IRREVERSIBILITY OF SULFATE SORPTION ON
GOETHITE AND HEMATITE

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Abstract. Sulfate ion adsorption and desorption experiments carried out on synthetic goethite and hematite
and natural hematite show adsorption to be a highly irreversible reaction. All oxides showed an increase
in sulfate ion adsorption with decrease in pH. Only a small fraction of sorbed sulfate was desorbable
after 48 hr, and only at a pH of 3. Extreme irreversibility of sulfate sorption on these common soil
minerals suggests that adsorbed sulfate is more immobile in watersheds than previously considered
and that recovery models which inherently assume reversibility may need to be modified.

1. Introduction

The Direct Delayed Response Program (DDRP) has been employed to assess the
long term effect of acid deposition. Indeed much of the Acid Rain literature
conclusions are geared towards a saturation-desorption phenomenon. Inherent in
the models (i.e. MAGIC) is the assumption of reversibility of sulfate adsorption
(Cosby et al., 1986; Hornberger et al., 1986), even though some literature suggests
that sulfate sorption is more irreversible in nature.

Sulfate ion retention in a soil depends on environmental conditions and site reac-
tion characteristics, with oxyhydroxide and clay minerals being important soil con-
stituents. Definition of constituent sorption characteristics and consideration of factors
which influence sorption are prerequisite to the modeling of sulfate ion sorption
in soils. When the sorption process on individual soil constituents is ascertained,
then parallel effects in whole soil behavior may be estimated.

Natural whole soil samples are a complex mixture of surfaces with a variety
of organic and inorganic species in the soil solution. Many soils have been examined
for sorption characteristics (Kamprath et al., 1956; Liu and Thomas, 1961; Chao
et al., 1962; Chang and Thomas, 1963; Barrow, 1967; Bornemisza and Llanos,
1967; Hasan et al., 1970; Sanders and Tinker, 1975; Couto et al., 1979; Singh,
1984), but derivations of mechanisms from soil studies is difficult due to their complex
nature, and the inability to specify specific reactions with certainty. The sorption
mechanisms of the individual constituents can be interpreted with less ambiguity,
since specific mineral components and surfaces can be more thoroughly characterized.
Extrapolation of experimental results for individual surfaces must be done with
cautions, however, because when placed back into the natural environment, con-

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Anion sorption on oxyhydroxide minerals has been studied fairly extensively (Bowden et al., 1973; Breuwsma and Lyklema, 1973; Parfitt and Russell, 1977; Parfitt and Smart, 1977, 1978; Sigg and Stumm, 1981; Borggaard, 1983), but only a few (Aylmore et al., 1967; Hingston et al., 1974; Russell et al., 1974) have examined desorption also. This paper presents results of sorption-desorption studies on the iron oxide, hematite, and hydroxide, goethite. These important soil minerals are easily prepared and known to sorb sulfate.

2. Experimental Methods

**Preparation of Materials**

Goethite was prepared by aging a solution of ferric nitrate, adjusted to pH 12, at 60 °C for 24 hr (Atkinson et al., 1968). Hematite was prepared by hydrolyzing ferric nitrate at 100 °C under reflux conditions for 18 d (Parks and DeBruyn, 1962). Precipitates were washed, filtered and vacuum dried. X-ray diffraction analysis (XRD) indicated that the materials obtained were goethite in the first case, and hematite with a small amount of goethite impurity in the second case. A sample of natural hematite was crushed and sieved. XRD analysis showed no crystalline impurities.

The surface areas of synthetic goethite and hematite, measured using the BET-N₂ adsorption method (Brunauer et al., 1938), were 44.1 and 43.2 m² g⁻¹, respectively, while the crushed natural hematite sample was 12.0 m² g⁻¹.

The pH of zero points of charge as determined by acid/base titrations were 7.1, 8.0, and 8.8 (all ± 0.05) for goethite, hematite and natural hematite, respectively.

All chemicals used were of analytical reagent grade.

**Sorption Experiments**

Goethite and hematite samples (0.1 g) were mixed with 25 to 50 mL of K₂NO₃ media of 10⁻² to 10⁻⁴ M concentration. These constant ionic strength suspensions were equilibrated for 24 hr at a constant pH value. Known amounts of sulfate were added K₂SO₄ to attain initial solution concentrations up to 5 mM. At preset time intervals (0.5 to 48 hr), the pH was recorded, and a sample of the suspension removed and filtered through 0.45 µm Millipore filter paper. The filtrate was analyzed for sulfate using ion chromatography.

**Desorption Experiments**

Reversibility was examined by leaching in a constant pH and ionic media. This was achieved by filtration and resuspension of a sample to which a known amount of sulfate had been sorbed. The ionic media and pH were the same as for uptake studies, and the ratio of solid to solution was kept constant. After a reaction time of 48 hr, the suspension was filtered and the filtrate examined for sulfate con-