instrument assembly. The weight loss measurements were done under isothermal conditions by keeping the samples at required temperature in a muffle furnace.

The un-doped and Cu-doped goethite samples were treated under reducing conditions in a 300ml capacity closed reactor having provisions for gas inlet, outlet, sampling, agitation, and temperature control within $\pm 1^\circ\text{C}$. Weighed amount of metal ion-doped goethite sample (2.5% w/v) was taken and experimental conditions maintained during the dissolution experiments were: acid concentration 0.7M, reaction temp 70°C, SO₂ 0.28M (stock solution of sulphurous acid was prepared by sparging sulphur dioxide in water in a closed reactor and dissolved sulphur dioxide in the solution was estimated volumetrically by KMnO₄ method (Vogel, 1991)). The total volume taken for each experiment was 100ml. The contents were allowed to react for two hours at 70°C and samples (~2ml each) were drawn at the desired time intervals. The slurries were filtered and analyzed.

3. RESULTS AND DISCUSSION

3.1. Characterization of the samples

The chemical analysis of various samples is given in Table 1. The Cu content in doped samples varied between 0.4 to 2.7%. It is observed (Table 1) that as the Cu content increased, the iron content also increased indicating an increased conversion of ferrihydrite to Fe₂O₃ rather than to goethite (Cornell and Giovanoli, 1988).

Table 1
Chemical analysis of various samples

Sample code	% Fe	% Cu	colour
G	62.18	0	yellow
CuG1	57.93	0.41	Yellow
CuG2	63.50	1.15	yellowish brown
CuG3	64.95	2.7	yellowish brown (darker than sample CuG2)

The color of the samples slightly varied from yellow to brownish yellow color. The XRD patterns of the samples are shown in Figure 1. All the samples contained crystalline goethite as the major phase with slight shift in the d-values of major peaks (Table 2). The intensity of major peaks as well as the ratio of relative intensity I_{110}/I_{111} decreased as the percentage of doping increased (Table 2) indicating increase in the proportion of untransformed/poorly crystalline material (Kumar *et al.*, 1990). The marginal decrease in all axis (Table 2) indicates increasing lattice distortion of goethite as the % doping of Cu(II) ion increases rendering the goethite fraction more unstable. However, in pure goethite samples the c-axis is slightly more than the reported value 3.015 (Subbanna *et al.*, 2003). The MCD value along (1 1 1) plane decreased as the doping of Cu(II) ion increased indicating that the formation of finer goethite particle in presence of Cu(II) ions takes place. The % weight loss in the temperature range of 120-400°C is shown in Figure 2. Considering that the % weight loss in this range corresponds to phase transformation of goethite to hematite, % goethite in the samples was estimated and is shown in Figure 2. The estimated goethite contents were 100, 89.2 and 67.75 for samples having 0.4, 1.15 and 2.7% Cu respectively. Since no hematite phase was observed from the XRD pattern, it is inferred that Fe₂O₃ is present in amorphous form. The surface area of the samples increased with increase in % Cu (Figure 3). The high surface area may be attributed to a combination of (i) the significant void space between individual crystallites (Mcgarvey and Owen, 1998) due to insertion of Cu(II) ion in the goethite matrix (ii) the finer goethite particle and (iii) increase in amorphous content of the doped samples (Mishra, 2003).

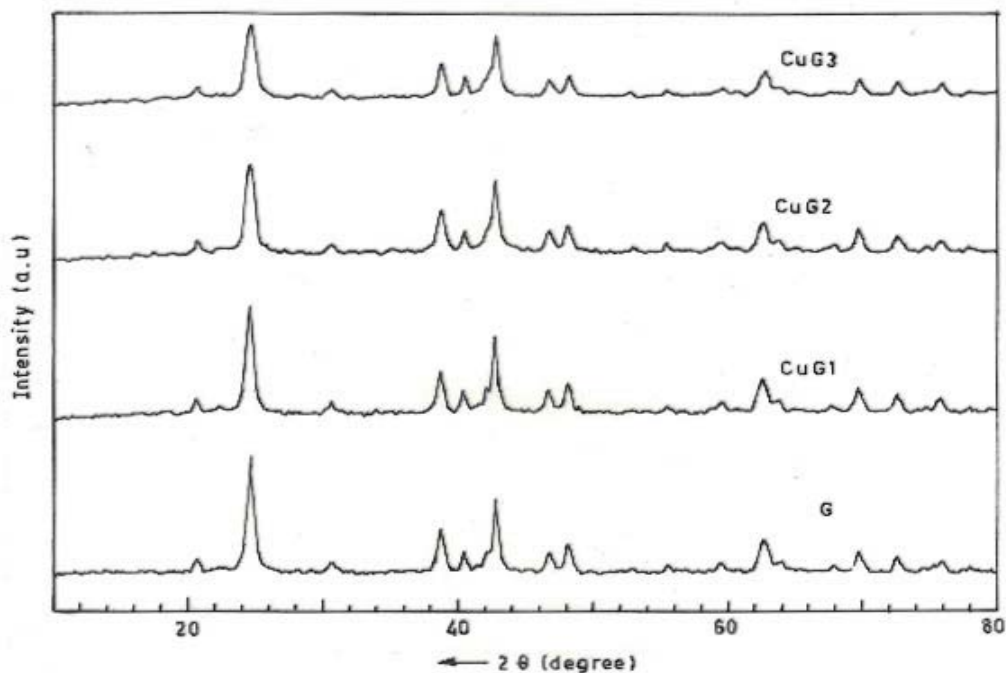


Figure 1. XRD pattern of the undoped and Cu(II)-doped goethite samples

Table 2
 Data from XRD analysis

Sample Code	Peak shift			Lattice parameters, Å			I_{110}/I_{111}	mcd ₁₁₁ , nm
	4.18	2.69	2.44	a	b	c		
G				4.6262	9.9724	3.0340	1.6021	29.824
CuG1	0	-0.00135	-0.0011	4.6251	9.9723	3.0325	1.2658	25.876
CuG2	0.0133	0.00365	0.00135	4.6216	9.9650	3.0288	1.222	22.79
CuG3	0.0067	0.004	0.0011	4.6149	9.5071	3.0272	1.189	10.57

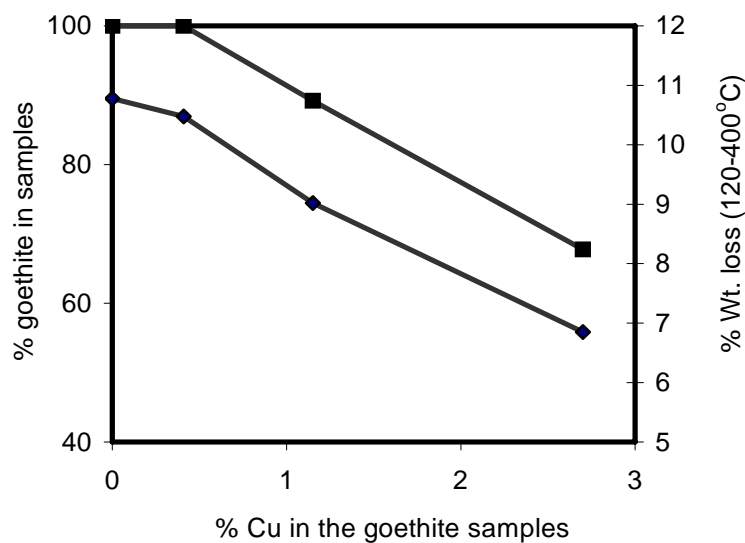


Figure 2. Effect of Cu(II) ion doping on % goethite content and % weight loss (120-400°C)

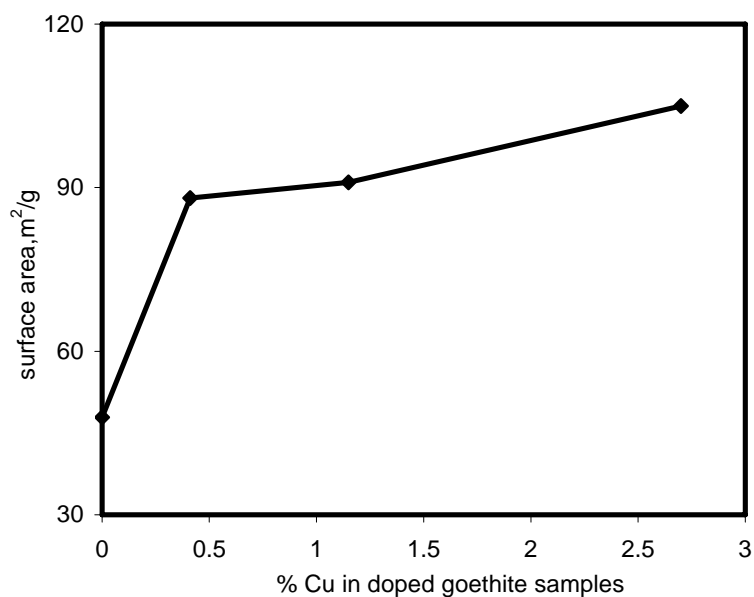


Figure 3. Effect of copper(II) ion doping on surface area

3.2. Dissolution behavior

3.2.1. Effect of percentage of doping on iron and copper dissolution

Figure 4 shows percentage dissolution of iron from pure and Cu-doped goethite samples. The total iron extraction in two hours time increased from 65.8 to 96.7% by increasing the Cu content from nil to 0.4%.

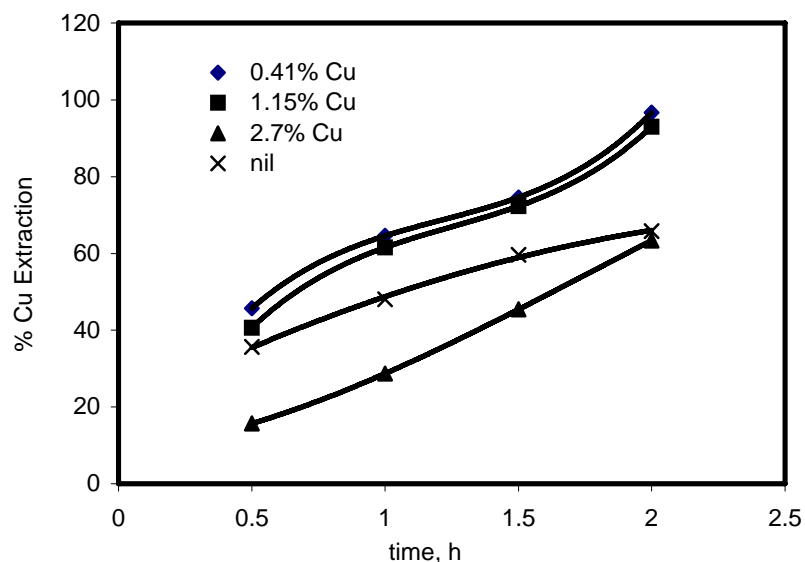


Figure 4. Effect of time on dissolution of Fe from un-doped and Cu-doped goethite (Conditions: $[H_2SO_4]=0.7M$, $[SO_2]=0.28M$ and $Temp=70^\circ C$)

For the samples containing 1.15 and 2.7% Cu, iron dissolution was 93.0 and 63.8% respectively. At lower concentrations, copper ion may get incorporated in goethite structure resulting in distorted octahedral structure (Cornell and Giovanoli, 1988), which would make the structure somewhat less stable than the pure goethite. The larger surface area (Figure 3) would also increase the extent of iron dissolution. But in

case of 2.7% Cu doped sample, since the goethite content was only 65%, iron dissolution is expected to be low. The percentage extractions of copper from Cu-doped goethite samples are shown in Figure 5. Copper extraction remained more or less the same for 0.4 and 1.15% Cu-doped samples (~82%) while it drastically decreased to 36.3 % for the sample containing 2.7% Cu indicating association of more copper with the non-goethite fraction of the sample. copper dissolution was found to be 1.14 and 1.13 respectively suggesting higher dissolution of iron as compared to copper. This trend is further confirmed from the results obtained with doped sample having 2.7% Cu. Here iron to copper dissolution ratio (Figure6) initially increased to 2.93 and after two hours it was found to be 1.74. Overall low dissolution of Cu (II) could be due to the fact that it prefers positions in hematite rather than in the goethite structure (Cornell, 1984).

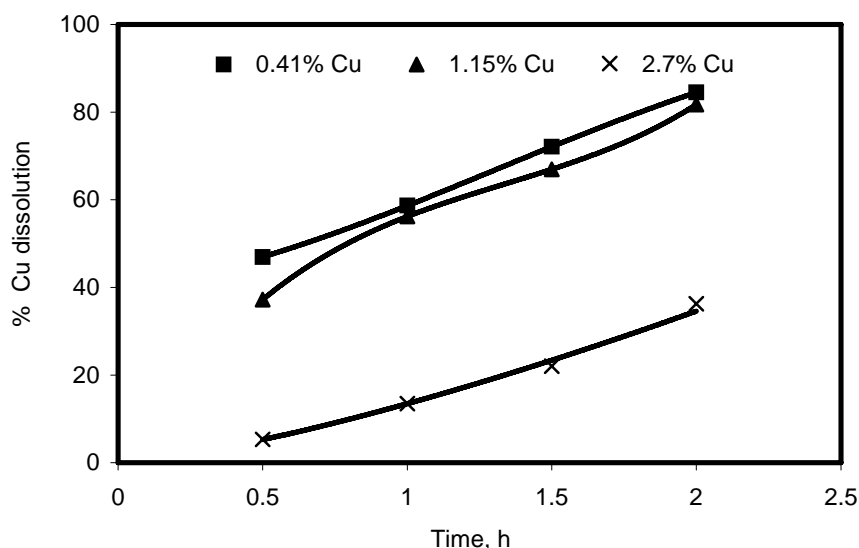


Figure 5. Effect of time on dissolution of Cu from Cu-doped goethite

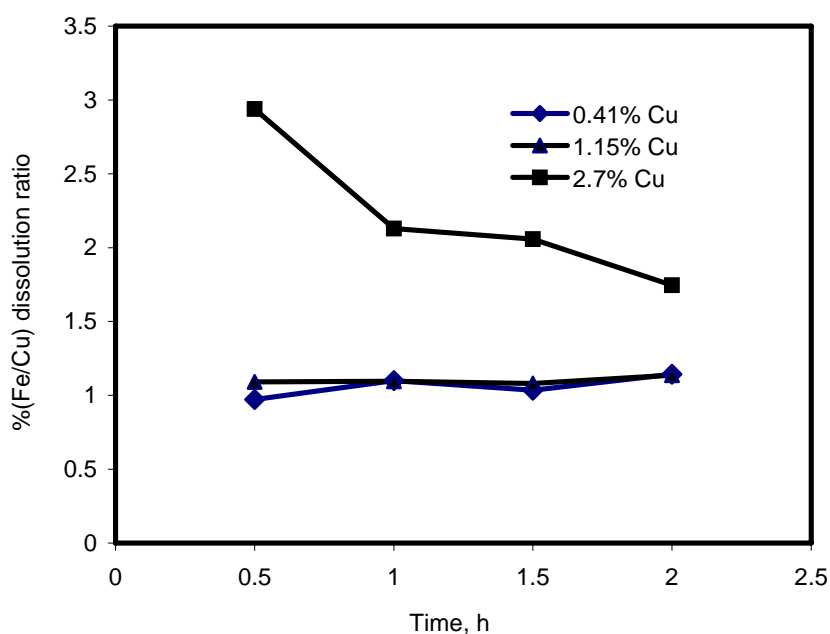


Figure 6. Plot for % (Fe/Cu) dissolution vs time (Condition: same as in Figure4)

3.2.2 Effect of presence of Cu (II) ion on iron dissolution

Catalytic effect of Cu(II) ion during reductive dissolution of metal oxides has been reported (Byerley *et al.*, 1979). During dissolution of Cu(II)-doped goethite, copper coming into solution may act as a catalyst. In order to investigate this aspect, experiments were carried out under same conditions as mentioned earlier with the addition of 200 and 500mg/l Cu(II) during dissolution of pure goethite. The results are given in Figure 7. It is observed that for 200mg/l Cu (II) in solution there is not much increase in iron dissolution whereas 500mg/l Cu(II) shows catalytic effect. Since in the present study the copper concentration remained below 200mg/l throughout the reaction, the catalytic effect of copper will not be there and the difference in dissolution is could be attributed to varying goethite content and surface area of the samples.

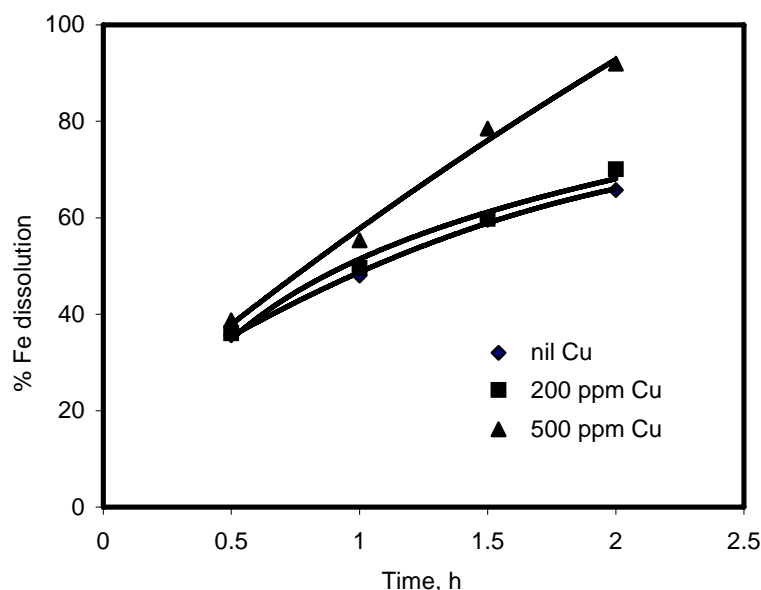


Figure 7. Effect of presence of Cu(II) ion on dissolution of Fe from un-doped goethite(Condition: same as in Figure 4)

4. CONCLUSIONS

- Cu(II) ion doped goethite samples prepared by co-precipitation method contained 58-65% total iron. The XRD patterns confirmed the formation of goethite as crystalline phase. There was slight shift in the d-values of major peaks. The intensity of major peaks as well as the ratio of relative intensity I_{110}/I_{111} decreased as the percentage of doping increased.
- Low concentrations of Cu (II) in the goethite matrix (up to ~1.15%) have marginal effect on the goethite content whereas at 2.7 % Cu doping, formation of goethite is reduced to ~65%.
- Doping of Cu (II) ion in goethite samples resulted in increase in the surface area.
- The surface area of doped sample containing 2.7% Cu was higher but the % dissolution of iron was only 65% indicating dissolution of only goethite fraction of the matrix. The difference in iron dissolution from pure and doped goethite has been explained on the basis of goethite content and surface area.

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