

## Original Research

## Core Ideas

- Decreasing quartz sand wettability leads to attractive hydrophobic interactions with colloids.
- In flow columns, transport of Fe oxide colloids is not affected by sand matrix wettability.
- The short-range hydrophobic attraction is probably counteracted by colloid surface roughness.

# Iron Oxide Colloid Mobility as Affected by Solid Matrix Wetting Properties

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The influence of porous media wettability on the mobility of colloids is mostly unknown. In the present work, organic-matter-coated goethite (OMCG) colloids were percolated through three saturated soil materials differing in wettability: untreated quartz sand and two variants of hydrophobized sand. For each type of sand, three ionic strength levels were applied. Derjaguin–Landau–Verwey–Overbeek (DLVO) and Lewis acid–base extended DLVO (XDLVO) interaction energy profiles were calculated according to contact angles and zeta potentials. Flow column results elucidated that decreasing sand wettability had no relevant effect on OMCG colloid mobility. In contrast, colloid retention increased with ionic strength in each type of sand packing. Classic DLVO interactions could predict trends in colloid retention by the respective characteristics of energy barriers and secondary minima. The extension with Lewis acid–base interactions in the XDLVO approach led to the prediction of significant short-range ( $\sim 2$  nm) attractive interaction energies between colloids and hydrophobized sand, which were not reflected by colloid breakthrough behavior. This was probably due to substantial energy barriers calculated for larger distances ( $\sim 27$  to  $\sim 75$  nm, depending on ionic strength) between the solid matrix and colloids. It is concluded that the distinct surface roughness of sand grains and colloids probably weakened the strength of the short-range attractive interactions, because larger amounts of surface area were still outside the effective distance for the short-range interactions predicted by XDLVO. Regarding colloidal mobility, we concluded for our saturated porous systems that near-surface attractive XDLVO interaction energies between OMCG colloids and hydrophobized sand did not significantly affect colloid mobility.

Abbreviations: DCDMS, dichlorodimethylsilane; DLVO, Derjaguin–Landau–Verwey–Overbeek; DOM, dissolved organic matter; OMCG, organic-matter-coated goethite; PV, pore volume; SEM, Scanning electron microscope; XDLVO, extended Derjaguin–Landau–Verwey–Overbeek.

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Research from the past decades has revealed that transport processes of colloids and solutes in soils can be strongly affected by the wettability of the solid matrix. Although most typical soil minerals have hydrophilic surfaces, their wettability can be decreased by the formation of organic matter coatings over time (Roberts and Carbon, 1972; Doerr et al., 2000; Lamparter et al., 2014). Soil water repellency leads to nonuniform wetting and water infiltration via preferential flow pathways at the profile (dm) scale (Bauters et al., 2003; Ziogas et al., 2003, Ganz et al., 2014). Due to preferential flow, parts of the seepage water can reach the water table much faster than in wettable soil, supporting groundwater pollution with cotransported contaminants (Bauters et al., 2003; Ferreira et al., 2003). In addition to the profile scale (Krueger et al., 2016), soil wettability also shows a considerable spatial heterogeneity at the pore (cm) scale (Bachmann et al., 2013; Krueger and Bachmann, 2017). At the pore scale, soil water repellency can decrease the transport of colloidal particles due to attractive hydrophobic interactions between the soil matrix and colloids (Goebel et al., 2013).

To explicitly include wettability effects on colloid transport at the pore scale, the classic Derjaguin–Landau–Verwey–Overbeek (DLVO) approach, consisting of van der Waals and electrostatic interactions, can be complemented with Lewis acid–base interactions (van Oss et al., 1990). This approach is termed XDLVO, for extended DLVO. Acid–base interactions can be up to two magnitudes stronger than electrostatic and van der

Waals interactions and can either cause hydrophobic attraction or hydrophilic repulsion (van Oss, 2006). Corresponding interaction energies originate from the influence of solid surfaces on the relatively well-ordered, three-dimensional, hydrogen-bonded network of water molecules in bulk water. If a solid surface features a sufficient number of polar groups (or Lewis sites) to outcompete the self-association of water molecules, it is readily wettable. Near the surface of hydrophilic materials, the hydrogen-bonding network of water molecules collapses. This leads to an increase in water density compared with bulk water, which causes repulsive interaction energies. In contrast, if its amount of Lewis sites is incapable of competing with self-association, the adhesion between the surface and water is low and the surface turns hydrophobic. At hydrophobic surfaces, water density is lower than in bulk water, leading to attractive interactions (Vogler, 1998).

In several cases, the inclusion of attractive hydrophobic interactions in the context of the XDLVO approach was required to describe colloid interactions that the classic DLVO failed to predict. For instance, the flocculation behavior of hectorite colloids could only be described by hydrophobic attraction (van Oss et al., 1990). Similarly, the transport of polystyrene microspheres in hydrophobized sand was significantly reduced as compared with hydrophilic sand, which could be explained by hydrophobic attraction. Moreover, increasing ionic strength led to stronger colloid retention in the hydrophobized sand due to lower energy barriers (Goebel et al., 2013).

The considerable retention of microspheres in hydrophobized sand reported by Goebel et al. (2013) indicates that soil water repellency and the associated hydrophobic attraction can strongly influence the mobility of colloids in soils. Given the common occurrence of soil water repellency (Doerr et al., 2000; Woche et al., 2005), these observations have relevant implications for the mobility of colloidal particles. However, the majority of colloid transport experiments are conducted in hydrophilic solid matrices and ignore the effects of water repellency. Therefore, it is important to determine whether the mobility of typical soil colloids such as Fe oxides is likewise affected by hydrophobic attraction originating from soil water repellency.

Iron oxide colloids were selected for this study because, besides their relevance in soil-forming processes, their mobility is relevant in the context of contaminant transport and remediation approaches. This is due to the fact that Fe oxides have a high affinity for the adsorption of multiple contaminants such as heavy metals and radionuclides (Sätmark et al., 1996; Kretzschmar and Sticher, 1997; Novikov et al., 2006; Hassellöv and von der Kammer, 2008).

Since the effects of particle wettability on preferential flow effects and associated solute transport is widely investigated, in our study, we focused on saturated porous systems with respect to organic-matter-coated goethite (OMCG) colloid transport to account explicitly for particle–colloid interactions under the exclusion of liquid–air interfaces.

This led to the three hypotheses of this study: (i) OMCG colloids are subjected to stronger retention in hydrophobized quartz

sand than in hydrophilic sand, (ii) OMCG colloid retention increases with ionic strength in both hydrophilic and hydrophobic sand, and (iii) due to the relevance of surface wettability, the XDLVO approach is required to predict the mobility of OMCG colloids in the respective solid matrices, whereas the classic DLVO approach is insufficient. To test these hypotheses, column breakthrough experiments were conducted. Hydrophilic OMCG colloids were percolated through three types of solid matrix materials: hydrophilic quartz sand and two variants of sand hydrophobized via dichlorodimethylsilane (DCDMS) treatments. For each sand type, experiments were conducted at three ionic strength levels (0.91, 2.77, and 5.53 mM.) This ionic strength range covers the range commonly found in soils of nonarid tropical and temperate climate zones (Naidu et al., 1991). From physicochemical surface properties of the applied materials, DLVO and XDLVO interactions were estimated and compared.

## Materials and Methods

### Materials Applied for Column Experiments

Quartz sand (Carlo Bernasconi AG) was washed with HCl to remove surface impurities; both the sand and the cleaning procedure are described in detail in Carstens et al. (2017). Zeta potentials were calculated via Smoluchowski's equation (Elimelech et al., 1995) from electrophoretic mobility measurements of quartz colloids ground to  $<2 \mu\text{m}$  (ZetaPALS, Brookhaven Instruments Corporation). Details on the hydrophobization of quartz sand with dichlorodimethylsilane are given in the supplemental material.

Goethite colloids in powder form (specification Bayferrox 920 Z, Lanxess) were brought into suspension in ultrapure water with sonication (Bransonic 221 Ultrasonic Cleaner) and coated with dissolved organic matter (DOM; Pahokee peat fulvic acid standard II, International Humic Substances Society). The final concentrations in the OMCG colloid suspensions amounted to  $37.0 \text{ mg goethite L}^{-1}$ ,  $1.0 \text{ mg DOM L}^{-1}$ , and, depending on the experimental variant,  $\text{CaCl}_2$  at ionic strength levels of 0.91, 2.77, and 5.53 mM. Colloid zeta potentials were measured at each ionic strength (ZetaPALS). Particle sizes of the colloids were measured with dynamic light scattering (ZetaPALS) immediately after sonication and after 2 h. Scanning electron microscope (SEM) images of the dry, uncoated goethite powder were produced with a Fei Quanta 200 SEM.

### Breakthrough Experiments

The experimental setup for the plexiglass column flow experiments was identical to the one described in Carstens et al. (2017) and its supplemental data. In total, 18 column experiments were conducted (three variants of quartz sand at three ionic strength levels; each run was conducted in duplicate). For the column experiments, columns were filled with 27 g of sand to a height of 10 cm. To achieve full water saturation, the wet-packing method (Saiers and Hornberger, 1996) was applied. For that, columns were filled with ultrapure water prior to slow insertion of the sand

grains. Column experiments for the present study were conducted in three operational phases: (i) injection of  $\text{CaCl}_2$  solution with the respective ionic strength of the subsequent colloid pulse, (ii) injection of OMCG colloid suspension with different ionic strengths (i.e., 0.91, 2.77, and 5.53 mM  $\text{CaCl}_2$ ), and (iii) column rinsing with  $\text{CaCl}_2$  solution at the respective ionic strength. For the entirety of experiments, the total amount of injected colloids had a mean pore volume (PV) of 6.88 with a SD of 0.15 PV. The effluent was collected every 4.13 min with a fraction collector ( $\sim 0.46$  PV each). Velocities are given as pore flow velocities (Darcy flux divided by porosity). The mean pore water velocity of all experiments amounted to  $1.82 \times 10^{-4} \text{ m s}^{-1}$  with a SD of  $5 \times 10^{-6} \text{ m s}^{-1}$ . Effluent colloid concentrations were measured photometrically with an ultraviolet-visible Varian Cary 50 spectrophotometer. Details are given in the supplemental material.

### DLVO and XDLVO Interactions

The classic DLVO approach includes electrostatic and van der Waals interactions, to which Lewis acid–base interactions are added in the XDLVO approach. The method of calculation followed the description outlined in Goebel et al. (2013), who approximated XDLVO interactions between quartz sand and polystyrene microspheres. In brief, van der Waals and Lewis acid–base interactions between a solid surface and a colloid immersed in water can be approximated via the van der Waals and Lewis acid–base surface free energies. The basic principle is the interrelation of solid and liquid interfacial properties through the solid–liquid contact angle (van Oss et al., 1988). To calculate surface free energies, contact angles of solid surfaces must be determined with three different liquids (two polar, one apolar) that have known surface free energy components. For that, sessile drop method contact angle measurements were conducted using ultrapure water, glycerol, and iodobenzene. Electrostatic interactions were calculated from zeta potentials and solution ionic strength.

## Results and Discussion

### Properties of Sand Matrices and Colloids

The DCDMS hydrophobization treatment yielded strongly water-repellent sand surfaces, increasing the water contact angle from  $23.4 \pm 3.9$  to  $100.8 \pm 8.8$  and  $111.4 \pm 10.2^\circ$  for the applied DCDMS concentrations of 0.1 and 0.3  $\text{mL kg}^{-1}$ , respectively (given as mean  $\pm$  SD). Further results concerning contact angles, zeta potentials, and particle sizes for quartz sand and colloids are given in the supplemental material.

### OMCG Colloid Breakthrough in Hydrophilic and Hydrophobic Quartz Sand

Total OMCG colloid retention for the nine combinations of sand wettability and ionic strength is given in Fig. 1. Colloid breakthrough curves are given in Fig. 2, depicted as means and ranges of the duplicate experiments (breakthrough curves for each individual breakthrough experiment are shown in Supplemental

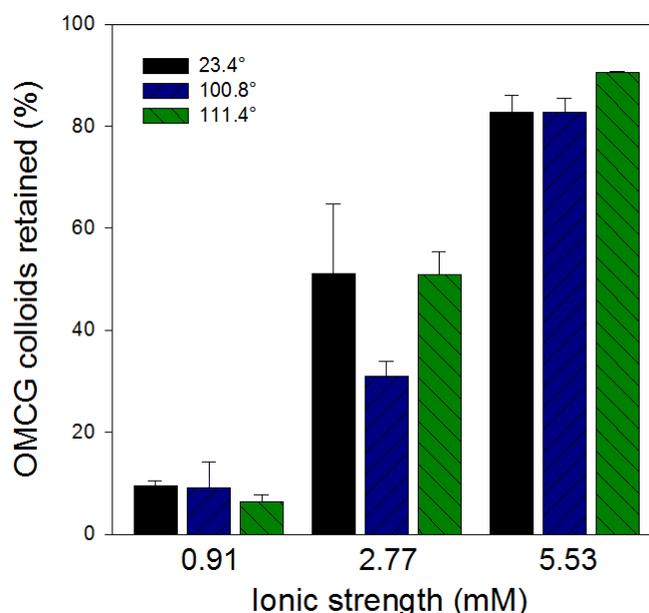


Fig. 1. Total amounts of organic-matter-coated goethite (OMCG) colloids retained in the columns, given as a percentage of the injected colloids. Results are shown for untreated quartz sand and the two dichlorodimethylsilane-hydrophobized variants of sand at the three applied ionic strength levels. Results are given as arithmetic means of two experiments; the bars denote the ranges.

Fig. S1). Neither early breakthrough (before 1 PV) nor long tailing of the colloid breakthrough was observed.

At 0.91 mM ionic strength, OMCG colloid retention amounted to  $9.5 \pm 1.0$ ,  $9.1 \pm 4.9$ , and  $6.3 \pm 1.4\%$  (in the order of decreasing sand wettability, given as means and ranges of the duplicates). There was a slight decrease in colloid retention with sand wettability, but the absolute differences in retention were too small to suggest a clear trend, especially with regard to the range of the  $100.8^\circ$  sand results. The high colloid mobility was probably caused by the negative zeta potentials of both the sand and colloids. These results are in agreement with previous studies showing that Fe oxide colloids coated with negatively charged adsorbants were highly mobile in negatively charged porous media (Kretzschmar and Sticher, 1997; Förstner et al., 2001; Tosco et al., 2012; Carstens et al., 2017).

At 2.77 mM, OMCG colloid retention ranged from  $51.1 \pm 13.6$  to  $31.0 \pm 3.0$  to  $50.9 \pm 4.5\%$ , in the order of decreasing sand wettability. Not only did the total retention show strong variation, but the ranges of the breakthrough curves were also considerably larger than those at 0.91 and 5.53 mM (Fig. 2). A statistical method was used to calculate the SD for the duplicate measurements of each wettability–ionic strength combination, according to Vermeulen (1953). For each combination, 23 pairs of measured  $C/C_0$  values were applied in this calculation method (details in the supplemental material). For the  $23.4$  and  $111.4^\circ$  sands, the SD was clearly higher at 2.77 mM than at the other ionic strength levels (Supplemental Table S4). For the  $100.8^\circ$  sand, the results also showed the highest SD at 2.77 mM

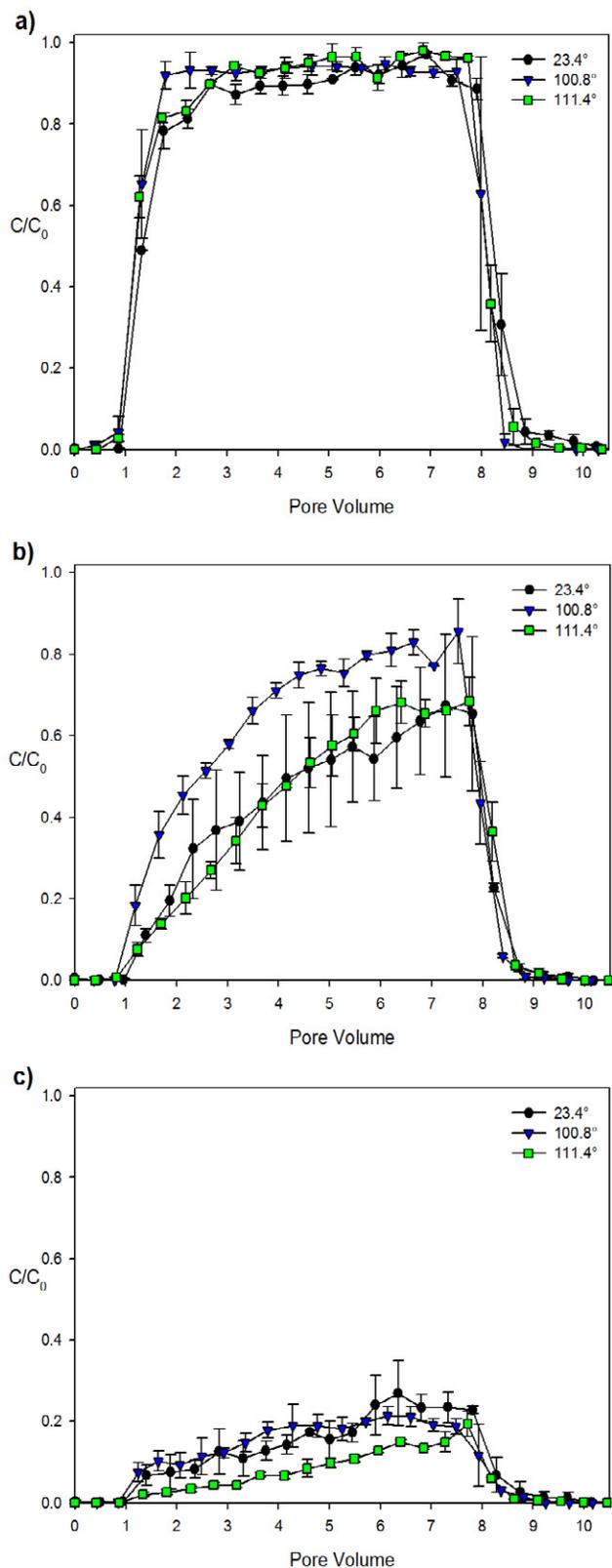


Fig. 2. Organic-matter-coated goethite (OMCG) colloid breakthrough curves at ionic strengths of (a) 0.91, (b) 2.77, and (c) 5.53 mM. The curves are shown for the three types of sand, denoted by the sessile drop method contact angle for water. Results are given as means calculated from the duplicate experiments, with the error bars indicating the value ranges. The  $y$  axis shows the effluent concentration divided by the input concentration ( $C/C_0$ ).

when two strongly differing pairs of values at the steeply ascending and descending slopes of the breakthrough curves at 0.91 mM were omitted. Although the variations were strongly related to the ionic strength level, there was no discernable relation to sand wettability, which is discussed below in the context of DLVO interactions. In fact, we have found a comparable pattern concerning goethite colloid breakthrough experiments at different DOM concentrations: whereas colloid breakthrough was highly reproducible at 0.0 and 1.0 mg DOM L<sup>-1</sup>, results varied widely at intermediate DOM concentrations (Carstens, unpublished data, 2017). Furthermore, the clear increase of colloid retention with ionic strength (Fig. 1) confirmed our second hypothesis and was well established by previous research on colloidal Fe oxides such as hematite and ferrihydrite (Kretzschmar and Sticher, 1997; Kuhnert et al., 2000; Tosco et al., 2012) and other colloid types, such as polystyrene microspheres (Goebel et al., 2013).

At 5.53 mM, OMCG colloid retention decreased from  $82.9 \pm 3.2$  to  $82.8 \pm 2.8\%$  and then increased to  $90.6 \pm 0.2\%$ , in the order of decreasing sand wettability. The last value may indicate slightly increased retention at the lowest wettability and the highest ionic strength. However, we did not consider this slight increase sufficient to prove our first hypothesis that decreasing wettability increases colloid retention for the following reasons: (i) at 5.53 mM, there was almost no difference in colloid breakthrough between 23.4 and 100.8° sands, despite the considerable difference in wettability as compared with the smaller difference between 100.8 and 111.4° sands; (ii) colloid retention slightly decreased with wettability at 0.91 mM; (iii) there were fluctuations of colloid breakthrough at the other ionic strength levels as well, especially at 2.77 mM; and (iv) the mean retention in the three sand types (for all ionic strength levels combined) amounted to 47.8, 40.9, and 49.3%, given in the order of decreasing sand wettability. Hence, the difference in retention between the most and least wettable sand is negligible (the retention in the 100.8° sand is lower due to the stronger colloid breakthrough at 2.77 mM).

Despite the considerable decrease of quartz sand wettability by the DCDMS treatments (Supplemental Table S1), there was no clear effect on breakthrough behavior of OMCG colloids. This result clearly shows us that OMCG colloid breakthrough behavior was in disagreement with the stronger retention of polystyrene microspheres in hydrophobized quartz sand than in hydrophilic sand (Goebel et al., 2013), which is discussed below in the context of XDLVO.

### DLVO and XDLVO Interactions Predictability of OMCG Colloid Retention with Classic DLVO

The basic trend that retention of OMCG colloids increased with ionic strength could be predicted with classic DLVO calculations. This was in agreement with previous research on OMCG colloids in quartz sand (Carstens et al., 2017) and other Fe oxide colloids (Ryan and Gschwend, 1994; Kuhnert et al., 2000; Tosco et al., 2012).

The width of energy barriers between OMCG colloids and sand surfaces clearly decreased with rising ionic strength, from 75 to between 38 and 27 nm (Fig. 3). Smaller energy barriers can lead to increased colloid retention at hetero-domains (i.e., favorable retention sites at which the energy barrier is absent due to surface charge heterogeneities and surface roughness) (Ma et al., 2011; Shen et al., 2012). Furthermore, the increasing ionic strength resulted in deeper secondary energy minima at higher ionic strength (Fig. 3). Secondary minima, which are caused by attractive van der Waals interactions that reach deeper into the bulk fluid than electrostatic repulsion, are known to increase colloid retention (Shen et al., 2012; Tosco et al., 2012; Goebel et al., 2013). Retention of OMCG colloids at 0.91 and 5.53 mM was relatively constant (Fig. 1 and 2), implying clearly unfavorable and favorable DLVO attachment conditions, respectively. In contrast, the stronger variations of colloid breakthrough at 2.77 mM (discussed above) may have been related to the intermediate magnitude of energy barriers and secondary minima at this ionic strength. We assume that, under the attachment conditions at 2.77 mM, the specific characteristics of the individual columns such as pore structures and pore velocity fields could have a higher effect on colloid mobility for this intermediate state between strong and weak adsorption vs. the more distinct attachment conditions at 0.91 and 5.53 mM.

Our third hypothesis was that the classic DLVO approach would be incapable of predicting OMCG colloid mobility, due to the pronounced differences in sand matrix wettability. However, as wettability did not clearly affect OMCG colloid mobility, the classic DLVO approach was sufficient.

It was notable that, at each ionic strength level, the magnitude of the secondary minimum varied for the three types of sand (Fig. 3). The deepest secondary minima were approximated for the 100.8° sand, which had the strongest van der Waals energy (Supplemental Table S1) and therefore the strongest attractive van der Waals interaction energy component of the three sand types. Standard deviations for the contact angle measurements, from which van der Waals interactions were calculated, were relatively high (Supplemental Table S1). Thus, variations in van der Waals interactions between the sand types may be overestimated. In agreement with that, the variations in secondary minima depth were generally not reflected in the breakthrough experiment results. A possible exception was the stronger OMCG colloid retention for the 100.8° sand than with the other sand types at 2.77 mM. However, this pattern was absent at 0.91 and 5.53 mM (Fig. 1). Furthermore, the similar colloid breakthrough in wettable and hydrophobized sand indicated that any potential changes in quartz sand zeta potentials caused by the DCDMS treatment, which could not be measured directly due to the large particle diameter, were likely to be small.

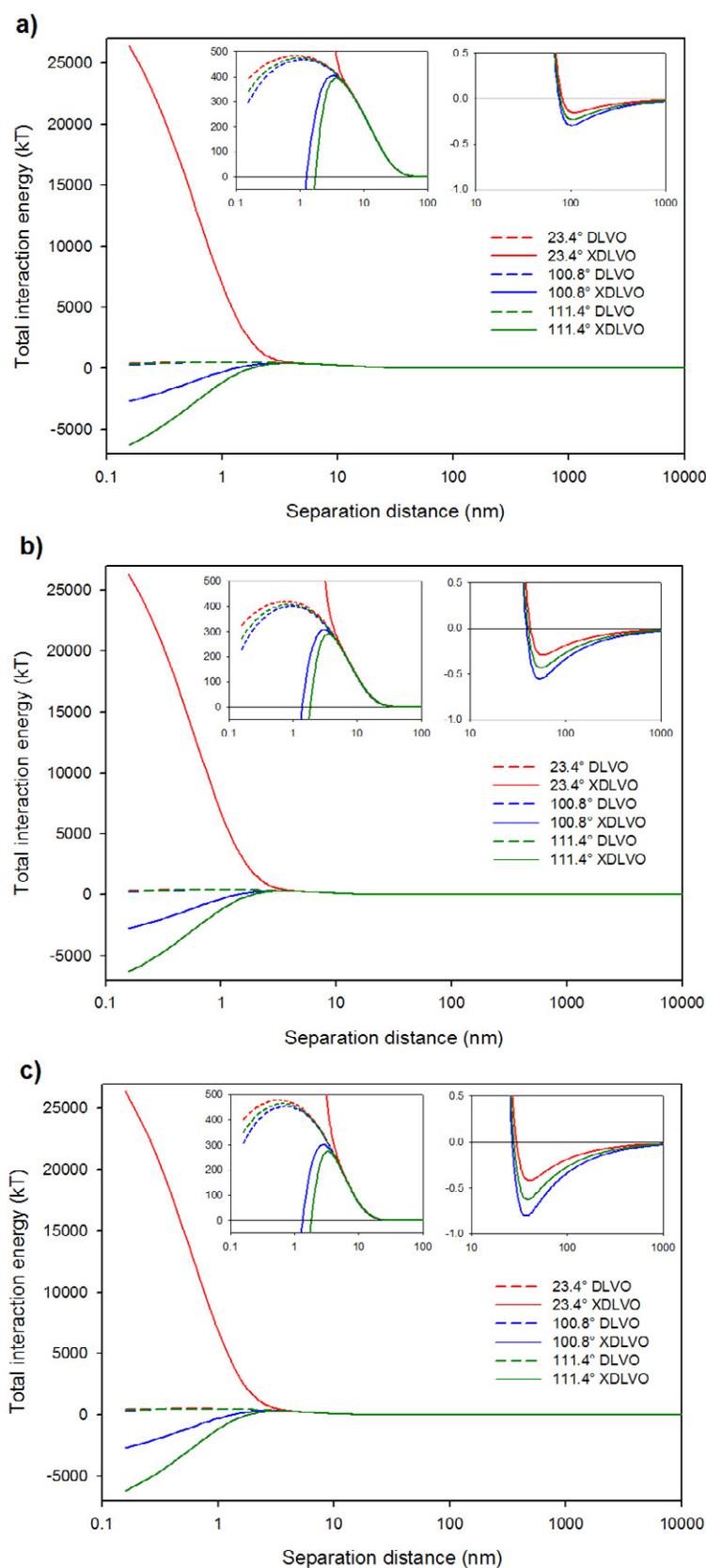


Fig. 3. Total Derjaguin–Landau–Verwey–Overbeek (DLVO) and extended DLVO (XDLVO) interaction energies at ionic strength levels of (a) 0.91, (b) 2.77, and (c) 5.53 mM for three types of quartz sand (water contact angles of 23.4, 100.8, and 111.4°).

## Predictability of OMCG Colloid Retention with XDLVO

The Lewis acid–base interaction energies estimated with the XDLVO approach led to substantial short-range ( $\sim 5$  nm) modifications of the classic DLVO interactions (Fig. 3). The acid–base interactions were considerably stronger than electrostatic and van der Waals interactions, in agreement with previous research (van Oss et al., 1990; Goebel et al., 2013). For a potential extension of DLVO with steric interactions, see the supplemental material.

Between the hydrophilic quartz sand and OMCG colloids, Lewis acid–base interactions were strongly repulsive at each ionic strength. Therefore, the energy barriers predicted with the classic DLVO approach were significantly increased with the XDLVO approach (Fig. 3). As both approaches predicted unfavorable attachment conditions, they were in agreement with the colloid breakthrough behavior at 0.91 mM ionic strength. The probable reasons for increased colloid retention at 2.77 and 5.53 mM, despite the presence of energy barriers, were discussed above in context of the classic DLVO approach.

For the two variants of hydrophobized sand, the XDLVO approach showed that Lewis acid–base interactions were attractive at each ionic strength, leading to short-range primary energy minima (Fig. 3). This effect was more pronounced for the more strongly hydrophobized sand. However, hydrophobization did not affect OMCG colloid transport and retention (see above, Fig. 1). Presumably, the short-range primary energy minima could not exert an influence due to the fact that substantial energy barriers remained between the surfaces. These considerations are in agreement with van Oss et al. (1990), who examined the aggregation behavior of hectorite colloids across a gradient of NaCl concentrations. At ionic strength levels considerably higher than in the present work ( $>200$  mM), electrostatic repulsion became weaker than hydrophobic attraction. This led to aggregation of the hectorite colloids. However, at ionic strength levels comparable with those in our work, short-range attractive hydrophobic interactions between hectorite colloids did not affect flocculation behavior, as electrostatic energy barriers remained between the negatively charged colloids.

In Goebel et al. (2013), XDLVO interaction energies between hydrophilic carboxylated polystyrene microspheres and untreated, as well as DCDMS-hydrophobized, sand (sessile drop method contact angle =  $112^\circ$ ) were calculated. Several results were in accordance with the present work: (i) energy barriers were present between colloids and both types of solid matrices, and (ii) the XDLVO approach predicted strong short-range repulsive interactions between colloids and hydrophilic sand, as well as strong short-range attractive interactions. However, their column breakthrough experiments led to the result that, although there was almost no retention in hydrophilic sand, the microspheres were retained in significant amounts in the hydrophobic sand, particularly at higher ionic strength. This retention occurred despite the fact that energy barriers remained between microspheres and quartz sand. The authors suggested that microspheres may have

overcome the energy barriers by wedging at grain-to-grain contacts or due to the presence of surface charge heterogeneities on the sand grains that led to the local absence of energy barriers. Subsequently, colloids could be retained in the primary energy well originating from the hydrophobic attraction. In contrast, Crist et al. (2005) reported no effect of solid matrix wettability on the mobility of hydrophilic microspheres; Goebel et al. (2013) explained the difference by their use of strongly hydrophobic sand (water contact angle =  $112^\circ$ ), whereas Crist et al. (2005) mixed water-repellent sand with hydrophilic sand at a ratio of 1:250.

The strong retention of microspheres in hydrophobic sand reported by Goebel et al. (2013) stood in marked contrast with the transport behavior of OMCG colloids in a comparable sand matrix in the present study. Hence, the question arose as to why microspheres were affected by short-range hydrophobic attraction with quartz sand, whereas OMCG colloids were not. A possible explanation is the difference in colloid surface roughness. Whereas polystyrene microspheres have almost perfectly smooth surfaces, goethite particles have very irregularly shaped surfaces, as seen in SEM images of the colloids applied in the present work (Fig. 4a and 4b).

Surface roughness is known to exert a strong influence on DLVO interaction energies. The DLVO energy calculations involving uneven instead of smooth surfaces show strong interaction energy profile deviations; both energy barriers and energy wells can be enhanced or removed (Shen et al., 2012). Furthermore, the distance between an approaching colloid and a rough surface is, on average, greater than with a smooth surface. Hence, the effects of near-surface interaction energies are reduced with increasing surface roughness (Hoek and Agarwal, 2006). This is likely to have meaningful implications for our study, as XDLVO energies show attractive interactions between OMCG colloids and sand to occur at very close separation distances less than  $\sim 2$  nm. For comparison, the surface topography analysis of one of the smoothest goethite surfaces found in nature still revealed surface roughness of 1.37 nm on the planar level (Ghose et al., 2010). Moreover, it was reported that, even under electrostatically favorable attachment conditions, the nano-roughness of positively charged goethite coatings on quartz sand was a hindrance for the retention of negatively charged carbon nanotubes. The goethite nano-roughness led to shallow primary minima susceptible to hydrodynamic or diffusive colloid removal (Zhang et al., 2016). With these considerations, it can be assumed that the near-surface attractive interaction energies could affect the almost perfectly smooth surfaces of polystyrene microspheres in Goebel et al. (2013), but they did not feature significantly for the rough, irregularly and needle-shaped shaped colloids in our study.

## Conclusions

Organic-matter-coated goethite colloids were percolated through three types of saturated quartz sand matrices with decreasing surface wettability, each at three different ionic strength levels. The results elucidated that colloid transport and retention,

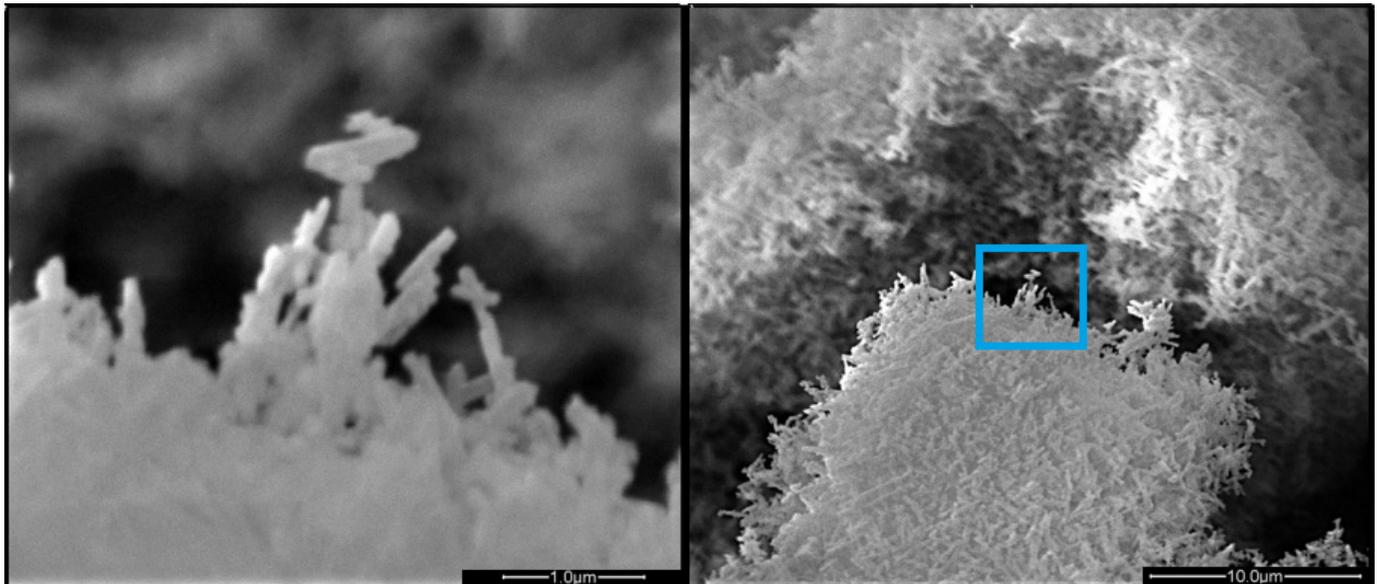


Fig. 4. Scanning electron microscopy (SEM) images of (a) goethite colloids (shown is the edge of an aggregate in dry powder before it is brought into suspension by sonication), and (b) an overview at a lower magnification. The blue box depicts the colloids shown in image (a).

although strongly affected by ionic strength, were not clearly modified by solid matrix wettability, which was against our expectation.

The classic DLVO approach was capable of predicting the higher colloid retention at increasing ionic strength in the form of decreasing energy barriers and deeper secondary minima. The XDLVO approach included Lewis acid–base interactions and thus took the differences in solid matrix wettability into account. That the deep primary energy wells predicted between hydrophobized sand and OMCG colloids did not affect colloid mobility behavior was probably due to the fact that energy barriers were still present.

These results were in marked contrast with a previous study, which showed that polystyrene microspheres were strongly retained in a hydrophobic sand in the presence of energy barriers. The retention was suggested to be due to local gaps in the energy barrier that permitted microsphere association with primary energy wells. We assume that the discrepancies in microsphere and OMCG colloid retention behavior were related to surface roughness. Whereas microspheres had smooth surfaces, OMCG colloids were irregularly shaped, which we illustrated in SEM images of the colloids. As the attractive Lewis acid–base interactions were estimated to occur at separation distances of  $<2$  nm, the pronounced surface roughness of OMCG colloids probably rendered these near-surface interactions ineffective.

We conclude that, in contrast with polystyrene microspheres, the mobility of Fe oxide colloids representing a typical soil colloid type was not affected in a meaningful way by decreasing solid matrix wettability. Hence, the effect of soil water repellency on the mobility of soil colloids may not be as large as suggested by previous experiments with model microspheres. This is probably related to the fact that the surface roughness of Fe oxides considerably weakens the short-range attractive hydrophobic interactions. Presumably, comparable processes are relevant

for other typical soil colloids as well. A promising objective for future studies would be to apply hydrophobic soil colloids (e.g., hectorite clay) in column flow experiments with a water-repellent solid matrix. In such a system, attractive hydrophobic interactions may be sufficient to overcome electrostatic energy barriers and thereby induce colloid retention. Further research should also focus on colloids that were similar in surface chemistry but different in surface roughness.

### Supplemental Material

The supplemental materials contains information on the applied materials (i.e. quartz sand and OMCG colloids). This includes the preparation method for hydrophobized sand, as well as contact angle and particle size data. Furthermore, details are given on the effluent measurements. All individual colloid breakthrough curves are presented (in the main manuscript, the mean of two replicate breakthrough curves is given for each experimental variant), and the calculation method for SDs for the breakthrough curves is described. Finally, a brief statement is given as to why it was not possible to include steric interactions in our DLVO and XDLVO approximations.

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