EXTRACTION OF METAL IONS SORBED ON HYDROUS OXIDES OF IRON(III)

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(Received March 11, 1985; revised June 3, 1985)

Abstract. Extraction of metal ions presorbed on Fe(III) hydrous oxide suspensions using 20 different chemical reagents has confirmed that bonding to several different sites can be involved. Up to half of the sorbed Cd was moderately weakly bound, and was displaced by Mg, Ca and Na chloride solutions but these reagents released little Cu or Pb, and < 20% of the Zn. Reagents which partially dissolved gel suspensions (e.g. mineral acids, EDTA, reducing agents) released > 80% of the sorbed metal ion, but a small fraction remained as a limited solubility interaction product in each case. Sorption and extraction behavior using samples containing goethite and/or hematite reflected the lower solubility of these solids in the various solutions. 'Aged' gels bound metal ions less strongly than freshly precipitated hydrous oxide. The extraction data has been interpreted in terms of displacement reactions, formation of complex ions, and specific adsorption (or coprecipitation). The significance of hydrous oxide formation in metal ion scavenging from natural waters and subsequent release processes has been considered.

1. Introduction

When Fe(III) compounds are leached from soils, sediments, or waste heaps, or are introduced into waterways via discharges such as acid mine waters they tend to reprecipitate at a new location in the form of hydrous Fe oxide gels (HFO). The coagulated colloidal particles have a high surface area per unit weight, and have the capacity to co-precipitate or adsorb large amounts of any metal ion present in associated aqueous phases. The affinity order for freshly precipitated HFO is said to be Pb > Cu > Zn > Ni > Cd > Co > Sr > Mg (Kinniburgh et al., 1976). Aging of the gel results in dehydration and molecular re-arrangement, and depending on conditions the product can be goethite (FeOOH) or hematite (Atkinson et al., 1968). These mineral forms exhibit different adsorption behavior. For example, the affinity sequence on goethite suspensions is reported to be Cu > Pb > Zn > Ni > Co > Ca > Mg > Sr (Forbes et al., 1976).

The factors which influence metal ion uptake by Fe(III) hydrous oxides have been investigated by many different groups. The ions studied include Cd$^{2+}$ (Gadde and Laitinen, 1974; James et al., 1975; Millward, 1980; Honeyman and Leckie, 1981); Zn$^{2+}$ (Gadde and Laitinen, 1974; Shuman, 1977; Kalbasi et al., 1978; Peneva and Paskaleva, 1981; Millward and Moore, 1982; Kinniburgh and Jackson, 1982); Cu$^{2+}$ (Davis and Leckie, 1978a; Millward and Moore, 1982); Pb$^{2+}$ (Gadde and Laitinen, 1973; Hildebrand and Blum, 1974; Swallow et al., 1980); Ni$^{2+}$, Co$^{2+}$ (Kinniburgh et al., 1976; Forbes et al., 1976; Gerth and Bruemmer, 1983; Schenck et al., 1983) and Hg$^{2+}$ (Shimomura et al., 1969; Forbes et al., 1974; Kinniburgh and Jackson, 1978; Inoue and Munemori, 1979; Parks, 1982).
In each study, the amount sorbed was found to be a function of the system pH, adsorbate ion concentration, and the ratio of adsorbate to adsorbent. For each metal ion there was a narrow pH band where the percentage of total metal ion sorbed increased from near zero to > 95%.

During the adsorption of Cu, Pb, Cd or Zn ions, one or two protons are released per mole of metal ion sorbed (Grimme, 1968; Gadde and Laitinen, 1974; Forbes et al., 1976) and this corresponds to M$^{2+}$ being bound to either one or two active sites. Different types of bonding sites exist on the surface of HFO, with bonding strengths for a given metal ion varying by an order of magnitude or more. Sites which strongly bind one metal ion are not necessarily preferred sites for other metal ions (Benjamin and Leckie, 1981, a,b).

Desorption studies have confirmed that sorbed metal ions can be associated with at least two different types of sites. The involvement of specific and non-specific sites in Zn retention by HFO was indicated by Ba$^{2+}$ displacing only a portion of the adsorbed ion (Kalabasi et al., 1978; Peneva and Paskaleva, 1981). Using a goethite suspension, extraction with HNO$_3$ released only about 39, 29, or 10% of sorbed Zn, Cd or Ni, respectively (Gerth and Bruegger, 1983). With sorbed Cu, the most strongly held fraction is believed to be co-ordinated to two surface hydroxyl groups (Padmanabham, 1983). Acidification of a Cu-HFO system to pH 1 released all sorbed metal ion (Davis and Leckie, 1978 a,b) but only 81% of Pb was released on lowering the pH of an HFO suspension to 2. Recovery was 56% using 'aged' solid phases (Gadde and Laitinen, 1973).

In the presence of NaCl, chloro-complex formation tends to reduce the amount of Pb (Swallow et al., 1980), Zn (Millward and Moore, 1982) and Cd (Millward, 1980) sorbed by HFO suspensions. With goethite-seawater systems, the Mg$^{2+}$ and SO$_4^{2-}$ ions present also influenced Cu, Pb, Zn and Cd uptake values (Balistrieri and Murray, 1982). Less than 0.1% of any Pb(II) pre-sorbed onto HFO, goethite or hematite was displaced by 0.1 M MgCl$_2$ (Hildebrand and Blum, 1974).

The various studies indicate that a change in chemical environment may result in release of toxic metal ions associated with hydrous oxides, but desorption processes have not been examined in great detail even though it is recognized that natural systems are dynamic.

The hydrous oxides of Fe (Al, Mn) are considered to play an important role in controlling solution metal ion levels, and to clarify the situation in regard to iron(III) hydrous oxides, a systematic study has been made of the amount of adsorbed Cu, Pb, Cd or Zn displaced when treated with any one of the twenty reagents sometimes used in soil/sediment analysis. In recent years extraction with chemical solutions has been used to evaluate the 'availability' of metal ions sorbed on sediment components but as shown in a recent review (Pickering, 1981), views differ on the suitability of different reagent sequences.