



Towards a new process for the flotation of quartz



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ABSTRACT

Results obtained from flotation experiments performed on three different quartz concentrates demonstrate that quartz can be floated in diluted solutions of hydrofluoric acid (HF) simply by the aid of frothers alone. The recovery was found to be highly dependent on the choice of frother and strongly positively correlated with the concentration of both frother and HF, as well as with the HF conditioning time. Experiments using HNO_3 instead of HF showed no flotation of quartz. Of the five different frothers tested, Brij 58 was found to produce the highest recovery. Good recoveries were also obtained for Dowfroth 400 and Flotanol C07, whereas Dowfroth 200 and MIBC failed to float any quartz. From experiments in which a given feed material were tested at two different particle size distributions it was found that highest recoveries were obtained for the finer feed. Chemical analysis of the floated products showed that these were significantly purer than their corresponding feed materials, and that most of the contaminating elements were concentrated in the sink fraction that remained in the cell. Contact angle measurements corresponded well with flotation recoveries.

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1. Introduction

Quartz is an important industrial mineral with a number of uses, spanning from foundry sand, abrasives, and filter media to its use as a raw material in the production of glass, silicon carbide and silicon metal. Accompanying the span in uses and applications, there is a corresponding span in the mineralogical and chemical purity of the respective quartz products.

The highest quality demands are put on quartz for the production of electronic grade silicon, but also quartz for solar grade silicon requires high quality concentrates consisting of pure quartz with a minimum of impurities in the crystal lattice. Hence, concentrates for such uses are highly priced commodities. Still, the subsequent down-stream chemical processing is far more costly and energy-intensive. Flotation is an indispensable tool in the production of high purity quartz concentrates for such uses, as most of the contaminating minerals can be floated with the appropriate collectors leaving the purified quartz behind in the sink fraction. This paper describes the results from initial experiments that could lead to a new and alternative process for the production of high purity quartz concentrates, or, alternatively, to rinse other mineral concentrates from small amounts of silica. As shown by this study, quartz can be floated in diluted solutions of hydrofluoric acid (HF) simply by the aid of frothers alone.

Traditionally, HF has performed two functions in the production of high purity quartz concentrates: Firstly, it has been used to activate feldspar prior to its flotation by amine collectors – thus enabling the separation of feldspar and quartz at low pH where the zeta-potentials of the former remains negative while that of the latter becomes close to neutral (Buckenham and Rogers, 1954; Peres et al., 2007). The difference in zeta potential is enhanced by adding HF at pH 2–2.5, thereby obtaining a further selective decrease in the zeta-potential of the feldspar. Secondly, HF is used as a leaching agent to clean the quartz surface (by partial dissolution) and remove surface-bound contamination. The process described in this study represents a third use of HF, in which the chemical is employed to produce a directly floatable quartz surface.

HF in aqueous solution is a weak acid, and only some 10% is dissociated in a 0.1 N solution (Sidgwick, 1950). However, the dissociation constant falls continuously with dilution. It was shown by Pick (1912) that this could be explained by assuming that the solution contains HF_2^- ions in addition to HF monomers and dissociated H^+ and F^- . The HF_2^- ions act as the conjugate base of a strong acid, i. e. no non-dissociated HF_2H will be present in solution. Hence, the degree of dissociative ionization of hydrogen fluoride in aqueous solution increases markedly as its added concentration increases. It is generally accepted that this reflects the progressive increase in the concentrations of complex anions with the general formula $\text{F}-(\text{HF})_n$. According to Bailar et al. (1989), hydrogen fluoride crystals contain long chains in which each hydrogen atom is believed to be

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covalently bonded to one fluorine atom and hydrogen-bonded to another. The existence of polymeric HF in solid acids has been inferred from crystallography and phase rule studies even though HF and HF_2^- were the only detectable species (Farrer and Rossotti, 1964). Ernsberger (1960) proposed that a significant proportion of silica tetrahedra surface OH^- ions are replaced by F^- ions under “less extreme conditions of acidity”, and that the resulting silicon atom coordination deficiency could lead to the continuous adsorption of further fluoride ions. This suggests that fluorine-coated quartz surface areas can be created under “less extreme conditions of acidity”, which in turn means that these areas could become hydrophobic and the particles readily floated without collectors provided that the surface coverage is sufficient.

Hydrofluoric acid is an industrial chemical that poses challenges with respect to health, safety and environment (HSE). Hence, when possible, alternative acids are preferred. However, the chemical's unique properties and role in quartz beneficiation combined with the high energy costs associated with downstream chemical processing of quartz for high purity applications still renders HF-based processes highly interesting. It is in light of this that the direct and collectorless flotation of quartz was investigated. The main purpose of this paper is to report and document initial experimental findings that could lead to a new process for flotation of quartz and production of high purity quartz concentrates. The paper does not seek to explain the mechanisms, but demonstrates the potential and points at the needs for further investigations.

2. Materials and methods

2.1. Materials

Three different quartz qualities were used in this study. The first material consisted of commercially available high purity quartz (NC4A) purchased from The Quartz Corp. This NC4A material had been washed and dried during production. Prior to flotation experiments, the material was given an additional wash with NaOH solution, rinsed with deionized water, dewatered and filtered. The second material was denoted ‘NC4A < 200 μm ’ and consisted of NC4A milled with ceramic balls and screened to produce the 40–200 μm size fraction. This fraction was then washed with deionized water, dewatered and filtered prior to the flotation experiments. The third material consisted of lump quartz from Vatnet, a small deposit in northern Norway. The lump quartz was crushed, milled with ceramic balls and screened to produce the 40–200 (<200) μm size fraction. This fraction was then washed with deionized water, dewatered and filtered prior to the flotation experiments. The particle size distributions of the three materials (Fig. 1) were determined by laser diffraction using a Coulter LS230, whereas the chemical compositions of the

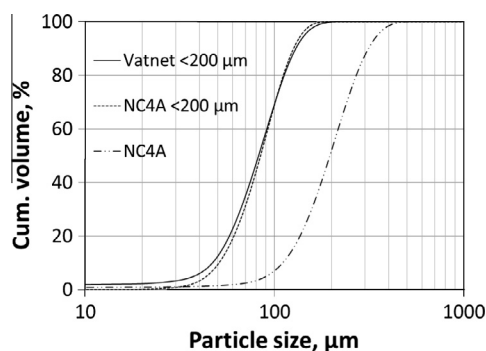


Fig. 1. Particle size distributions of the different quartz materials.

‘Vatnet < 200 μm ’ and the NC4A were obtained from ICP-MS analysis using a Perkin-Elmer DRCII.

2.2. Reagents

Hydrofluoric acid (HF) 40% from Merck was used in concentrated form. Sodium hydroxide (NaOH) from J.T. Baker, Brij 58 from Acros Organics, Dowfroth 200 and Dowfroth 400 from Nasaco, Flotanol C07 from Clariant and MIBC from Sigma-Aldrich were all prepared as 1 wt% solutions with deionized water. An overview of the frothers is shown in Table 2.

2.3. Flotation experiments

A Maelgwyn Mineral Services self-aerated flotation machine with a 1 L Plexiglas cell was used in the batch flotation studies. With the exception of a few batches that were used to study the effect of the conditioning time of the initial HF condition step, all the flotation experiments were conducted by first conditioning individual 100 g batches of feed material with 0–50 ml of 40% HF and 900 ml deionized water for 5 min. Then, 1 ml 1 wt% frother solution was added, followed by a further 2 min of conditioning. Following these two conditioning steps, air was introduced to the cell at a superficial gas velocity of 0.44 cm/s (4 L min⁻¹) and 2 min of flotation was performed (until barren froth). A second and a third consecutive flotation step was performed on the same batch by repeating the 2 min of conditioning with 1 ml 1 wt% of frother solution prior to 2 min of flotation. Hence, four final products were produced for each batch (i.e. three floated products and the remaining sink product). Both conditioning and flotation were conducted at an impeller speed of 50%, and deionised water was added to maintain pulp level during flotation. The pH during flotation was effectively determined by the buffering effect of the HF solution, and was found to be stable at 2.8–2.9. As a control, pH was measured with a Metrohm 744 pH meter immediately prior to the first flotation step.

In addition to the early flotation experiments a second series of flotation experiments were conducted on Vatnet quartz in order to do a flotation kinetics study. The differences from the experiments described above was that all of the frother solution was added initially prior to flotation and that the flotation froth was collected separately every 30 s for two min (0–30 s, 30–60 s,

Table 1
Chemical composition of NC4A and Vatnet quartz.

Element	Quartz material (feed)	
	NC4A (ppm)	Vatnet < 200 μm (ppm)
Al	3	3
B	<10	<10
Ba	<1	<1
Be	115.9	201.4
Ca	11.1	10.4
Cr	721.7	651.0
Cu	<1	<1
Fe	<0.03	21
Ga	<200	<200
K	<0.2	<0.2
Li	1.4	0.7
Mg	31.6	34.8
Mn	389.4	280.8
Na	7	8
P	1.4	2.7
Pb	0.2	0.3
Ti	<0.2	2.0
Zn	7.7	8.3
Zr	1.8	0.8

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