

Specific surface free energy component distributions and flotabilities of mineral microparticles in flotation—An inverse gas chromatography study



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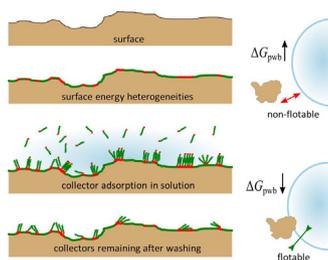
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HIGHLIGHTS

- Mineral microparticle surfaces exhibit heterogeneous surface free energies.
- Wettability heterogeneities are well characterized by inverse Gas Chromatography.
- Surfactants have most effect on and reduce the high energy sites of surfaces.
- Surface area fraction relevant to render a surface flutable is less than 1%.
- Energy-of-interaction vs. flutability correlate stronger at small fractional area.

GRAPHICAL ABSTRACT



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ABSTRACT

In fundamental flotation studies often the contact angle with water is used to describe wettability of a mineral surface and it is correlated with flutability. A more fundamental parameter however is the specific surface free energy related to the contact angle via Young's equation. Inverse gas chromatography (iGC) has recently been proven to be a suitable method to determine specific surface free energy components and their distributions of particulate surfaces. In this study the pure minerals quartz (SiO_2), fluoro-apatite ($\text{Ca}_5[\text{F}(\text{PO}_4)_3]$), and magnetite (Fe_3O_4) are examined for flotabilities and surface energy component distributions considering different methods of sample treatment and the effect of the collectors sodium oleate and dodecyl ammonium acetate. The parameter of specific net free energy of interaction between bubbles and particles immersed in water ΔG_{pwb} resulting from the complex surface energy analyses is introduced and used to evaluate the hydrophobicity of the mineral surface in correlation to microflotation recoveries. The results lead to the hypothesis that only small fractions of the surface and their change of wettability by flotation reagent adsorption will inherently define the flutability of minerals. Consequently, the main purpose of the amphiphilic collector molecules seems to be the reduction of high specific surface free energies of small fractions of the surface that lead to a strong attraction between particle surface sites and water molecules rather than the hydrophobization of the entire mineral surface, a new paradigm in flotation science.

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1. Introduction

Flotation is a well-established and widely used separation process in minerals engineering and recycling. Nevertheless, scien-

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tifically, the complex synergistic and antagonistic micro processes are underlying ongoing research and controversial discussions [1–7]. Since flotation is a separation method based on the different wettabilities of the particles to be separated, many researchers have been looking for functions of the flotation recovery and contact angles against water as a parameter to account for wettability [1,8–10]. However, the determination of particle wettability is not a straight forward task as classic sessile drop contact angle determinations or the captive bubble method should be avoided on powder samples for the porosity and roughness effects are typically not assessable and penetration methods like the Washburn method are very much structure dependent [11–13]. Furthermore does the sole determination of a contact angle between a surface and the polar solvent water not allow for the description of the surface wettability, as specific and aspecific interactions need to be distinguished [14–17]. Consequently, two surfaces with the same water contact angle can actually be very much different with respect to their hydrophobicity [18]. We apply the relatively new but established method of inverse gas chromatography iGC [19–23] which is capable of describing the wettability of solids by determination of the specific surface free energies of minerals in flotation as has been presented by Mohammadi-Jam [24] recently.

The total specific surface free energies of the interfaces (solid (s) or liquid (l) in gas) in a three phase contact γ^t are related to the contact angle by Young's equation in Eq. (1) [18]. The total specific surface free energy is by assumptions of additivity [14,25] a sum of the disperse interactions γ^d and the quadratic mean of the Lewis acid/base interactions γ^+/γ^- , respectively. Consequently, the contact angle is not the immanent physical parameter of wettability (i.e. hydrophobicity or hydrophilicity) as shown in Eqs. (1) and (2).

$$\gamma^t = \gamma^d + 2 \cdot \sqrt{\gamma^+ \cdot \gamma^-} \quad (1)$$

$$\gamma_{s,l}^t = \gamma_s^t + \gamma_l^t - 2 \left(\sqrt{\gamma_s^d \cdot \gamma_l^d} + \sqrt{\gamma_s^+ \cdot \gamma_l^-} + \sqrt{\gamma_l^+ \cdot \gamma_s^-} \right) \quad (2)$$

To thermodynamically evaluate whether the particle-bubble contact in water (pwb) is favorable, the specific free energy of interaction ΔG_{pwb} as introduced by van Oss is calculated following Eq. (3) [18].

$$\begin{aligned} \Delta G_{pwb} = & \left(\sqrt{\gamma_p^d} - \sqrt{\gamma_b^d} \right)^2 - \left(\sqrt{\gamma_p^d} - \sqrt{\gamma_w^d} \right)^2 \\ & - \left(\sqrt{\gamma_b^d} - \sqrt{\gamma_w^d} \right)^2 + 2 \cdot \left[\sqrt{\gamma_w^+} \left(\sqrt{\gamma_p^-} + \sqrt{\gamma_b^-} - \sqrt{\gamma_w^-} \right) \right. \\ & \left. + \sqrt{\gamma_w^-} \left(\sqrt{\gamma_p^+} + \sqrt{\gamma_b^+} - \sqrt{\gamma_w^+} \right) - \sqrt{\gamma_p^+ \gamma_b^-} - \sqrt{\gamma_p^- \gamma_b^+} \right] \quad (3) \end{aligned}$$

The more negative ΔG_{pwb} the stronger the hydrophobic effect and the more favorable for the particle to form a three phase contact with a hyper-hydrophobic gas bubble when dispersed in water as

depicted in Fig. 1. This approach is similar to the investigations of Holysz and Chibowski [16] where they used the parameter of work of water spreading onto the mineral surface.

Consequently, there should not be a search for the relation of flotation response (recovery of hydrophobic particles) based on the parameter of contact angle with water but rather the net energy of interaction between a bubble and a particle immersed in water taking the specific surface free energy components into account.

The iGC method not only allows for determining the specific surface free energy components of the entire powder surface but can also determine the heterogeneity of surface energies by detecting the specific surface free energy over the fraction of particle surface coverage [19,26]. Hence it can be investigated if e.g. the high energy surface sites at heterogeneities are responsible mainly for hydrophilicity/hydrophobicity because these sites will primarily be covered with collectors when conditioning with flotation reagents.

One drawback of iGC for flotation studies is that the measurement takes place on dried powders but flotation is characterized by particle bubble interactions in a pulp. Therefore we investigated how the preparation of the mineral particles, after collector conditioning to achieve a dry powder, influences both the flotation response after resuspending and the specific surface free energy results of iGC. We tested washing the collector covered minerals with water only and with water and subsequent acetone before drying in an oven at 50°C. We furthermore look at collectors with chemical or physical adsorption mechanisms. The minerals chosen are pure minerals of fluoro apatite $\text{Ca}_5(\text{F},\text{PO}_4)_3$ (APA), magnetite Fe_3O_4 (MAG) and quartz SiO_2 (QRZ). The collectors are the anionic sodium oleate (NaOl) and the cationic dodecyl ammonium acetate (DDAA). It is well known that NaOl is chemisorbed by calcium-oleate precipitation on apatite under basic conditions whereas DDAA is physisorbed [27–29]. Chemisorption also takes place for NaOl and magnetite by covalent binding to ferric ions on the magnetite surface [30]. For quartz and DDAA physisorption of the cationic collector on the negatively charged surface at close to neutral pH is the presumed mechanism of interactions [31]. We have not found a reference in the literature testing the washing effect on the remaining particle surface wettability.

The direct comparison of iGC results and flotation has so far only been reported by the McGill group of Kristian Waters by Ali [19] and most recently by Mohammadi-Jam [21,24]. Mohammadi-Jam presented a conclusive study on the wettability of pyrite and a correlation of flotability and the work of adhesion, a similar parameter like the free energy of interaction ΔG_{pwb} used here. However they did not focus on the effect of the fractional coverage of the probe molecules of the iGC measurement, which would show surface energy distributions and thus changes in heterogeneity. The unique point of this work therefore is to shed light on the heterogeneity of surface energy components with respect to floatabilities of minerals.

As a result of this study of surface free energy components distributions we present the hypothesis that the collector molecules'

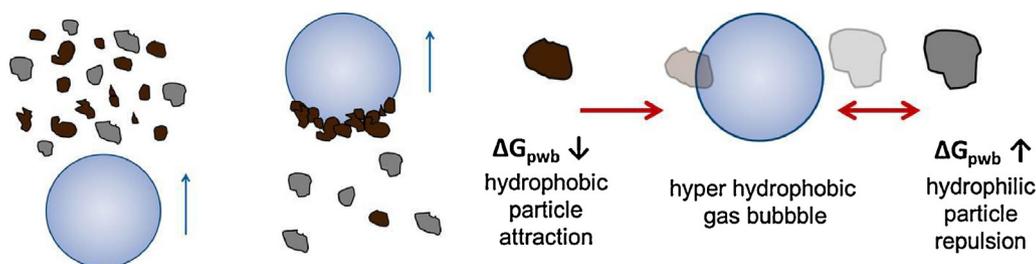


Fig. 1. (left) Schematic of a rising gas bubble picking up hydrophobic brown particles leaving behind the hydrophilic gray gangue, (right) schematic presentation of hydrophobic attraction and repulsion for negative and positive free energy of interaction, respectively, of a particle interacting with the hyperhydrophobic bubble in water.

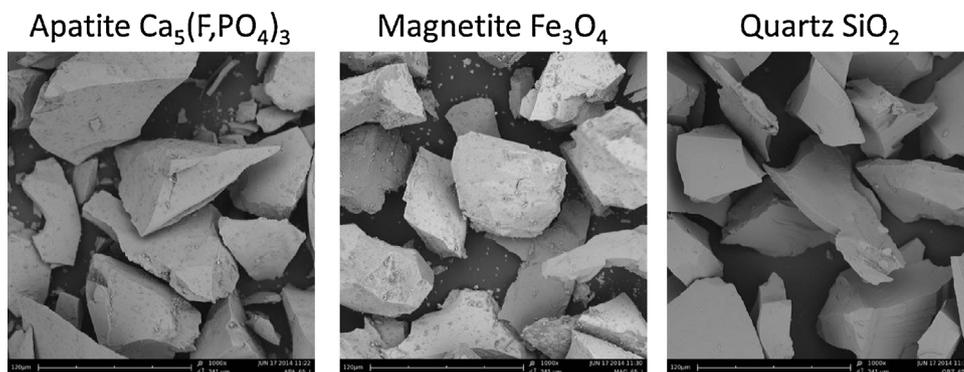


Fig. 2. Back scattered electron scanning electron micrographic images of the crushed and milled minerals used in this study (before ultrasonication and filtration) showing irregular shapes with sharp edges and for apatite and magnetite adhering very fine material.

main purpose is to reduce the small area fractions of high energy surface sites of naturally hydrophilic mineral particles which lead to a strong particle-water attraction. Intriguingly, only a small fraction of the naturally heterogeneous surface of mineral particles is relevant for a particle to attach or not attach to a bubble and thus be floatable or not. This is similar to the discussions by Ho et al. in [32] when they were looking at the relation of surface energy distributions, as defined by Thielemann et al. [33], on the crystal shape and effect of milling of D-mannitol crystals.

2. Materials and methods

2.1. Minerals and chemicals

The minerals used are pure large crystalline samples of fluoro apatite and magnetite from Minas Gerais, Brazil and quartz from Madagascar. They were crushed using a lab jaw crusher (Fritzsche, Germany), milled in a continuous screen outlet lab ball mill with a 500 mm sieve (FIA, Germany) and lab sieved to achieve a fraction between 71 μm and 100 μm (quadratic openings). The hard and abrasive quartz mineral particles have been washed with 1N HCl to remove iron impurities after milling. In Fig. 2 back scatter electron micrographs are being presented showing fine adhering particles both on the surfaces of apatite and magnetite. Because they are appearing in a similar gray scale it can be assumed that these are fine apatite or magnetite particles, respectively.

To investigate the effect of the fine adhering particles we prepared additional samples of all particles after ultrasonication (US) of water based suspensions in a bath and subsequent filtration and drying before conditioning, microflotation and iGC.

The following Table 1 shows measured granulometric properties of the minerals, namely the volumetric mass density using gas pycnometry (Micromeritics), the mass specific surface areas by the BET N_2 -adsorption method (Micromeritics) and particle sizes of the distributions determined with laser diffraction (Sympatec HELOS). The densities show classic literature range values of the respective minerals. It is noticeable that the specific surface area is very high

Table 1

Granulometry of the mineral particles used, density ρ by gas pycnometry, specific surface area S_m with and without ultrasonication (US) and filtration by BET-method, particle sizes (10%, 50% and 90% quantiles) by wet laser diffraction.

mineral	ρ in g/cm^3	S_m in m^2/g		particle sizes in μm		
		pure	US	x_{10}	x_{50}	x_{90}
apatite (APA)	3.20	0.40	0.20	23.7	68.4	103.8
magnetite (MAG)	4.91	0.20	0.16	43.2	78.5	115.6
quartz (QRZ)	2.65	0.09	0.09	48.6	82.2	123.1
finer apatite (APA*)	3.20	0.67	–	3.31	55.7	81.9

for apatite and lowest for quartz which is both due to smaller particles within the fraction and adhering finest particles which can be (partially) removed by ultrasonication as noticeable for apatite and magnetite looking at the specific surface area. For the investigations of the effect of sodium oleate conditioning concentrations on apatite, we used a smaller fraction of apatite, with properties for APA* given in Table 1.

We used sodium oleate (NaOl) from Fluka as received. The water is in any case demineralized tap water with 10^{-2} mol/l KCl as salt background. Acetone is from Carl Roth and used as received. Dodecyl ammonium acetate is synthesized by acidification of dodecyl amine with acetic acid, both from Sigma Aldrich.

2.2. Sample Preparation/Microflotation

For the flotation recovery studies a single gas capillary Halimond tube is used with a volume of 110 ml at a solid volume concentration of 0.4%, corresponding to 1.21 g APA, 1.85 g MAG and 1 g QRZ, respectively, at an air flow rate of $50 \text{ cm}^3/\text{min}$ under thermostatic conditions at 30°C for 1 min. One half of the milled samples were treated with ultrasound before conditioning as stated above.

- I These samples are the pure minerals used for **microflotation** in 10^{-2} mol/l KCl solution as well as **iGC**.
- II Conditioning of the samples in 5×10^{-4} mol/l of collector at pH 8 for APA with both collectors and MAG with NaOl and QRZ with DDAA only for 15 min. Then part of these samples and pulps are directly used for **microflotation only**.
- III One part of the conditioned particles in II is filtered and washed on the filter with 110 ml 10^{-2} mol/l KCl solution and subsequently 110 ml deionized water. Then the particles are oven dried over night at 50°C and used for **iGC**. To check the remaining flotability after the washing step the particles are resuspended in 10^{-2} mol/l KCl solution and used in **microflotation**.
- IV Another part of the particles of II is washed with water as in III and then furthermore washed with 110 ml of the less polar solvent acetone. Then these samples are oven dried like above and investigated in **iGC**. Additionally like in III a fraction is resuspended in the KCl solution for **microflotation**.

For studying the effect on sodium oleate conditioning concentration with the finer apatite APA* the particles were water washed only as in procedure III.

2.3. Inverse gas chromatography

The samples of the preparation steps (above) I, III and IV are investigated as dry powders using inverse gas chromatography.

The measurement device is the surface energy analyzer SEA of the company Surface Measurement Systems for determination of the disperse and Lewis acid/base components of the specific surface free energy γ^d , γ^+ , γ^- , respectively [26,34] at target surface coverages $(n/n_m)_{\text{target}}$ between 0.5% to 10%, where the total specific surface free energy is given by $\gamma^t = \gamma^d + 2 \cdot (\gamma^+ \cdot \gamma^-)^{0.5}$. The determination at different surface coverages allows for assessing the surface energetic heterogeneity of the samples [19,26]. Beforehand, the mass specific surface areas of the particles S_m are determined with the N_2 BET method using Micromeritics FlowSorb II 2300 as presented in Table 1. For iGC the following probe gas molecules (HPLC grade from Sigma Aldrich) are used in a helium carrier gas with a flow rate of $10 \text{ cm}^3/\text{min}$: hexane, heptane, octane, nonane and decane for the disperse component and the monopolar ethyl acetate and dichloromethane with Lewis acid and Lewis base properties, respectively. The column is operated at 0% humidity and 90°C for the experiments with APA, MAG and QRZ and 30°C for APA* with varying NaOH concentration in the conditioning step, respectively. The higher temperature for the first campaign were chosen to assure a clean surface by guaranteeing desorption throughout the measurements but from experiences in the first campaign in the second one with APA* a stable less erroneous measurement setting was found for 30°C . A sample mass is chosen so that a surface area of 0.5 m^2 is obtained. The sample is tapped vertically for 10 min in a 3 mm inner diameter silanized glass column with 30 cm length and closed with inert silanized glass wool. Before the measurement the samples are conditioned at 100°C for 5 h in a Helium gas flow of $10 \text{ cm}^3/\text{min}$. The specific surface free energy components are calculated using the peak maximum of the probe molecule retention curves and the Schultz approach for the disperse components as well as the van Oss Chaudhury and Good method with Della Volpe scale for the Lewis acid/base components [25,35]. The calculations use the peak maximum retention time and the actual fractional surface coverage $(n/n_m)_{\text{actual}}$ of the individual probe molecules and fitting of the retention volume versus fractional surface coverage by a simple exponential law for interpolation and extrapolation of comparable surface coverages n/n_m also allowing for calculation of propagated error of measurement and fitting determination. For the disperse component analysis the probe molecules hexane, heptane, octane, nonane and decane were measured but only heptane to decane was used for calculation based on the coefficient of determination being highest for the fit as explained in Fig. 3 and following the guidelines in [36].

The principle of determination of the specific surface free energy components using the Schultz method [21,37] at a given surface coverage is depicted in Fig. 3 for two different probe molecule surface coverages n/n_m .

The basic measured parameter in iGC is the net retention time of the gas molecules which is used to calculate the retention volume V_N plotted as the energy of interaction on the ordinate with R and T being the gas constant and the absolute temperature, respectively. The abscissa values are the cross section areas a times the square root of the disperse component of the specific surface free energy γ_1^d of the probe molecules. The homologue of the alkanes will enable determination of the disperse component of the particle specific surface free energy γ_s^d from the slope of the fitted linear function. The orthogonal distance of the monopolar Lewis base and Lewis acid molecules ethyl acetate and dichloromethane allows for calculation of the Lewis acid and Lewis base specific surface free energy of the solid γ_s^+ and γ_s^- , respectively.

For the calculations in Eq. (3) besides the specific surface free energy components of the particles, the ones of water and the gas

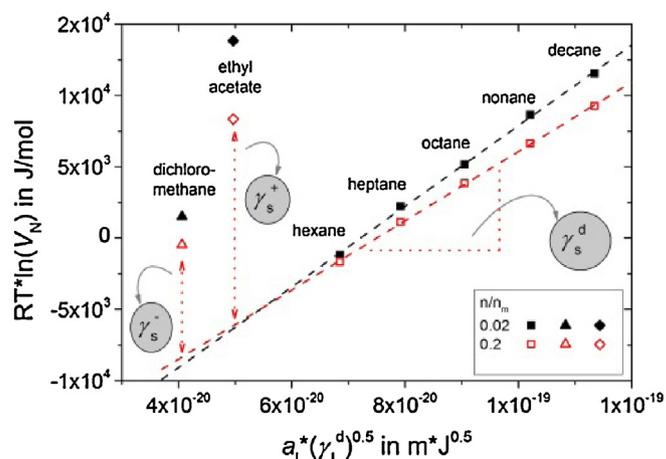


Fig. 3. Schematic graph of the Schultz-method showing the plot of probe molecules in the $RT \ln(V_N)$ vs. $a_1(\gamma_1^d)^{0.5}$ presentation to determine the disperse and Lewis acid/base components of the specific surface free energy at a two fractional surface coverage of 2% and 20%; the lines are to guide the eye.

Table 2

Specific surface free energy components of water (at 30°C and 90°C) and air bubbles used in the calculations below.

fluid	T/K	γ^d in mJ/m^2	γ^- in mJ/m^2	γ^+ in mJ/m^2
water ^a	303	21.5	25.2	25.2
	363	18.0	21.1	21.1
gas (bubble) ^b	–	0.0	0.0	0.0

^a Values calculated using the database of the VDI-GVC in [39].

^b As assumed by van Oss in [38].

bubble are necessary as well and given in Table 2. Van Oss is making the assumption that gas bubbles are hyper hydrophobic and the specific surface energy components are zero [38].

3. Results and discussion

3.1. Flotabilities

The microflotation results for the samples prepared are presented for apatite and both collectors in Fig. 4 and for magnetite with NaOH as well as quartz with DDAA in Fig. 5.

It can be seen that the pure (collectorless) apatite has a relative high recovery of about 10% which is most probably due to entrainment of the fine particles enriched in the apatite fraction more prominently than for the other two minerals with 10% quantile particle of only $24 \mu\text{m}$ as opposed to $43 \mu\text{m}$ and $49 \mu\text{m}$ for magnetite and quartz, respectively. The chemisorbing collector NaOH without washing and resuspending (preparation II) has the highest recovery without influence of ultrasonic treatment. The water washing and resuspending, i.e. remaining hydrophobicity, shows much less recovery (preparation III) for the sample with attached finest particles (no US). However, when removing the finest particles by US a similar recovery can be achieved. Consequently it can be assumed that the finest particles present in the sample without US will adsorb a lot of the collectors and are removed in preparation III. For the physisorbing collector the US does not affect the recovery after the washing procedure. It even shows the opposite behavior. In this case it could be the case that the physisorbing collector cannot detach the finest particles at the washing step but those still adhering particles reduce washing off of the collector. For iGC investigations to be put in context with microflotation results it was important that the hydrophobicity due to the sample preparation (washing) is not reduced too drastic, this is the case for all samples studied. However it shows the need to compare iGC results with

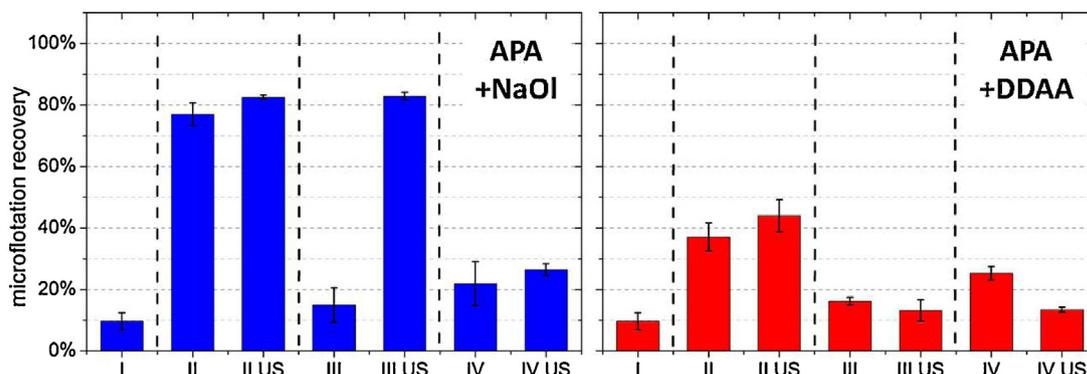


Fig. 4. Recoveries of microflotation for apatite and sodium oleate (left) and dodecyl ammonium acetate (right) and the sample preparations I, II, III and IV mentioned in 2.2; error bars are 95% confidence intervals.

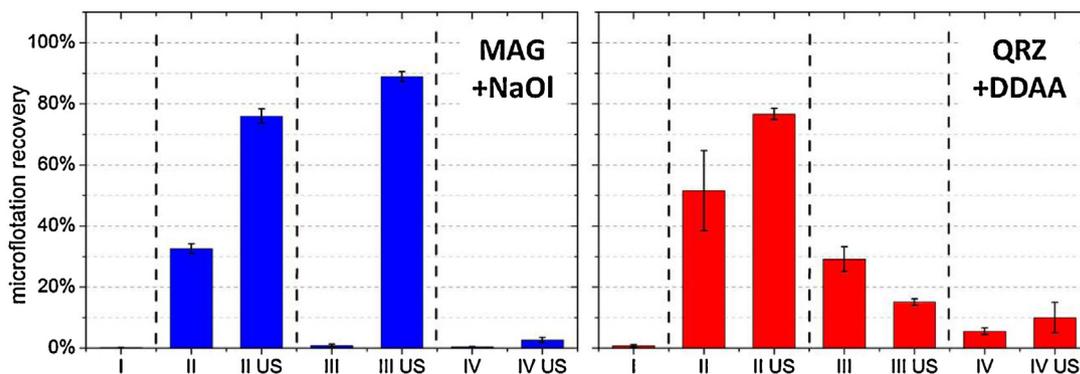


Fig. 5. Recoveries of microflotation for magnetite and sodium oleate (left) and quartz and dodecyl ammonium acetate (right) and the sample preparations I, II, III and IV mentioned in 2.2; error bars are 95% confidence intervals.

the resuspended recoveries rather than the flotation results without acknowledging the effect of sample treatment. In other words, sample pre-treatment is crucial for iGC investigations.

For the chemisorbing combination of NaOI on magnetite (Fig. 5 left) the tendencies in sample preparation and impact on recoveries is similar to the chemisorbing NaOI on apatite (Fig. 4 left). As well is the tendency of the physisorbing combinations of DDAA on quartz (Fig. 5 right) and apatite (Fig. 4 right) similar. The washing and resuspending seems to not be able to detach all of the collectors from the surface as it was assumed. With acetone, so a less polar washing after water washing reduces the recovery and thus remaining hydrophobicity for magnetite with NaOI as well as quartz and DDAA but increases recovery for the not ultrasonic treated apatite with both collectors which is an interesting finding to be discussed and furthermore studied in the future. The ultrasound may not only have an effect on the particles in terms of dispersing fine attached ones but also on the mechanism of adsorption of the collector. Due to this unknown effect of ultrasound the samples of the second campaign were not ultrasound pretreated.

The microflotation results of the second campaign of apatite APA* with varying sodium oleate concentration in the conditioning step and with the water wash only procedure (III in 2.2) are presented in Fig. 6.

One can see a clear dependency with higher recovery and thus better flotability, thus higher hydrophobicity, for a higher sodium oleate conditioning concentration. Surely there is a lack of experimental data for the residual NaOI concentration on the particle surface after the conditioning and water washing procedure. Nevertheless, the microflotation recovery shows an indirect expected effect that can be checked with the specific surface free energy components distribution as measured with iGC and the particle bubble interaction parameter as seen in the next paragraphs.

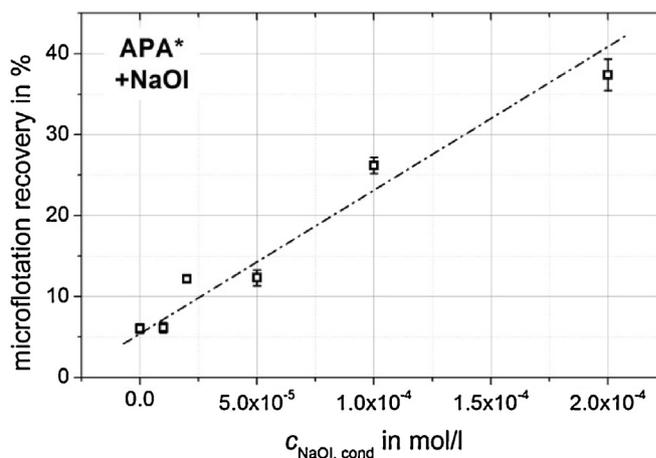


Fig. 6. Microflotation recoveries of APA* samples after water washing, drying and resuspension in collectorless solution, conditioned at different NaOI concentrations $C_{NaOI,cond}$; error bars are 95% confidence intervals, the line is to guide the eye.

3.2. Specific surface free energy component distribution

The heterogeneity of the three specific surface free energy components of all the samples of the three minerals with their respective collectors are summarized in the nine graphs in Fig. 7 with the surface coverage of the iGC probe molecules on the abscissae. It needs to be emphasized that a degressively falling curve shape is expected and increase with fractional surface coverage is only due to erroneous data as reflected with the error bars as a result of error propagation due to the various linear and non-linear regressions involved in the iGC method. Propagation of errors in

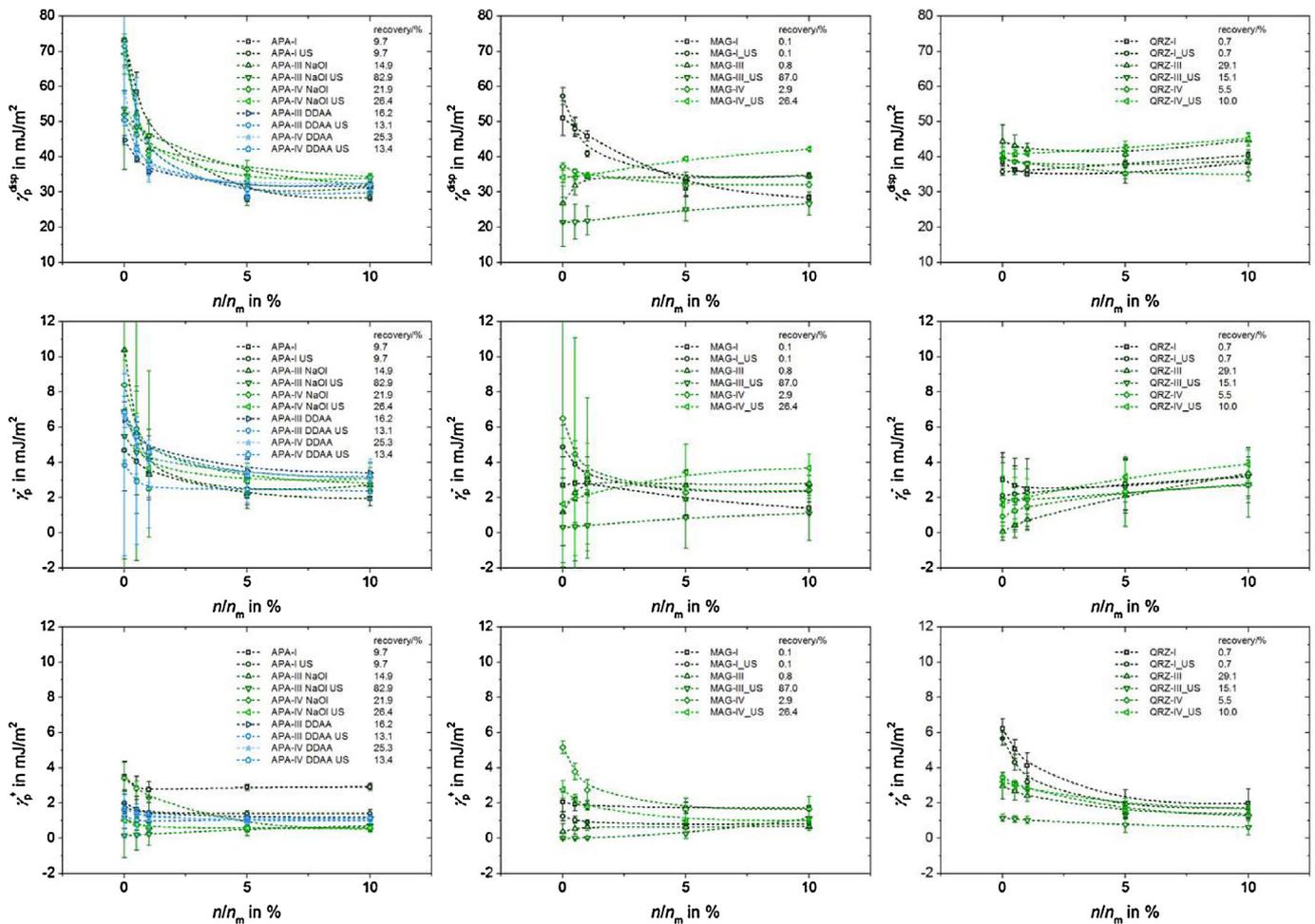


Fig. 7. Specific surface free energy components γ^{disp} , γ^- and γ^+ as a function of the fractional surface coverage in the iGC investigations n/n_m for (from top to bottom) the disperse γ^{disp} , the Lewis base γ^- and Lewis acid γ^+ components and the minerals (from left to right) APA with NaOl and DDAA, MAG with NaOl and QRZ with DDAA and different sample preparation methods with given resulting microflotation recoveries after resuspending shown in the individual legends; error bars are 95% confidence intervals, the lines are to guide the eye.

poor samples is furthermore the reason for the trust area reaching negative surface energies which is physically not possible.

For small surface coverages higher energies are detectable especially for the pure samples and stronger for apatite and magnetite than quartz which is due to the occurrence of high energy surface sites due to the finest particles attaching. The average surface energy of all surface sites as a limit value of the declining functions seems to be reached at 10% surface coverage already looking at the apatite sample and the disperse component. The limit values of the disperse component often used to describe the surface energy is lowest for apatite and highest for quartz, so the natural hydrophilicity of quartz is expected to be highest and for apatite lowest. This might additionally explain the rather high flotation recovery for apatite without collector. The effect the collectors have for apatite and magnetite is most significant at low surface coverages for the disperse component of interactions. Consequently, the collectors tend to adsorb primarily on a small fraction of the particle surface on high energy sites reducing the high energy and thus reducing the hydrophilicity of those sites. A clear tendency for the effect of the collector action on the Lewis base components is not to be seen, however as reported in the literature [24] the basic values are higher than the acidic ones but not as dramatically higher as reported in Holysz et al. [16] which is due to a different measurement technique and evaluation. The high Lewis acid values for

apatite as well as quartz however are reduced due to the collectors as in [24]. For magnetite the small Lewis acid component of the collectorless sample is increased by the collector values similar to the ones found for apatite and NaOl. No clear effect of the adsorbed collector on the disperse specific surface free energy is seen for the quartz samples. The heterogeneity of the surface energies (intensity of decrease of energy over surface coverage) is drastically reduced for apatite and magnetite. It seems that the apatite surface is most heterogeneous followed by magnetite, whereas quartz is least heterogeneous. This could be due to the initial grain sizes of the samples where larger grained crystals are used for magnetite and quartz and finer grained crystals for apatite. Furthermore could apatite show the strongest heterogeneity due to its semi soluble nature and thus different calcium mineral species as patches on the surface, for which, due to lack of measurement techniques, this hypothesis cannot be tested. However, because of the stronger tendencies and the higher heterogeneities for the second campaign apatite was continued to work with (APA*), without ultrasound treatment in the conditioning and washing step and with the water washing step only. Furthermore was a smaller particle size fraction used because preliminary studies showed more reproducible iGC results and possibility to investigate at 30 °C as the iGC column temperature. The specific surface free energy component plots against

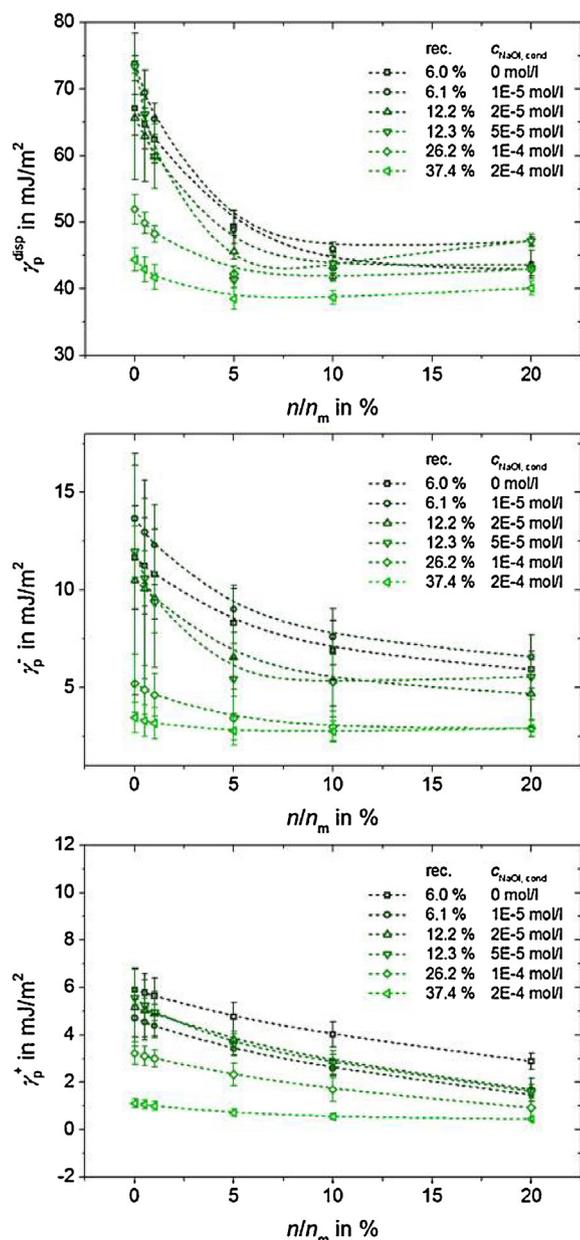


Fig. 8. Specific surface free energy components, from top down: disperse γ_p^{disp} , Lewis base γ_p^- and Lewis acid γ_p^+ as a function of the probe molecule fractional surface coverage n/n_m for the apatite samples APA* with different sodium oleate concentrations in the conditioning step C_{NaOl} of the minerals and given resulting recoveries after resuspending; error bars are 95% confidence intervals, the lines are to guide the eye.

the fractional iGC probe molecule surface coverages are shown in Fig. 8.

For all three surface energy components a decrease for all iGC probe molecule surface coverages is noticeable with increasing sodium oleate conditioning concentration and thus increasing floatabilities. As for the results above the decrease is more pronounced for smaller surface coverages, i.e. for small area fractions of higher surface energy sites. This systematic evolution leads to the conclusion that the collectors are mostly responsible for the reduction of high energy surface sites and thus a more energetically homogeneous surface. It is this effect that prominently leads to an improved flotability. In the next paragraph the flotability is

correlated with the thermodynamic quantity presented in Eq. (3) including all three specific surface energy components.

3.3. Flotability vs. free energy of interaction of particles and bubbles in water

As mentioned in the introduction, the flotation response, i.e. the recovery of particles, should be put in context to a fundamental parameter to account for hydrophobicity other than some contact angle with water. This paper introduces in this context the free energy of interaction ΔG_{pwb} between two different surfaces, here particle and bubble, immersed in a fluidic phase, here water, as a fundamental thermodynamic parameter expounding for the hydrophobic behavior of minerals as opposed to the often referred contact angle. Theoretically the flotation recovery shall be indirectly proportional to the energy of interaction, for the particle hydrophobicity increases with decreasing energy of interaction with a gas bubble in water. Below this assumption is challenged for energies of interactions calculated for different probe molecule surface coverages measured in iGC and samples of various floatabilities given in 3.1.

The following three graphs in Fig. 9 show the free energy of interaction ΔG_{pwb} based on the iGC measured specific surface free energy components between particle surface coverage and using equation (3) and the values for water and air given in Table 2 as a function of the flotation recovery from the microflotation study, for apatite APA with NaOl and DDAA, magnetite MAG with NaOl and quartz QRZ with DDAA, respectively.

For apatite APA and both collectors the assumed relation of increasing flotation recovery with increasing absolute (negative) energy of interaction holds true for the small surface coverages $n/n_m < 0.01$ but less for the high surface coverages exceeding $n/n_m = 0.05$. The same basically holds true for MAG and QRZ samples as well. Despite the large error and scattering of the data, this supports the hypothesis that the flotability of particulate material is mostly increased due to changes at small fractions of the overall surface (less than 1%) which initially show a high energy before conditioning and hydrophobization. The experience of the campaign with APA, MAG and QRZ with the different sample preparations presented in 2.2 led to the second campaign with the smaller apatite fraction APA* and different collector conditioning concentrations $C_{\text{NaOl,cond}}$ and the water washing procedure only and iGC column temperatures of 30 °C. The ΔG_{pwb} /flotability plot of this campaign is presented in Fig. 10 together with reevaluated data presented on barite flotability by Holysz et al. [16] and pyrite flotability by Mohammadi-Jam et al. [24].

The results clearly approve and emphasize the well working concept of correlating the specific surface free energy component results (as with iGC) with flotation using the concept of the free energy of interaction ΔG_{pwb} . Again, one can see a clear correlation especially for the small fraction of high energetic surface sites which correspondingly should be the sites the collectors adsorb primarily and more strongly holding on to the collectors even after the water washing step.

The data of Holysz et al. from [16] shows the same tendency, but due to a different determination of the surface free energy components using zeta potential and contact angle measurements the magnitude of the Lewis base component γ_p^- is very high and thus the line is shifted with respect to the ordinate axis ($\Delta G_{\text{pwb}} = f(\gamma_p^-)$). Furthermore with this method nothing can be said about the fractional surface effects, i.e. n/n_m is not valid. But the slope of the curves let's assume that the method developed by Holysz et al. is sensitive towards the high energy surface effects as iGC is for $n/n_m < 0.01$.

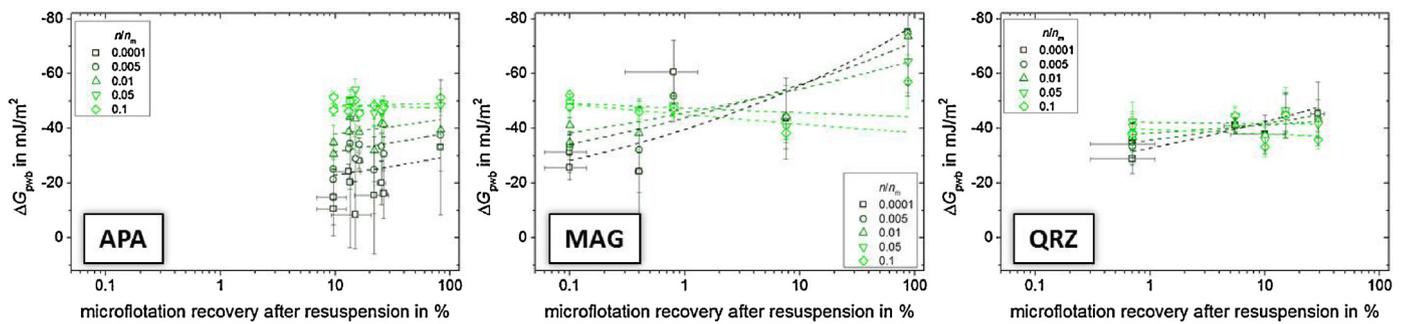


Fig. 9. Free energy of interaction between a particle and a bubble in water ΔG_{pwb} as a function of the microflotation recovery after resuspending with the parameter of probe molecule fractional surface coverage n/n_m for, from left to right: apatite, magnetite and quartz samples with the respective collectors; the lines show the fit of the data to the function $\Delta G_{pwb} = a \cdot (n/n_m)^b$; error bars are 95% confidence intervals, the lines are to guide the eye.

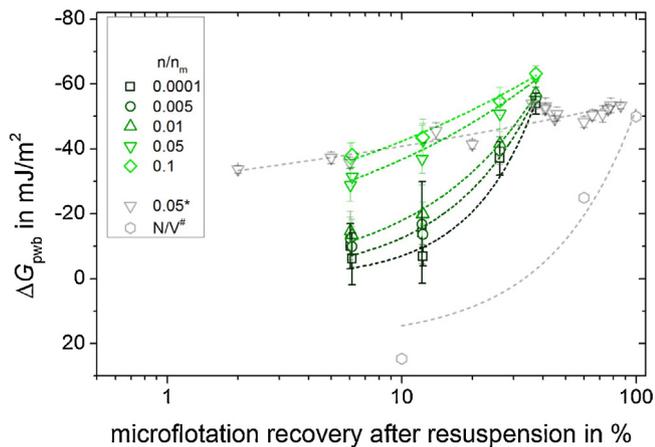


Fig. 10. Free energy of interaction between a particle and a bubble in water ΔG_{pwb} as a function of the microflotation recovery after resuspending with the parameter of probe molecule fractional surface coverage n/n_m for the apatite samples APA* with different conditioning concentrations of sodium oleate; the grey data with $n/n_m = 0.05$ and the (*) asterisk is calculated using the data for the pyrite samples in [24] at a fractional surface coverage of 0.05 as communicated by the author of [24]; the grey data with the (#) hash character is calculated using the data for barite samples in [16] where there is no value for the fractional surface coverage; all lines show the fit of the data to the function $\Delta G_{pwb} = a \cdot (n/n_m)^b$; error bars are 95% confidence intervals, the lines are to guide the eye.

4. Conclusions

The novel findings of this study can be summarized as follows:

1. Through inverse Gas Chromatography iGC it is possible to assess the distribution of the specific surface free energy components of particulate solid surfaces, i.e. disperse, Lewis base and Lewis acid, respectively.
2. The specific surface free energy components can be used to calculate the free energy of interaction between a particle and a bubble in water as a measure of hydrophobicity which is due to the distributed character a function of fractional surface area (iGC probe molecule fractional surface coverage).
3. The measure of hydrophobicity is an important factor in the flotation process and an important part of the flotability characteristic of a particle, i.e. the separation parameter in flotation (amongst size and shape).
4. In order to perform iGC analyses the solid particle phase needs to be dry, contrary to flotation separation which is occurring in the pulp phase.
5. We presented the impact of sample preparation necessary for dry iGC measurements on the flotability by means of resuspending particles in microflotation studies.

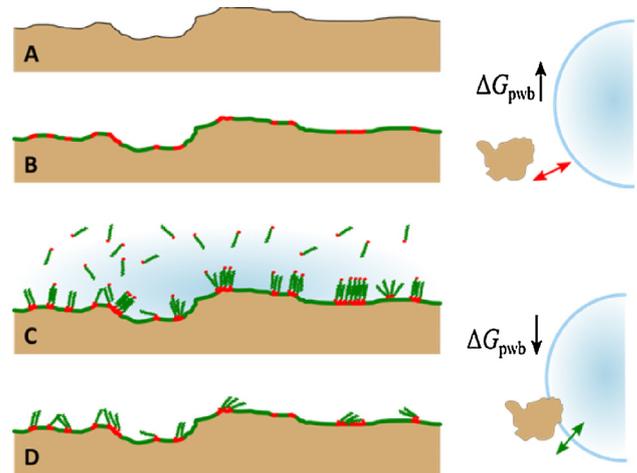


Fig. 11. Schematics of a Gedankenexperiment of a particle with a heterogeneous surface regarding specific free energy, where the red color refers to a high energy before and after adsorption of amphiphilic collector molecules with low energy hydrophobic tails and high energy functional head groups leading finally to a flotability for a low overall specific free energy of interaction. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

6. We showed that both physi- and chemisorbing ionic collectors dodecyl ammonium acetate and sodium oleate, respectively, on the salt type mineral apatite, the oxidic mineral magnetite and the silicate mineral quartz remain on the surface after the washing procedures as shown by higher recoveries than without collectors involved.
7. We showed that it is more logical to compare the results of iGC with the resuspended flotation recoveries of the dried particles.
8. The energy of interaction between a particle and a gas bubble in water using all specific surface free energy components of the three interacting phases is best to describe the particle hydrophobicity as the fundamental value of flotation to be correlated to the flotation recovery.
9. The iGC method presented cannot account for potentially flotation determining effects occurring in the suspended state of particles, e.g. through double layer interactions [40,41].

Thus this study brings up the following conclusions, which are graphically summarized as a Gedankenexperiment in Fig. 11:

- A The collector mainly causes the reduction of the high specific surface free energies of only a small fraction of the particle surfaces, most probably the edges and surface morphological heterogeneities.

B Consequently, the heterogeneities of the surface free energies are reduced by the adsorbed collector.

C Even though the overall highest recoveries are achieved in this study with the chemisorbing collectors the relation of flotation recovery and free energy of interaction is shown for the small surface coverages for both cases.

It is now important to gather more data and understand the impact of surface heterogeneity in terms of specific surface free energies for hydrophobization of mineral particles for flotation studies. This can only be achieved by continued investigations using inverse gas chromatography.

Furthermore there is the task to develop flotation process models including the fundamental interaction parameters of wettability presented, instead of the contact angle [42,43].

Finally, this could also explain latest findings on the effect of the particle morphology on flotation of sand blasted quartz particles and the observed enhanced flotation for rougher surfaces [44], in other words more high energy surface sites for the collector to adsorb on.

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