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ScienceDirect
Solid State Sciences 10 (2008) 1342–1351
Solid State Sciences
www.elsevier.com/locate/ssscie

Comparative studies of ferric green rust and ferrihydrite coated sand: Role of synthesis routes

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Received 4 October 2007; received in revised form 24 January 2008; accepted 31 January 2008
Available online 8 February 2008

Abstract

A comparative study of ferrihydrite and ferric green rust coated sand prepared by three synthesis routes has been outlined in the present contribution. The two minerals displayed inverse properties in terms of quantity of deposited iron for all three methods investigated. For ferric green rust coating, a newly proposed synthesis route named as dry contact method was efficient for the maximum quantity of iron with almost full coverage area. Considering the similar parameters, the modified wet synthesis method designated as reactive method provides the optimum results for ferrihydrite coated sand. These coatings have been characterised by different surface analysis techniques. In particular, due to the excellent sensitivity of miniaturised Mössbauer Spectrometer (MIMOS) it was possible to detect the lowest iron content (0.1 Fe w/w%). A distinct approach based on tribology between crystallised ferric green rust and sand has been proposed to explain the relatively high quality of coating using dry contact method.
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Keywords: Green rust; Ferrihydrite; Iron coated sand; Mössbauer spectroscopy; MIMOS; X-ray photoelectron spectroscopy

1. Introduction

Iron oxide coated sand materials exhibit coating of various chemically synthesised iron oxide onto natural sand substrates. These materials are promising candidates for the elimination and fixation of pollutants such as inorganic and organic compounds in soils, sediments and in contaminated water [1–6]. The coated sand materials are much more favourable over pure iron oxide and uncoated silica. As a result of bound iron oxides, an increase in the specific surface area of the resulted coated sand provides a better adsorption efficiency of organic compounds and heavy metals [7–9]. In addition, due to the surface charge modifications and grain size effect, resulting materials are more adapted for high scale applications such as wastewater treatment/filtration.

Iron oxide coated sand or clay prepared by addition of base to an acidified Fe(III) solution in the presence of respective particles results in different types of coatings such as amorphous, poorly crystalline [10–12] or crystalline [13]. Furthermore, Xu and Axe [14] have also suggested that the synthesis route affects the crystallinity of coating and the particle size of silica which influences the quality of coating. In addition, several studies have been done to evaluate the characteristics of coatings such as the formation of Fe–O–Si bond at the oxide–coating interface [13], lack of repulsive forces on chemical interactions at the oxide–quartz interface [15] and effect of particle size on the oxide–substrate interaction [16]. Some interesting investigations on elemental determination, distribution and the structure of coatings have also been carried out [17–19]. In addition to investigations on laboratory made coatings imitating natural ones, studies that concern optimisation of the coating processes and examination of fundamental questions regarding substrate–coating interactions,

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doi:10.1016/j.solidstatesciences.2008.01.033

adhesion of coatings and interfacial phenomenon are yet to be addressed and extensively investigated.

The present investigation deals with the systematic study of natural sand substrate coated by iron oxide minerals. Ferrihydrite (FH) and green rust (GR) are the two minerals selected as coating materials in the present study. GRs are Fe(II)–Fe(III) hydroxysalt compounds with double layered hydroxide structure composed of brucite-like alternate interlayers of anions and water molecules with the chemical formula $[Fe^{II}_{(1-x)}Fe^{III}_{x}(OH)_2]^{+x}\cdot[(x/n)A^{n-}\cdot mH_2O]$ where x varies from 0.25 to 0.33 [20–24]. The exact crystalline structure of GR depends on the interlayer anions which are categorised as GR1 with planar anions e.g. Cl^- and CO_3^{2-} and GR2 with three-dimensional anions e.g. SO_4^{2-} [20–23]. In the present investigation the ferric GR is obtained by complete oxidation of carbonated GR. Previous investigators [25,26] have reported on coating of GR on metallic substrates but studies about the coating of GR on the natural substrates are not yet investigated. We report here, to the best of our knowledge, the very first study on GR coated sand. FH is one of the most abundant and reactive iron oxyhydroxide minerals. The use of iron oxide as a coating material is rather conventional but the studies related with the optimisation of coating for two different iron minerals such as partially crystalline FH and well crystallised GR are limited. It is, however, interesting to study these minerals due to differences in their surface charges, grain size, poorly crystalline versus crystalline character. The concept of poorly crystalline versus crystalline character has previously been studied for soil segregation [27] and authors have reasoned that poorly crystalline FH increases the soil aggregation due to its higher reactivity as a consequence of large surface area.

The two minerals were coated on the sand surface by three different methods designated as dry contact method (D), wet contact method (W) and reactive method (R). The three methods used were hypothesized to involve different interactions such as physical/mechanical and chemical bonding interactions between substrate and coating material which may play an important role in macroscopic and microscopic adhesion and morphology of coatings.

One major objective of present study concerned the optimisation and establishment of the synthesis routes for iron coated sand to obtain a reliable model material for further experiments such as reactivity in a column or in a batch which are useful for various applications. Thus, key points discussed emphatically are centered on synthesis of coated material devoid of free iron particles and the maximum amount of coated iron. We are presenting the very first results on the comparison of the effect of synthesis routes on the mineralogy, quantity and macroscopic adhesion for coating of two minerals on sand at room temperature. The properties of coatings for two minerals under the same synthesis routes are also outlined. Such studies directly address questions related to stability, quantity of Fe and chemical/physical interactions between the coating and the substrate. These coated materials were characterised by various surface techniques such as Mössbauer Spectroscopy (using miniaturised Mössbauer Spectrometer i.e. MIMOS), X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). Furthermore, quantitative analysis was done by XPS, Energy Dispersive Analysis by X-rays (EDAX) and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

2. Experimental

2.1. Pre-treatment of sand

In the present investigation the quartz sand (150–300 μm) of Fontainebleau (Prolabo) was soaked in 1 M HCl solution and then washed thoroughly in order to remove traces of other minerals. The treatment of sand with H_2O_2 was done to remove organic matter [28]. Finally, the sand was extensively depurated by using deionized water and then oven dried at 110 °C.

2.2. Synthesis routes for the coating

Three methods explored for the synthesis of coatings designated as wet contact, dry contact and reactive method, are based on the conditions employed.

2.2.1. Wet contact method

The concept of wet contact method involves preparation of minerals, mixing of mineral solutions with sand for the genesis of coating and finally thorough washing to remove free and loosely bound particles. Detailed description of coating methods used for the two minerals is given below.

2.2.1.1. Synthesis of ferric green rust and ferrihydrite. The ferric GR was prepared by co-precipitation method explained in previous studies [29–31]. Preparation of an Fe(II)–Fe(III) solution was done by dissolving appropriate amounts of $FeSO_4\cdot 7H_2O$ and $Fe_2(SO_4)_3\cdot 5H_2O$ salts to provide a final concentration of Fe of 0.4 M. Mixed Fe(II)–Fe(III) GR was prepared by blending the mixture of Na_2CO_3–NaOH solution with the Fe(II)–Fe(III) solution. Thorough mixing of these two solutions resulted in carbonated GR [GR $(CO_3)^{2-}$] of the formula $[Fe^{II}_4Fe^{III}_2(OH)_{12}]^{2+}\cdot[CO_3, 3H_2O]^{2-}$. Finally the ferric GR was obtained by oxidising the carbonated GR through controlled addition of H_2O_2 solution using a peristaltic pump [24]. The reaction was monitored and the final pH achieved was 10.2.

The synthesis of FH was done by using a conventional precipitation method illustrated in literature [32]. NaOH (1 M) solution was added continuously to $FeCl_3$ solution (0.2 M) as a neutralising source and the final pH was adjusted and maintained to 7.5 throughout the synthesis period. Prior to mixing with sand, these minerals were extensively washed by distilled water.

2.2.1.2. Synthesis of coated sand. Synthesis of coated sand was done with some modification of the methods employed in previous studies [13,33]. After overnight aging of prepared minerals, the pH was maintained and stabilised to pH 7.5 and sand was mixed with the suspension. In order to coat the mineral on the sand substrate the mixture was then subjected to mixing through multiple cycles of alternative stirring and

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