

Short communication

Non-HF collectorless flotation of quartz

Erik Larsen*, Przemyslaw B. Kowalczyk, Rolf Arne Kleiv

Department of Geoscience and Petroleum, Norwegian University of Science and Technology, Sem Sælandsvei 1, N-7491 Trondheim, Norway



ARTICLE INFO

Keywords:

Flotation
Quartz
Sulphuric acid
Sodium fluoride
Contact angle

ABSTRACT

Pure mineral flotation experiments have demonstrated that quartz can be floated without a collector, in solutions containing an inorganic acid (e.g. H_2SO_4) and sodium fluoride (NaF). Excellent quartz recoveries, similar to that of previous investigations with aqueous solutions containing hydrofluoric acid (HF), have been achieved with lower fluorine concentrations and a more optimal F/H ratio when combining separate sources of H and F instead of using only HF.

1. Introduction

Quartz is an important industrial mineral with various applications, and its flotation with anionic collectors when activated with cations, or with cationic collectors, have been well-known for quite some time (Glover, 1928; Wark, 1936). More recently it has been shown that quartz can be easily floated, without the use of collectors, in a solution of HF and frother (Larsen and Kleiv, 2015), and that it can be selectively floated from feldspar and other impurities in such a system (Larsen and Kleiv, 2016). The water contact angle on quartz was shown to be significantly larger after HF-treatment, and consequently the HF-treated quartz was rendered sufficiently hydrophobic for flotation without the use of a collector. Thus, considering the previous findings of the excellent floatability of quartz treated with HF and floated without a collector, the idea of the present work is simply based on replacing HF by combining separate sources for hydrogen and fluorine, in order to investigate the floatability of quartz with the combined reagent system.

2. Materials and methods

2.1. Materials

A high purity quartz was used in this study (Table 1). The quartz sample was dry milled in a polyurethane coated mill with 25 mm Y-stabilized ZrO_2 balls, and screened on a Rotap sieve shaker with Tyler standard 38, 74 and 104 μm screens. The $-38 \mu m$ fraction was used for wettability measurements, while $-38 \mu m$, $38-74 \mu m$ and $74-104 \mu m$ fractions were used for batch flotation experiments.

2.2. Particle size distribution

Particle size distributions of the quartz fractions were measured with a Malvern Mastersizer 3000 (laser diffraction), using a refractive index of 1.54 and an absorption index of 0.01. Particle size distributions of the samples are shown in Fig. 1 and Table 2. Table 2 also shows the specific surface area calculated by the Mastersizer software.

2.3. Reagents

Hydrofluoric acid, 48% HF (Sigma-Aldrich), sulphuric acid, 96% H_2SO_4 (Merck), and NaF (Sigma-Aldrich) were added to the solutions in their concentrated form. Brij 58 (Acros Organics), a polyoxyethylene (20) cetyl ether with a molar mass of 1123 g/mol, was prepared as a 1 wt.% solution before addition. Heptane (VWR) was used as reference liquid in the wettability measurements.

2.4. Flotation experiments

Flotation was performed with a self-aerated mechanical flotation machine from Maelgwyn Mineral Services, using a 1.2 L Plexiglass cell. A 50 g of quartz was conditioned with chemicals and 900 ml deionized water for 20 min (unless otherwise stated). A frother solution was then added, followed by a further 1 min of conditioning, prior to air introduction at a superficial gas velocity of 0.55 cm/s (5 L/min). Water was added to maintain a pulp level during flotation, while flotation was performed until barren froth. pH was measured prior to flotation using a Metrohm 744 pH meter.

* Corresponding author.

E-mail address: erik.larsen@ntnu.no (E. Larsen).

<https://doi.org/10.1016/j.mineng.2019.01.014>

Received 15 October 2018; Received in revised form 2 January 2019; Accepted 10 January 2019

Available online 17 January 2019

0892-6875/© 2019 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Table 1
Chemical analysis (ICP-MS) of quartz used in this study (ppm).

Al	B	Ba	Be	Ca	Cr	Cu	Fe	Ga	K	Li	Mg	Mn	Na	P	Pb	Ti	Zn
14.4	< 1	2.2	< 10	< 200	< 0.06	< 0.1	6.6	< 0.05	< 0.03	< 0.4	< 0.2	< 0.2	< 0.02	< 1	0.3	< 0.2	< 0.7

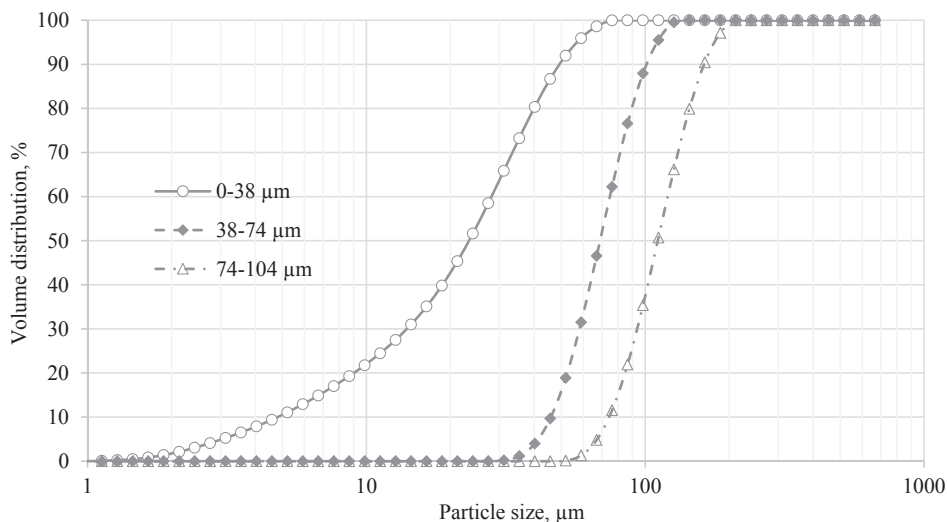


Fig. 1. Particle size distributions of the quartz fractions.

Table 2
Particle size distribution parameters and specific surface area of the quartz fractions.

Sample	D ₅ (μm)	D ₁₀ (μm)	D ₅₀ (μm)	D ₉₀ (μm)	D ₉₈ (μm)	Spec. surf. area (10 ⁻² m ² /g)
0–38 μm	3.0	4.8	23	49	65	19.5
38–74 μm	41	46	69	102	121	3.5
74–104 μm	67	74	111	163	193	2.1

2.5. Wettability measurements

A Biolin Scientific Sigma 700 force tensiometer was used to measure the capillary force liquid weight gain on –38 μm non-treated and

chemically treated samples. All chemically treated samples were conditioned for 20 min (unless otherwise stated), filtered and dried at 40 °C prior to measurements. The capillary constant of the sample material was determined by first measuring weight gain with the heptane wetting reference liquid (contact angle, $\theta \approx 0^\circ$), while the contact angle for water was found after measuring the weight gain on another similarly treated sample in deionized water. A modification of the Washburn equation (after Siebold et al., 1997) was used for the calculations:

$$\frac{w^2}{t} = \frac{c \cdot \rho^2 \cdot \gamma \cdot \cos\theta}{\mu} \tag{1}$$

where w = weight gain, t = flow time, c = capillary constant, ρ = liquid density, γ = liquid surface tension, θ = contact angle, μ = liquid viscosity.

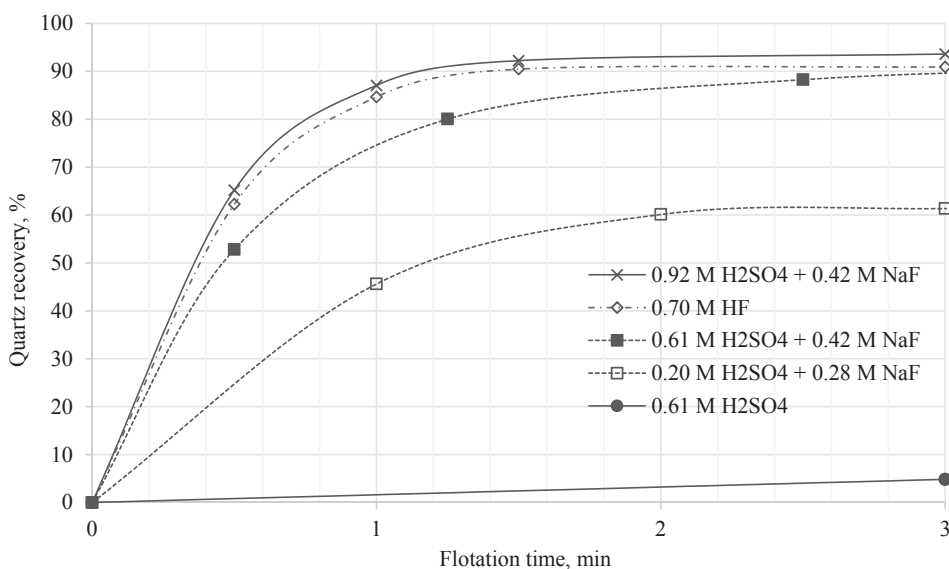


Fig. 2. Quartz recovery vs. flotation of fraction –38 μm (2 · 10⁻⁵ M Brij 58 as frother).

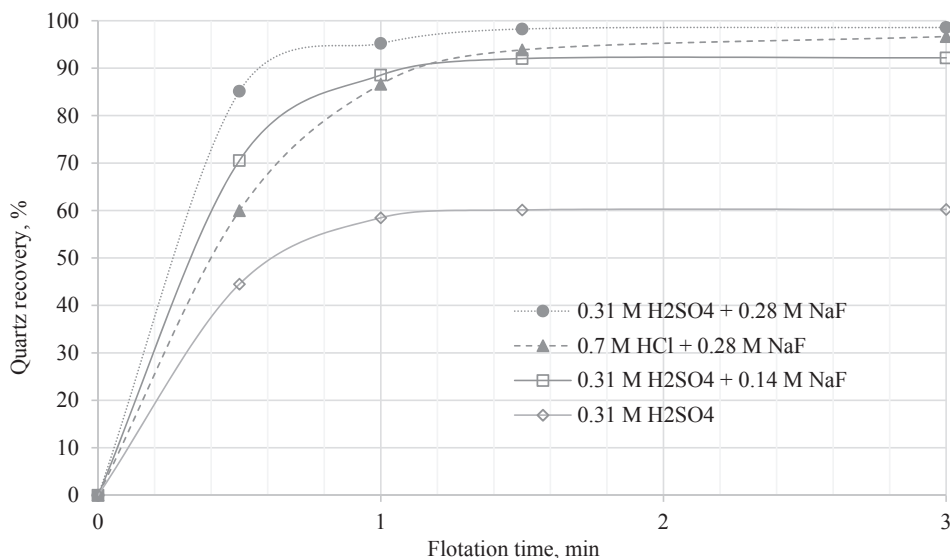


Fig. 3. Quartz recovery vs. flotation time of fraction 38–74 μm ($2 \cdot 10^{-5}$ M Brij 58 as frother).

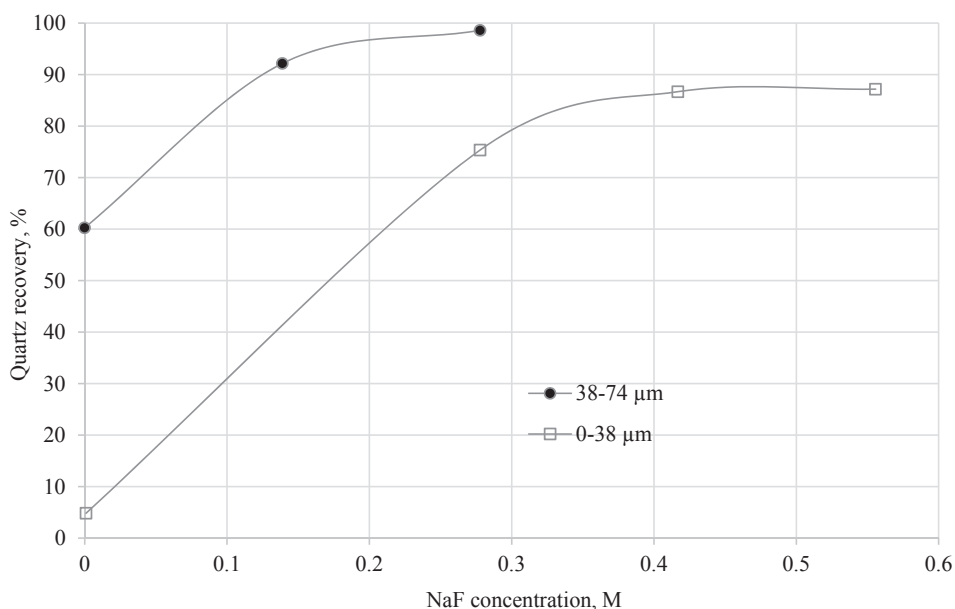


Fig. 4. Quartz recovery vs NaF concentration at 0.31 M H₂SO₄ ($2 \cdot 10^{-5}$ M Brij 58 as frother).

3. Results and discussion

3.1. Flotation of quartz

Figs. 2 and 3 show the quartz recovery as a function of flotation time for fractions $< 38 \mu\text{m}$ and 38–74 μm under various chemical conditions. There was no flotation of quartz in pure water, with only frother, or with NaF and frother. Quartz started to float when it was treated with H₂SO₄ and frother, and with H₂SO₄, NaF and frother. The recovery of quartz increased with the increase in the concentration of H₂SO₄ and NaF. The results show that flotation of quartz with 0.92 M H₂SO₄ and 0.42 M NaF showed similar flotation kinetics and maximum recovery (R_{max}) to that of flotation with 0.70 M HF alone, while flotation with 0.61 M H₂SO₄ + 0.42 M NaF showed similar R_{max} to that of 0.70 M HF, but at a slightly longer flotation time. The amount of H⁺ was higher (1.2 M vs 1.0 M) and F⁻ was lower (0.4 M vs 1.0 M) in a system of H₂SO₄ and NaF compared to HF alone. It indicates that the F-to-H ratio is not optimal in a system with HF only.

In Fig. 3, flotation with 0.7 M HCl + 0.28 M NaF show similar final recovery as that of 0.31 M H₂SO₄ + 0.28 M NaF. Although the flotation with HCl display a slightly slower rate of flotation, this shows that acids other than H₂SO₄ can be used in the process.

Figs. 2 and 3 show that the 38–74 μm fraction requires substantially less chemicals compared to that of the 0–38 μm fraction, in order to achieve similar recoveries. A recovery of 91% was achieved with 0.61 M H₂SO₄ + 0.42 M NaF for the 0–38 μm fraction, while a similar recovery (92%) was achieved with 0.31 M H₂SO₄ + 0.14 M NaF for the 38–74 μm fraction. This difference in recovery is likely due to the large difference in specific surface area between the fractions (Table 2).

Fig. 4 shows the quartz recovery of fractions < 38 and 38–74 μm at 0.31 M H₂SO₄ and varying amounts of NaF, while Fig. 5 shows the quartz recovery of fraction $< 38 \mu\text{m}$ at 0.42 M NaF and varying amounts of H₂SO₄. It can be clearly seen that the maximum recovery of quartz (after 3 min) increased with NaF concentration, and the optimum concentration of NaF with 0.31 M H₂SO₄ was ca. 0.25 M for fraction 38–74 μm . For finer quartz particles higher concentrations of both acid

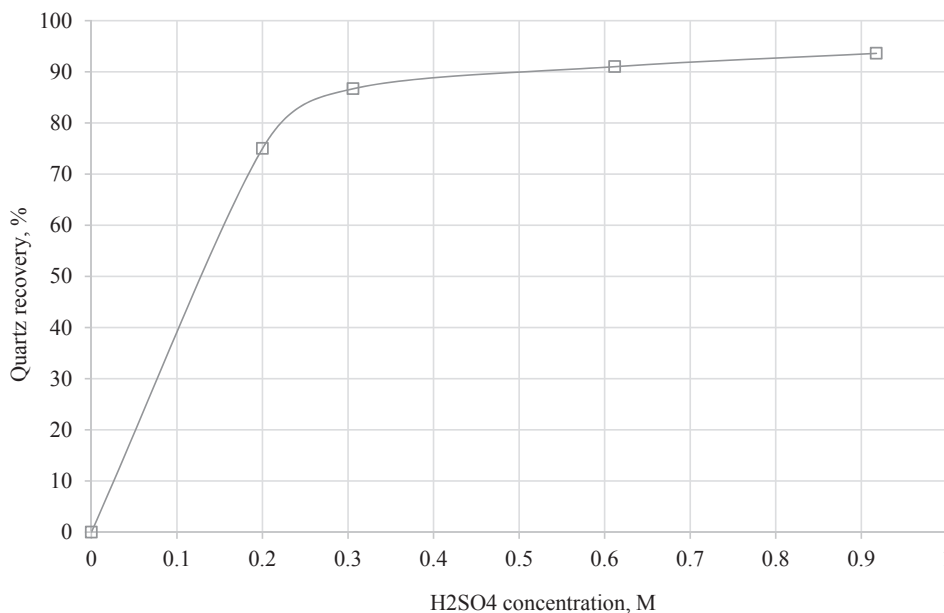


Fig. 5. Quartz recovery vs H₂SO₄ concentration at 0.42 M NaF of fraction 0–38 μm ($2 \cdot 10^{-5}$ M Brij 58 as frother).

Table 3

Contact angle measurements on quartz, 0–38 μm.

Conditions	Contact angle, °
No treatment	41 ± 2
0.8 M NaF	39 ± 2
Brij 58 (1 min cond.)	53 ± 2
1.2 M HF/H ₂ SO ₄ (with or without Brij 58)	80 ± 2
0.2–0.9 M H ₂ SO ₄ + 0.3–0.42 M NaF	82 ± 2

and NaF are required to achieve high recovery.

3.2. Contact angle

Table 3 shows results from the contact angle studies on the 0–38 μm fraction. The non-treated sample displayed contact angle of $41 \pm 1^\circ$. This is quite similar to our previous results (Larsen and Kleiv, 2015). Conditioning with a frother Brij 58 increased the contact angle only slightly, while acid treatment (HF or H₂SO₄) with or without NaF or Brij 58 rendered the quartz hydrophobicity to contact angle equal to 80°. This indicates that acid treatment or acid treatment combined with NaF creates a hydrophobic surface, while NaF or Brij 58 alone does not render the quartz surface sufficiently hydrophobic for it to float. The contact angle results correlate with the flotation results.

4. Conclusions

The investigations demonstrate that quartz can be floated in solutions of an inorganic acid (e.g. H₂SO₄) together with NaF and a frother Brij58. Quartz recoveries were achieved with lower F concentrations

and lower F/H ratios when combining separate sources of H and F, compared to using only HF. Experiments with NaF and the frother showed no flotation of quartz.

Wettability measurements showed an increase in the contact angle of quartz after conditioning with H₂SO₄ or with H₂SO₄ together with NaF, while NaF or Brij58 alone has apparently little or no effect on the contact angle of quartz. The contact angle results correlate with flotation data.

Acknowledgments

The authors wish to thank the Department of Geosciences and Petroleum, NTNU, for the use of its laboratory resources.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mineng.2019.01.014>.

References

- Glover, H., 1928. Flotation of some oxide and silicate minerals. Flotation Fundamentals, Part 1, Section E. Utah Eng. Exp. Sta. Tech. Paper 1, 77–101.
- Wark, I.W., 1936. The physical chemistry of flotation. VII. Trimethylammonium bromide as a flotation agent. J. Phys. Chem. 40, 661–668.
- Siebold, A., Walliser, A., Nardin, M., Oppliger, M., Schultz, J., 1997. Capillary rise for thermodynamic characterization of solid particle surface. J. Colloid. Interf. Sci. 186, 60–70.
- Larsen, E., Kleiv, R.A., 2015. Towards a new process for the flotation of quartz. Min. Eng. 83, 13–18.
- Larsen, E., Kleiv, R.A., 2016. Flotation of quartz from quartz-feldspar mixtures by the HF method. Min. Eng. 98, 49–51.