Super-hydrophobic powders obtained by froth flotation: properties and applications

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Super-hydrophobic materials offer a wide range of industrially relevant applications such as water-repellent construction materials, surface or textile coatings and oil sorbents. Hydrophobic modification of mineral particles is at the heart of the froth-flotation process. I show here that froth-floated fluorite crystals display super-hydrophobic properties: they form highly stable monolayers on flat and curved ("liquid marble") water surfaces, surround themselves with a gaseous plastron when submerged and selectively disperse and increase the density of oil in an oil–water mixture. I show that resuming the main steps of the flotation process using oleic acid functionalization provides an easy way to render low-solubility calcium salts (CaCO₃, CaF₂) hydrophobic. I study the potential of hydrophobic crystal monolayers to mitigate freshwater evaporation losses for water management: surprisingly, I find that even very compact, polydisperse crystal layers do not reduce water evaporation rates. I finally present a new method based on hydrophobic modification and X-ray scanning at an air–liquid interface to determine the cleavage planes of ground mineral powders with potential applications in mineralogy and catalysis.

Introduction

The production of durable, abrasion resistant, low-cost super-hydrophobic material and coatings is today one of the key challenges of materials science.¹ The most obvious application of super-hydrophobic materials is water repellency, which is of interest for clothing, building materials, paints, self-cleaning optics, to cite just a few applications. Other highly promising perspectives offered by these materials include viscous drag reduction² on watercraft, anti-icing,³ oil-spill remediation,⁴ water decontamination, anti-fouling⁴ and anti-corrosion effects.¹ Hydrophobic particulate materials have been the focus of considerable attention because powders have an increased surface-to-volume ratio compared to bulk material, thus reinforcing the interfacial effects characteristic of hydrophobic materials. The granular nature of powders adds further interesting physical properties to this material, such as the ability to flow and mold itself into the shape of its container, and porosity with respect to gases. Applications of hydrophobic powders include oil spill remediation,⁴,⁶–⁸ water filtration⁹,¹⁰ and decontamination, water-repellent filling material in areas that need to be protected from water infiltration or water freezing (e.g., pipes, junction boxes). They are also sold as a toy (kinetic sand or magic sand) for educational purposes.¹¹ Because of their many promises and exotic physical properties¹²,¹³ a variety of methods have been described over the past decades to produce hydrophobic particles, ranging from silane vapor deposition on silica,¹⁴,¹⁵ polystyrene⁶⁰ or lycopodium¹¹ particles to carbon-functionalization of zeolite ash.²⁷

Hydrophobic modification of mineral particles is at the heart of the froth flotation process (Fig. 1), an industrial technique developed to separate minerals from their gangue.¹⁸ In the first step of froth flotation, the raw ore is ground and mixed with surfactants that selectively adsorb to the mineral particles that one wishes to separate. After surfactant adsorption, gas is injected in the ore-surfactant slurry; the hydrophobic particles adhere to rising air bubbles and concentrate at the liquid surface, forming a froth, which is collected by skimming. The skimmed mineral powder obtained after froth flotation is, de facto, an intrinsically hydrophobic powder (lest the surfactant be removed after collection).

In the froth flotation process, hydrophobicity is a means (to separate the mineral) rather than an end in itself. This has led to the paradoxical situation that many recent surface chemistry papers¹⁴,¹⁷,¹⁹–²² describe how to produce hydrophobic low-solubility mineral particles by addition of surfactant without referring to the fact that these methods have been developed more than a century ago and are currently in use in the mining industry; in fact, froth-floated minerals constitute an abundant and economically interesting source of hydrophobic powders, because the flotation step is already integrated in the industrial process of these minerals. This situation is due in part to the lack of reports documenting the macroscopic hydrophobic behavior (marble formation, monolayer formation, bulk behavior of the powder in water, oil etc.) of mineral ores collected after froth flotation. In surveying the literature, I was...
also surprised to find that although magic (hydrophobic) sand has been used for decades for leisure and educational purposes, no scientific studies describe or explain the fascinating properties of this material. The main goal of this report is therefore to fill these gaps. I proceed by systematically comparing the wetting properties in water and oil of a non-floated, pure mineral (fluorite) to those of the same mineral collected after froth-flotation processing. I show that the main steps of froth flotation can easily be reproduced in the laboratory to produce hydrophobic powders. I then present two novel applications of hydrophobic powders: (1) their use as a tertiary to produce hydrophobic powders. I then present two novel froth-discuss my results concerning the hydrophobic properties of losses, (2) their use in mineralogy and catalysis to determine the self-assembled hydrophobic cover on water to limit evaporation steps of froth

Materials & methods

**ATR-IR**

Crystals were pressed against the ATR diamond (diameter: 6 mm, refraction index \( n = 2.4 \)) of a Vertex 70 (Bruker Optics) spectrometer equipped with a monoreflexion ATR MIRacle platform (Pike, US) and an MCT detector. The incidence angle was 45°; the penetration depth of the beam in CaF\(_2\) (\( n = 1.43 \)) ranges from 1 to 10 \( \mu m \) for the wavelengths shown in Fig. 2a.

**SEM**

A small amount of powder was dispersed on metal tape on an aluminium SEM holder. The holder was then gently tapped to remove excess powder. The samples were next electropolated with a conductive carbon layer. Scanning electron microscopy images were acquired on a JEOL JSM-6510 instrument, at 10–15 kV acceleration voltage, secondary or backscattered electron images were collected.

**X-Ray powder diffraction**

For standard powder analysis, a small pellet of powder was pressed in a cylindrical hole (~1 cm diameter, 3 mm deep). For the determination of cleavage planes, the minerals were first dispersed at the air-liquid (glycerol) interface as described in [28]. Samples were then analyzed on a Siemens D5000 diffractometer in \( \theta-2\theta \) mode with an angular step \( \Delta \theta = 0.01^\circ \).

**Contact angle measurement**

A small amount of mineral powder was deposited and flattened on a piece of double-sided scotch tape with a spatula. The layer was made thick enough that the deposited droplets did not contact the underlying scotch tape. A 10 \( \mu L \) water drop was thereafter deposited on the powder layers. I was unable to deposit less than 10 \( \mu L \) on the floated powders because smaller drops adhered to the pipette cone rather than to the powder film. Contact angles were measured with ImageJ. On non-treated synthetic powders (CaCO\(_3\) and CaF\(_2\)), the drop completely wetted the powder layer (\( \theta = 0^\circ \)).

**Surface functionalization of CaF\(_{2}\) and CaCO\(_3\) salts**

The ratio of oleic acid to mineral mass was determined by estimating the surface-to-volume ratio of the crystals based on their average size (~10 \( \mu m \), see Fig. 5). 2 g of precipitated CaF\(_2\) (Sigma, 99% purity, ref. 01123) or CaCO\(_3\) (Sigma, ref. 398101) was dispersed in 50 mL NaOH solution, pH 11, to which either 1 \( \mu L \) (oleic acid to mineral mass ratio 0.44 \( \mu g \) g\(^{-1}\)) or 10 \( \mu L \) (ratio 4.4 \( \mu g \) g\(^{-1}\)) of oleic acid (Sigma) was added. At pH 11, the carboxylic acids of the oleic acid are deprotonated and can bind to calcium at the mineral surface. The mineral, lye and oleic acid solution was next stirred for 30 min; the solution was then filtered and the mineral powder dried on a 50 °C plate for 6 hours. At higher oleic acid to mineral mass ratios (44 \( \mu g \) g\(^{-1}\)), a significant amount of soap (calcium oleate) also formed and could not be dissociated from the rest of the calcium carbonate powder.

**Evaporation rate measurements**

4 circular Petri dishes, 14 cm in diameter and initially filled with 80 g of tap water, were placed at room temperature and subject to a light, uniform breeze (air conditioning). Two samples were covered with a monolayer of CaF\(_2\) (geological origin, froth floated) by sprinkling and blowing the powder on the liquid surface until it formed a dense layer. Excess powder was blown away from the interface. Evaporation was compared with that...
from a bare water interface (two samples). The mass of water in each dish was measured at different time intervals.

**Results**

I examined two fluorite samples: (1) fluorite originating from a geological source, which had an orange hue and had been isolated by froth-flotation, hereafter referred to as CaF$_2$,$\text{f}$ (2) pure synthetic fluorite, hereafter referred to as CaF$_2$,$\text{s}$, a white powder obtained from the precipitation of NaF and CaCl$_2$. I first present a brief chemical and morphological analysis to characterize each sample type, and then describe and quantify their wetting behavior.

**Chemical and morphological characterization of synthetic and froth-floated fluorite crystals**

ATR-IR spectra and scanning electron microscopy of CaF$_2$,$\text{s}$ and CaF$_2$,$\text{f}$ are shown in Fig. 2. ATR-IR (Fig. 2a) shows that CaF$_2$,$\text{f}$ contained traces of quartz (peaks around 600–1300 cm$^{-1}$) and CaF$_2$,$\text{s}$ crystals were relatively uniformly sized cubes with well-defined, sharp edges and smooth (100) faces (Fig. 2b, top panels). CaF$_2$,$\text{f}$ crystals were strongly polydisperse and their crystalline habit could not be identified morphologically (Fig. 2b, bottom panels). Big (~50–100 μm) CaF$_2$,$\text{f}$ appeared covered with small (~5–10 μm) adhering CaF$_2$,$\text{s}$ particles (Fig. 2b, bottom, inset), yielding an overall “bushy”, rough
morphology. XRD powder diffraction spectra of CaF$_{2,\text{ff}}$ and CaF$_{2,s}$ sample were identical to that of pure CaF$_2$ as reported in the Minicryst database$^{25}$ (data not shown).

**Froth-floated fluorite is ultra-hydrophobic and oleophilic**

Fluorite is almost insoluble in water ($K_d = 3.9 \times 10^{-11}$). Like most insoluble ionic salts, CaF$_{2,s}$ dispersed when mixed with water, resulting in a white, turbid solution which became clear as the crystals sedimented. In contrast, when I dipped a spoonful of CaF$_{2,\text{ff}}$ (Fig. 3a) in water, the powder dropped to the bottom of the container as one cohesive block (Fig. 3c); it did not disperse. I could easily deform this block to any desired shape.

When I removed the block of powder from water, it was dry (Fig. 3d). As the CaF$_{2,\text{ff}}$ powder crossed the interface, a significant fraction remained at the water surface, forming a “skin” (Fig. 3b). The block of powder submerged in water had a metallic shine (Fig. 3c) due to total internal reflection of light, indicating that the powder was surrounded by a film of gas. When the film of gas was destabilized by boiling the solution or by vacuum pumping, the CaF$_{2,\text{ff}}$ particles dispersed in the solution. This shows that it is the air entrained by the particles as they cross the air–water interface that is responsible for the cohesion of the powder block in water; the fluorite particles in the submerged block are not directly in contact with water. I quantified the wettability of both fluorite types by measuring the contact angle of water drops on films of powder (Fig. 3e, Materials & methods). I found contact angles of $\sim 156 \pm 4^\circ$ ($n = 5$ drops, ±SD) for CaF$_{2,\text{ff}}$. On CaF$_{2,s}$, water drops completely wetted the powder substrate. As the contact angle of water on froth-floated CaF$_2$ exceeds 150$^\circ$, it qualifies as an ultra-hydrophobic material. CaF$_{2,\text{ff}}$ crystals could wrap themselves around spherical water droplets (“armored drop” or “liquid marble”$^{12,13}$) and stabilize them even after they were transferred on a hydrophilic (metallic) substrate (Fig. 3f). I further measured capillary rise in small cylindrical pillars of compressed synthetic and floated CaF$_2$: whereas water quickly rose in the CaF$_{2,s}$ column, I did not observe any capillary rise in the CaF$_{2,\text{ff}}$ sample (Fig. 3g).

I further examined the behavior of CaF$_{2,s}$ and CaF$_{2,\text{ff}}$ in binary oil:water solutions (Fig. 4a). After agitation, the synthetic CaF$_{2,s}$ crystals remained in the water phase and gradually sedimented to the bottom of the container. For CaF$_{2,\text{ff}}$–oil–water ternary mixture, the phase diagram depended on the mineral particle concentration. At low mineral-in-oil concentrations ($0.09 \text{ g mL}^{-1}$), CaF$_{2,\text{ff}}$ concentrated and dispersed in the oil phase on top of the water, coloring it orange. When the quantity of CaF$_{2,\text{ff}}$ was high enough ($0.16 \text{ g mL}^{-1}$), a fraction of the oil phase sank because the density of the oil–CaF$_{2,\text{ff}}$ slurry had exceeded that of water. I found that most ($\sim 95\%$) of the oil sank at mineral concentrations of $0.29 \text{ g mL}^{-1}$ (Fig. 4a). The calculated average density of the oil–CaF$_{2,\text{ff}}$ slurry at this

![Fig. 3](image-url) (a–d) Behavior of froth-floated fluorite powder (CaF$_{2,\text{ff}}$) at the air–water interface, in water, and when removed from water. (e) Contact angle of a water drop ($10 \mu\text{L}$) on a pellet of CaF$_{2,\text{ff}}$. (f) A drop of water ($10 \mu\text{L}$) can be completely covered by CaF$_{2,\text{ff}}$ crystals (“armored drop” or “liquid marble”); this drop remains spherical even when put in contact with a hydrophilic (metal) substrate. (g) Compared capillary rise in pillars of froth-floated and synthetic fluorite. No rise occurs in the froth-floated sample.
Compared SEM images of the synthetic CaF$_2$ and CaCO$_3$ crystals deposited and are stable at a liquid interface (Fig. 7a and b) (2) –render the powder hydrophobic so that the crystals can be easily deposited at the air–water interface. Stabilization of the crystals at the air–water interface is facilitated by hydrophobic modification of the surface of the crystals (e.g., with fatty acid collectors as described above). This suggests a straightforward two-step procedure (Fig. 7) to determine the cleavage plane of any ground mineral powder: (1) surface modification to render the powder hydrophobic so that the crystals can be easily deposited and are stable at a liquid interface (Fig. 7a and b) (2) –θ–2θ XRD scan of the crystals at the liquid interface (Fig. 7c and d).

I have validated this method for ground froth-floated CaF$_2$,ff (Fig. 7d) and for ground CaCO$_3$,ff. After the hydrophobic particles are deposited at the air–water interface, the only remaining diffraction peak is (111) for CaF$_2$ and (104) for CaCO$_3$, i.e., the respective main cleavage planes of these minerals. I emphasize that for CaF$_2$, the cleavage plane could not have been determined from the mere examination of the morphology of the CaF$_2$ sample described above: the refined CaF$_2$,ff particles are polydisperse, so the gaps between large particles can be filled with smaller particles, making the monolayer very compact (see Fig. 6, inset). I measured that only ~6–7 g of CaF$_2$,ff crystals are required to cover a 1 m$^2$ liquid surface. Surprisingly however, I found that evaporation rates (see Materials & methods) were not affected by the presence of a compact crystal monolayer (Fig. 6). Average evaporation rates were 30.7 ± 0.1 mg s$^{-1}$ m$^{-2}$ for the bare surface and 30.8 ± 3.4 mg s$^{-1}$ m$^{-2}$ for the CaF$_2$ covered surface.

Can water evaporation rates be reduced by covering with a monolayer of hydrophobic particles?

Across the world, freshwater is valued as a critical natural resource. In countries subject to high seasonal contrast (Australia, India, Africa, etc.), freshwater lakes fill up during the rain season and are used as reservoirs during the dry season. Limiting evaporation loss of freshwater during the dry season is therefore a critical issue.$^{26}$ Several methods have been developed to mitigate freshwater evaporation rates, ranging from Langmuir monolayers,$^{27}$ to thicker chemical films or plastic covers that reduce the exposed surface. I showed (Fig. 2b) that hydrophobic froth-floated mineral particles form stable, micrometer thick films at the air–water interface. Being thicker (~1–10 μm) than monolayers (~10 nm), they are mechanically and chemically more stable with respect to wind, surface waves or UV/bacterial degradation. These particles spread naturally on the surface of water, making them readily applicable to large water reservoirs. A high surface coverage (>90%) can be achieved because the CaF$_2$,ff particles are polydisperse, so that large gaps between large particles can be filled with smaller particles, making the monolayer very compact (see Fig. 6, inset). I measured that only ~6–7 g of CaF$_2$,ff crystals are required to cover a 1 m$^2$ liquid surface. Surprisingly however, I found that evaporation rates (see Materials & methods) were not affected by the presence of a compact crystal monolayer (Fig. 6). Average evaporation rates were 30.7 ± 0.1 mg s$^{-1}$ m$^{-2}$ for the bare surface and 30.8 ± 3.4 mg s$^{-1}$ m$^{-2}$ for the CaF$_2$ covered surface.

The cleavage plane of minerals can be determined by θ–2θ XRD scans of froth-floated particles at the air–water interface

When a mineral is ground it breaks along its cleavage planes: the cleavage planes make up most of the physical surface of ground crystals. We have recently found that crystals deposited at the air–water interface are spontaneously oriented by surface tension forces so that their most extended physical surface lies parallel to the air–water interface. Stabilization of the crystals at the air–water interface is facilitated by hydrophobic modification of the surface of the crystals (e.g., with fatty acid collectors as described above). This suggests a straightforward two-step procedure (Fig. 7) to determine the cleavage plane of any ground mineral powder: (1) surface modification to render the powder hydrophobic so that the crystals can be easily deposited and are stable at a liquid interface (Fig. 7a and b) (2) θ–2θ XRD scan of the crystals at the liquid interface (Fig. 7c and d).
crystals (see Fig. 2b, bottom panel): this method therefore provides important, non-trivial information on the physical faces expressed in a ground powder.

**Discussion**

I showed that whereas synthetic CaF$_2$ displays the usual hydrophilic properties of an ionic salt, froth-floated CaF$_2$ behaves as a super-hydrophobic material. I documented several enthralling phenomena (Fig. 3 and 4) resulting from the combined granular and hydrophobic nature of this material, such as water drop stabilization, surface film formation, non-dispersibility and oil-densification in binary oil–water mixtures. I designed a simple oleic acid functionalization protocol inspired from froth flotation techniques to make synthetic fluorite and calcite crystals hydrophobic (Fig. 5). While the fact that froth-floated minerals are hydrophobic is not new, I could not find any reports documenting the macroscopic properties resulting from this simple surface treatment; furthermore, many authors report on CaCO$_3$ functionalization by fatty acids$^{4,15,20-22}$ without apparently being aware that the technics they describe are used in the froth-flotation process. One purpose of this work is therefore to refresh this fact to the community of scientist working on hydrophobic materials. Froth flotation, a technic which has been refined for over a century in the mining industry to separate mineral particles as a function of their affinity to different surfactants, provides
a straightforward industrial source of hydrophobic mineral powder. I finally examined two novel applications of hydrophobic powders to reduce water evaporation rates (Fig. 6) and determine the cleavage plane of mineral powders (Fig. 7).

Some investigators claimed that fluorite is an inherently hydrophobic mineral based on the fact that water contact angles of cleaved natural fluoride monocrystals (presumably the (111) face) reached up to 100°; in addition, molecular dynamics simulations showed that water is depleted in the vicinity of the (111) CaF₂ plane, which could explain this hydrophobicity. Upon compiling other values of contact angle measurements on native CaF₂, I found that most reported values fall in the range 20°–50°; they significantly differ from the contact angle of the freshly cleaved 104 face of CaCO₃ (θ ~ 50° (ref. 32)), a hydrophilic mineral. Based on my observations on the effects of minute amounts of surfactant, it is possible that some of the very high contact angles of water on cleaved geological fluorite measured by Zawala et al. may be due to contamination or adsorption of organic material. My observations do not support the view that fluorite is inherently a hydrophobic mineral, because the pure synthetic CaF₂ crystals displayed hydrophilic properties.

Laborie et al. recently reported results on the use of monodisperse micrometric hydrophobically functionalized polystyrene particles to limit water evaporation rates; they found that a single particle layer did not modify the evaporation rate, similarly to what I found here using polydisperse hydrophobic fluorite crystals (Fig. 6). This behavior is due to the fact that the water vapor concentration profile above holes (spaces between crystals) is 3D, contrary to the case of the bare surface, where the vapor profile is stratified (1D). Consequently, the evaporation rate per unit surface trough the micron-sized holes in the monolayer is higher than the average evaporation rate per unit surface of the bare interface; the resulting average evaporation rate through the particle monolayer ends up being ~equal to that of the bare interface. Achieving evaporation reduction on flat interfaces with hydrophobic particles would therefore require a complementary component like a binder to fill the gaps between the particles; the particles could also be added to existing polymer-based evaporation reduction liquids.

I presented a new method (Fig. 7) to measure the cleavage planes of a mineral. This method provides information on the physical faces expressed in a ground powder and could have important applications in mineralogy and catalysis. It will be interesting to test the methods on minerals where more than one cleavage plane is present. The liquid on which the particles are deposited could additionally be modified (e.g. ethanol, glycerol, oil) to optimize attachment of the particles at the interface and make it applicable to crystals that are soluble in water.

The unique properties of hydrophobic powders (granular, hydrophobic, high surface-to-volume, porous) will no doubt reveal more, as of yet unforeseen applications of this material.

Conflicts of interest

There are no conflicts to declare.
Acknowledgements

I thank Guillaume Wang (MPQ, Paris Diderot) for help with SEM sample preparation, SEM image acquisition and analysis, Hélène Bouquerel (IPGP) for assistance in performing the sieve analysis, Pascale Chenevier (CEA) for providing fluoride samples, Patrick Guenoun (CEA) and Corinne Chevallard (CEA) for access to the X-ray diffractometer and ATR-IR spectrometer, Vincent Fleury (MSC) and Ameya Murukutla (CRI, Paris) for discussions on applications of hydrophobic powders.

Reference


24 http://lisa.chem.ut.ee/IR_spectra/paint/ﬁllers/quartz/


