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## INTRODUCTION

Iron(II) oxide coating on soils/sediments is reported to be the most important factor for controlling the sorption of radioactive metals in groundwater systems. Various forms of Fe(II) oxides occur in nature; they exist in both crystalline and amorphous forms. Our review indicated that goethite ( $\alpha$ -FeOOH) is one of the most common iron oxides present in subsurface sediments. Therefore, it is important to understand the reactive chemistry of U(VI) with goethite-coated sand (GCS). Our overall objective is to develop scalable reaction models to predict uranium fate and transport in subsurface environment. In this paper, we focus on U(VI) interactions with well-characterized, synthetic goethite-coated sand.

## OBJECTIVES OF THE PRESENT WORK

- To identify a standard protocol to synthesize pure goethite-coated sand.
- To characterize the goethite-coated sand synthesized using various methods.
- To analyze the interaction of U(VI) with the goethite-coated sand.
- To predict the adsorption characteristics using surface complexation models

## SYNTHESIS OF GOETHITE-COATED SAND

The following two methods were used for synthesizing goethite-coated sand:

1. Homogeneous suspension method using ferrous chloride or ferrous sulphate (Schwertmann and Cornell, 2000).
2. Heterogeneous suspension method using pure goethite (Scheidegger et al., 1993).

The schematics of the synthesis protocols are shown in Fig. 1a and 1b. The goethite coating by homogeneous suspension reaction was attempted with both ferrous sulphate and ferrous chloride as iron source (Fig. 1a). In case of heterogeneous suspension method, pure goethite was synthesized first using Fe(II) nitrate and then it was coated onto the acid washed quartz as shown in Fig. 1b. The goethite coated sand obtained from both the methods were shown in Fig. 2. Since the loss of iron during heterogeneous coating process was less (ranging only 4 to 6% of Fe was coated on to the sand grains), the same goethite suspension can be reused to coat several batches of sand. The sand synthesized with the used goethite suspension had iron content within the expected range for the heterogeneous coating method. Scanning electron microscopy (SEM) and powder X-ray diffraction (XRD) were used for characterizing the morphology and phase identification, respectively. Dithionite-sulphate-bicarbonate (DCB) and AOD (ammonium oxalate in dark) extractions were performed to quantify the iron content of the sand. DCB can remove the crystalline iron along with free iron oxides whereas AOD extracts the amorphous iron (Table 1). The surface area of goethite and GCS was measured using multipoint BET.

## CHARACTERIZATION

SEM images along with energy dispersive X-ray spectrum (EDX) were obtained on gold sputtered samples to identify goethite crystals. Since the iron oxide coating forms an uniform layer onto quartz it is difficult to identify the form of iron oxide coating onto pure quartz in a homogeneous system. Hence, a precipitate sample was directly analyzed. The SEM image of the precipitate showed typical acicular (needle shaped) particles indicating the coating on the quartz is goethite (Fig. 3a). Also, the SEM image of the sand after DCB extraction reaffirmed that the coated iron was indeed goethite (Fig. 3b). In the case of heterogeneous system, we first precipitated pure goethite crystals and validated it based on its morphology and XRD (Fig. 4). The XRD pattern matched the peak of synthetic goethite. The GCS from the heterogeneous system indicated goethite deposition onto the quartz pores that were formed due to rigorous acid washing of the un-coated sand. The SEM images and the corresponding EDX spectrum (Fig. 5a and 5b) show the differences in the iron concentration between a representative surface and pore site on the coated sand.

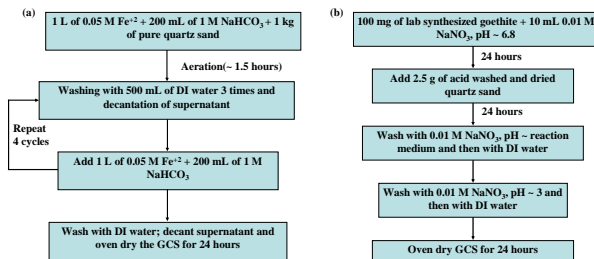


Figure 1. Synthesis of Goethite-Coated Sand (GCS). (a) Homogeneous suspension reaction; (b) Heterogeneous suspension reaction

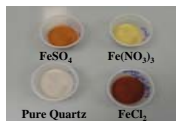


Figure 2. Goethite-coated sand synthesized from various systems

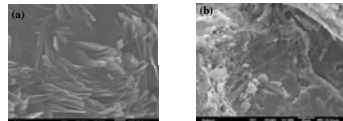


Figure 3. (a) SEM image of precipitate from homogeneous system; (b) GCS from homogeneous system after DCB extraction

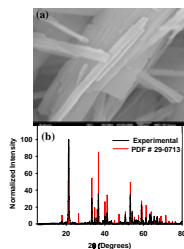


Figure 4. (a) Pure goethite; (b) powder XRD pattern of goethite

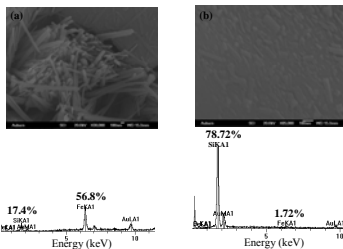


Figure 5. Goethite-coated sand from heterogeneous system and its corresponding EDX spectra. (a) Pore; (b) Surface

The iron analysis indicated that the homogeneous system resulted in about an order of magnitude higher iron content than the heterogeneous system. This correlated well with BET surface area measurements. The estimated surface area of the homogeneous system was about 6 times higher than the heterogeneous system. Table 2 shows the comparison between the two different protocols adapted to synthesize goethite-coated sand.

Table 1. Surface Area and DCB extractable iron from different systems

	BET Surface Area (m <sup>2</sup> /g)	DCB Iron (%)	AOD Iron (%)
Homogeneous- Fe(II) chloride	0.44	0.55	0.15
Homogeneous- Fe(II) sulphate	0.38	0.37	0.03
Heterogeneous- Fe(II) nitrate	0.07	0.03	-
Heterogeneous- Reused goethite	0.08	0.05	-
Pure goethite	53.30	67.57	3.00

Table 2. Assessment of the methodologies used for synthesizing goethite-coated sand

	Homogeneous Suspension Method	Heterogeneous Suspension Method
Iron content	High and easy to control	Less and dependent on reaction conditions
Verification of iron oxide as goethite	Difficult by imaging and powder XRD	Easier to confirm since pure goethite is coated onto the sand
Iron source	Percentage of input iron source coated onto the sand was 21%	Percentage of input iron source coated onto the sand was 4% - 6%
Purity of goethite coating	Chances of forming poorly crystalline iron oxides is high	Crystalline goethite can be checked for purity since coating is a separate step
Surface area of coated sand	High	Low
Time taken for the process	2 days	More than 2 weeks

## SORPTION AND DESORPTION EXPERIMENTS

Batch sorption isotherm experiments were performed using 10 g L<sup>-1</sup> of homogeneous sand and 100 g L<sup>-1</sup> of heterogeneous sand. The initial concentration of U(VI) was varied between 0 to 5 mg/L. The pH and ionic strength of the solution was fixed at 4.2 ± 0.1 and 0.1 M, respectively. The experiments were performed at room temperature (21 ± 1°C). After 48 hours, the samples were filtered, acidified and analyzed using kinetic phosphorescence analyzer (KPA). The desorption studies were performed at a higher solid to solution ratio (750 g L<sup>-1</sup>) with heterogeneous-system sand. Desorption was initiated on equilibrated samples that had higher U(VI) adsorption. This was accomplished by replacing 80% of the aqueous phase with the background solution. The samples were allowed to equilibrate for 8 days and analyzed.

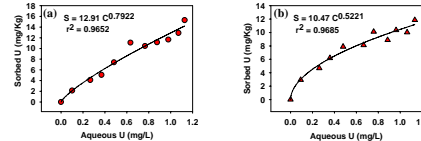


Figure 6. Adsorption of U(VI) to GCS from homogeneous system. (a) Fe(II) chloride; (b) Fe(II) sulphate

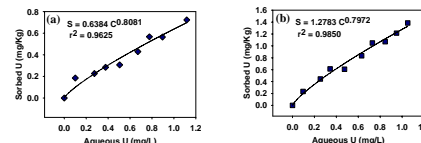


Figure 7. Adsorption of U(VI) to GCS from heterogeneous system. (a) Fe(III) nitrate; (b) Reused goethite

## EXPERIMENTAL AND MODEL RESULTS

Batch adsorption results were fitted using the Freundlich equation. The results in sorption capacity and sorption affinity of ferrous chloride system was higher than sulphate system (Fig. 6a and 6b). This is primarily due to the presence of higher iron in the chloride sand. Within the heterogeneous system, higher sorption was observed GCS than the Fe(II) nitrate (Fig. 7a and 7b), which is also due to the different content. However, the sorption affinity of both the sands for U(VI) were similar (Fig. 8).

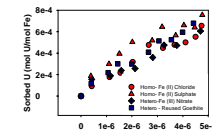


Figure 8. Adsorption of U(VI) after normalizing to iron content

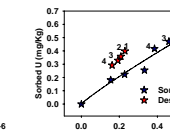


Figure 9. Desorption of U(VI) to solid solution ratio (750 g L<sup>-1</sup>)

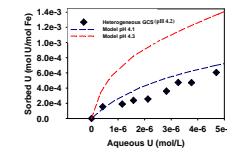


Figure 10. Adsorption of U(VI) to GCS in comparison with SCM prediction

When the sorption of U(VI) onto all the different sands were normalized to their iron content similar adsorption pattern was observed (Fig. 8). Desorption of heterogeneous GCS indicated that a portion of U(VI) could not be desorbed surface complexation model (SCM) developed for predicting the sorption of U(VI) on ferrous oxide (HFO) by Waite et al. (1994) was used to model this system. The model over-predicted the experimental results (Fig. 10). This might be due to the different surface area of HFO and goethite. Also the surface complexation constants in model were based on U(VI) sorption to amorphous HFO, not for crystalline goethite have influenced our model results.

## CONCLUSIONS

- Goethite-coated sand can be prepared using either homogeneous or heterogeneous system.
- The homogeneous method is the best approach to control the amount of iron onto the sand.
- SEM of the GCS indicated the heterogeneous system had higher Fe concentration pore spaces.
- Irrespective of the coating method, U(VI) adsorption on GCS can be normalized to iron content.
- A portion of the U(VI) is irreversibly sorbed onto GCS (based on heterogeneous system).
- The HFO model over-predicted the experimental results possibly due to different surface area and equilibrium constants.

## ACKNOWLEDGEMENTS

This work was funded by USDOE's ERSF program grant no: DE-FG02-06ER642