

Laboratory-prepared iron oxide coatings on sands: Submicron-scale small-strain stiffness

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ABSTRACT

Chemical weathering of iron-bearing rock minerals results in the formation of iron oxides, which can chemically adsorb onto soil surfaces, and/or absorb into their molecular structure. The objective of this paper is to use laboratory-prepared, iron oxide-coated sand to study the role of iron oxide coatings on the small-strain stiffness of coarse-grained soil. Ottawa sands were geochemically coated with iron oxides of goethite and hematite via a heterogeneous suspension reaction in the laboratory. Specimen preparation techniques were chosen to ensure that the soils were not cemented during preparation. SEM images, ICP analysis, and geotechnical index tests were used to characterize the submicron-scaled iron oxide coatings, and the bender element method was used to measure the shear wave velocities of uncoated and the two iron oxide coated sands. Contact mechanics and submicron scale mechanistic approaches were explored to interpret the experimental data, and results indicated that small-strain stiffness of iron oxide coated sands was higher than that of uncoated sands. Results also suggested that a small-strain stiffness behavioral hierarchy associated with iron oxide thermodynamic stability may exist. This study demonstrated that iron oxide coatings significantly influence sand grain-to-grain behavior, even in the absence of cementation or augmented contact area effects, due to an increase in the number of particle contacts present in the iron oxide coated sands.

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1. Introduction

Iron oxides are present in the geologic environment due to physical and chemical weathering of iron bearing minerals. In soils, oxides can be found as discrete coatings that are integrally bonded to a carrier mineral, such as silica sand. While weathering results in the alteration of many soil properties, including fabric and stress history, this study examines the effect of chemical weathering on the alteration of the surface properties of individual sand grains, and its implications for the engineering behavior of sands. Because iron oxides can occur as individual particles that are chemically bonded to sand surfaces, the presence of the oxides results in a substantial alteration to the nanoscale properties of the soil grains. This study examines the effect of two geochemically mature iron oxides, goethite and hematite, on the physical and small-strain mechanical behavior of oxide coated sands.

1.1. Chemical weathering of igneous rock-forming Fe(II) minerals

Physical and chemical weathering act simultaneously to alter the properties and behavior of geo-materials. Once physical weathering

takes place (e.g., through jointing and micro-fracturing), rock surfaces are exposed to environmental chemical attack. Physical weathering occurs as freeze–thaw, wetting–drying, and pressure-release mechanisms (Bland and Rolls, 1998), while chemical weathering involves hydration, dissolution, precipitation, hydrolysis, oxidation–reduction, ion exchange, and carbonation reactions (Gidigas, 1976; Drever, 2005). Such a varied suite of processes affects mineral composition, texture, structure, and chemical properties of both parent rock and soils. In the soil geochemical environment, the major chemical weathering agents are water, oxygen, carbon dioxide, and organic acids (the latter derived from vegetation decay).

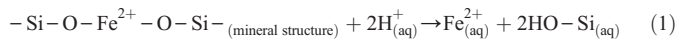
Water and oxygen are abundant at the Earth's surface; consequently, inorganic aqueous chemistry, including redox, is a good framework in which to analyze chemical weathering (Gidigas, 1976; Dixon and Weed, 1989; Martini and Chesworth, 1992; Faure, 1998; Cornell and Schwertmann, 2003; Drever, 2005; Nordstrom, 2005). Most specifically, this work is focused on the weathering chemistry of iron oxides in humid tropical climates with vertical drainage that is nearly-free draining. Iron is the third most abundant cation species in rock minerals, with an average concentration of 51 g of iron per kg of rock. Thus, iron plays a significant role in several hydro-geochemical processes that dominate the composition of surface and ground waters, such as dissolution of silicate minerals, sulfate reduction/pyrite formation, and pyrite oxidation/formation of hydrous ferric oxides. Iron occurs in several oxidation states, with +2 (Fe²⁺, Fe(II),

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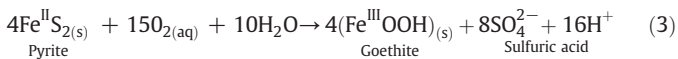
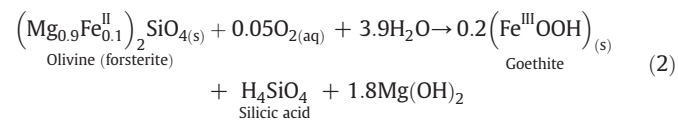
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or ferrous iron) and +3 (Fe^{3+} , Fe(III), or ferric iron) being the most abundant. In igneous rocks, most iron exists in the ferrous Fe(II) form within the mineral molecular structure.

The most abundant ferrous rock minerals are (in order of decreasing thermodynamic stability): ferrous silicates (e.g., the phyllosilicate biotite, the chain silicate pyrobole, and the nesosilicate olivine), ferrous sulfides (e.g., pyrite FeS_2), and ferrous carbonates (e.g., siderite FeCO_3). The pH of pure water in equilibrium with the atmosphere is approximately 5.66, while water buffered by the carbonate system typically exhibits a pH slightly under 7. When acidic water contacts iron-bearing rock minerals, the abundant free protons in the water attack the outermost mineral surfaces and surface-bonded cations are displaced via electrostatic repulsion, i.e., protolysis, and in turn, these displaced cations hydrolyze and migrate into the bulk electrolyte. Meanwhile, further proton-to-proton repulsion forces at the mineral surface create “channels” for more acidic water to attack the mineral within. In the process, Fe^{2+} cations from the rock mineral are released:



Once the $\text{Fe}^{2+}-\text{O}-\text{Si}$ bonds in ferrous silicates are broken, the overall molecular structure weakens. Furthermore, in-situ oxidation of ferrous iron may also take place, which yields a charge imbalance and further mineral breakdown. Consequently, Fe^{2+} cations, which are highly soluble in water, are released into subsurface soil and water environments. Once exposed to dissolved oxygen, which is the major electron acceptor in natural systems, ferrous iron Fe(II) can be oxidized to yield ferric iron Fe(III), which is then rapidly hydrolyzed. In contrast to Fe(II), Fe(III) has very low solubility, thus permitting rapid nucleation, precipitation, and growth of ferric oxides, hydroxides and oxy-hydroxides (this group is generically called “iron oxides”). Representative reactions that summarize this mechanism are as follows:



Reaction (2) can indeed be generalized to any mafic silicate mineral such as pyroxenes, amphiboles and mica (biotite) reacting with oxygen and water. These processes take place in terrestrial and marine environments at typical water $\text{pH} > 3$. Below $\text{pH} 3$, abiotic Fe(II) oxidation is very slow, and is almost exclusively bio-mediated. The by-products of the reactions above (acids and bases) may be readily leached away. However, the fate of strong acids such as sulfuric is commonly responsible for acid mine drainage (Rose and Elliott, 2000).

The well known, horizon-based, soil taxonomy framework specifies that iron oxides accumulate predominantly in the B-horizon, along with clay minerals, mostly kaolinite (Miller, 2001). Nevertheless, successive cycles of dissolution, transport, and re-precipitation may yield iron oxide adsorption on other soil horizons (Cornell and Schwertmann, 2003). Unlike quartz sands and silts, which are “primary” minerals, clays and iron oxides are commonly named “secondary” minerals.

1.2. Iron oxides

Iron oxides occur in a variety of forms, and have several commonly encountered amorphous precursors, which include hydroxides and oxy-hydroxides (Table 1). In particular, ferric oxy-hydroxide goethite ($\alpha\text{-FeOOH}$) is the most abundant iron oxide weathering product (Cornell and Schwertmann, 2003); however, it is not usually the direct

Table 1

Iron oxides, listed in order of increasing thermodynamic stability (Cornell and Schwertmann, 2003).

Category	Name	Chemical formula
Ferric hydroxide	Amorphous ferric hydroxide	$\text{Fe}(\text{OH})_{3(\text{s})}$
Ferric oxy-hydroxide	Limonite (obsolete term)	$\text{FeOOH} \cdot n\text{H}_2\text{O}$
	Akaganéite	$\beta\text{-FeOOH}$
	Ferrihydrite	$\text{Fe}_4(\text{OH})_{12} \text{ to } \text{Fe}_5\text{O}_3(\text{OH})_9$
	Lepidocrocite	$\gamma\text{-FeOOH}$
	Goethite	$\alpha\text{-FeOOH}$
Ferric oxide	Maghemite	$\gamma\text{-Fe}_2\text{O}_3$
	Hematite	$\alpha\text{-Fe}_2\text{O}_3$

iron oxide product. Instead, an amorphous precursor, such as ferrihydrite, lepidocrocite, or akaganéite is formed first, depending on the environmental conditions. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is a more mature iron oxide that is often present in soils of tropical and sub-tropical regions, favored by higher temperatures and water activity. In soil profiles, iron oxides are usually poorly crystalline, show impurities and defects, and their crystals are submicron-sized. Various chemical species (e.g., silicates, phosphates, and organic matter) usually interfere with crystal growth in the soil solution or prevent the precursors from transforming into iron oxides. Amorphous iron oxides have larger specific surface and higher solubility than their crystalline counterparts (Alexander and Cady, 1962). Relatively crystalline goethite and hematite prevail in mature tropical and subtropical soil profiles (e.g., oxisols and ultisols), with iron oxide content in these soils ranging from <1 to up to several hundred mg/g.

Iron oxides carry relatively high surface charge. This feature, in addition to their high specific surface, makes iron oxides usable as sorbents of heavy metals (Szecsody et al., 1994; Xu and Axe, 2005). Indeed, ferrihydrite is one of the most important sorbents in chemical applications, due to its large specific surface of up to $800 \text{ m}^2/\text{g}$ (Cornell and Schwertmann, 2003).

Chemical interactions between iron oxides (e.g., aggregation) render cementation-like effects which in turn favor the formation of soil clusters (Zhang et al., 2003). Intra-cluster bonding forces are generally much higher than inter-cluster forces. Because aggregation is surface-charge-, pH-, and ionic strength-dependent, it is therefore reversible. Aggregation is common in tropical soils with relatively high iron oxide content, and goethite-hematite mixtures are predominant. In arid and semi-arid regions, iron oxide rich soils can harden, thus forming “iron-stone concretions” and “indurated horizons” (Gidigas, 1976); such soil profiles are commonly called laterites or ferricretes.

1.3. Iron oxides in soil mechanics

Iron oxides are important in the geotechnical study of residual soil mechanics, where they commonly occur as cementing or coating agents in soils (Mitchell and Soga, 2005). The majority of studies on residual soil mechanics are based on field samples of lightly to heavily cemented soils. Millard (1962) (cited by Gidigas, 1976) studied tensile strength of African “concretionary gravels” and correlated the strength with iron oxide content. Similarly, tensile properties of semi-arid African soils were assessed in a laboratory investigation through the addition of the iron oxide ferrihydrite to the soil samples (Breuer and Schwertmann, 1999). In terms of small strain measurements in iron-rich, gravel-like materials, shear wave velocities were not found to correlate well with compaction degree (Sawangsurriya et al., 2008). Due to the difficulty of quantifying the behavior of coated soils, some laboratory based studies have removed iron oxides from fine-grained soils using strong chemical reductants (e.g., the Dithionite–Citrate–Bicarbonate method), and then measured index, hydraulic, and compressibility properties (Townsend et al., 1971; Rao et al., 1988;

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