EFFECf OF PRETREATMENT ON THE ELECTROKINETIC PROPERTIES
OF QUARTZ

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ABSTRACT


Effects of various commonly used pretreatments such as desliming, ultrasonic scrubbing
and leaching with dilute nitric, hydrofluoric and sodium hydroxide solutions on the elec-
trokinetic properties of quartz in aqueous solutions are reported. The study showed that
treatments with various reagents often used in mineral processing research in the past to
clean minerals can affect, sometimes severely, the electrokinetic properties of quartz. The
change in these properties during subsequent aging is also found to be governed by the
type of treatment used. This study also shows the need in mineral research for standardiza-
tion of mineral preparation techniques in order that the discrepancy in data reported for
surface properties in literature can be minimized.

INTRODUCTION

To conduct basic studies on the surface chemical properties of natural min-
erals, it is necessary to prepare them in the desired size fraction and then
clean the surface from impurities that are originally present as well as that
introduced during the preparation. For this purpose, mineral particles have
been subjected in the past to pretreatments varying from simple mechanical
cleaning and washing to severe leaching treatments. Such a multitude of pre-
treatments possibly accounts for the differences in values reported for surface
properties of the same mineral (Somasundaran, 1970). A typical example of
the effect of pretreatment on surface properties is the variation in values
reported for zeta potential of quartz after various pretreatments (Fujii, 1965).
As can be seen from Fig. 1, the different treatments do produce considerably
different zeta potential values; shifts in zeta potential that can result due to the
temperature variation from 25°C to 35°C is much smaller than those shown here
(Somasundaran and Kulkarni, 1973).

The purpose of the present work was to study and evaluate systematically
the effects of pretreatments on the electrokinetic properties of quartz as a
function of aging time, pH and ionic strength. The time dependence of the
electrokinetic properties can yield information on the extent of surface insta-
Bility imparted by pretreatments.
Fig. 1. Zeta potential of quartz subjected to different treatments as a function of pH. 
1 = HNO₃-leached quartz, equilibrium zeta potential; 2 = HCl-leached quartz, ionic strength
5·10⁻⁴ N, 25°C Fujii (1965); 3 = Ground quartz, ionic strength 5·10⁻⁴ N, 25°C Fujii (1965);
4 = HF-leached quartz, ionic strength 5·10⁻⁴ N, 25°C Fujii (1965).

EXPERIMENTAL

Minerals and pretreatments

Brazilian quartz of 28 x 65 mesh size prepared by rollcrushing, magnetic
cleaning and sieving was used for all the tests. The washed quartz was sub-
jected to the following pretreatments before determining its zeta potential:

Treatment No. 1. The sized quartz was deslimed several times with triple dis-
tilled water and it was immediately tested without aging.

Treatment No. 2. This treatment consisted of desliming a sample of the min-
eral with triple distilled water and leaching it in warm 23% nitric acid solution
for one hour. The mineral was then washed with the water till the pH of the
solution approached the natural pH (5.9–6.2) of the mineral-distilled water
system, and stored in cleaned polypropylene bottles at a pH of 2.8 until use.
A pH of 2.8 was selected for storing because it has been established earlier
that it is desirable to condition a mineral in a solution that is at a pH close to
its point of zero change (Somasundaran, 1970).
Treatment No. 3. A part of the sample which has undergone treatment No. 2 was treated with 10% HF solution for fifteen minutes and then washed repeatedly with triple distilled water until the pH of the solution approached natural pH (5.9—6.2). This mineral was then washed with 0.1N NaOH for two hours and subsequently rinsed with triple distilled water and stored at a pH of 2.8.

Treatment No. 4. This treatment consisted of contacting part of the quartz subjected to treatment No. 3 with 0.1N NaOH at 65°C for 170 hours and then with 0.01N NaOH at 65°C for 350 hours followed by washing with triple distilled water several times. The sample was then stored at a pH of 2.8 at room temperature.

Treatment No. 5. Part of the mineral sample aged at a pH of 2.8 for about four months after treatment No. 2 was washed with triple distilled water and then subjected to ultrasonic irradiation for fifteen minutes.

Test procedure

The experiments essentially involved determination of zeta potential of the pretreated quartz using the streaming potential technique as a function of aging time at various pH values keeping ionic strength and temperature constant, and at various ionic strengths keeping pH and temperature constant. Streaming potentials were measured using an automated set-up described in a recent publication (Somasundaran and Kulkarni, 1973). The special features of this set-up included provisions for control of operating temperatures and for making automatic measurements for prolonged intervals.

RESULTS

The zeta potentials obtained under various conditions are compared with those obtained for quartz subjected to treatment No. 2, the latter treatment being selected as a control for comparison because it was considered to be a moderate but sufficiently effective treatment. The equilibrium zeta potential obtained for quartz subjected to treatment No. 2 is given in Fig. 2 as a function of pH. The required aging time varied from two hundred to several hundred hours.

Figs. 3 and 4 give the zeta potentials obtained at an ionic strength of 10^{-2}N as a function of pH for the quartz treated as in No. 2 and No. 5, respectively, at various equilibration times. While there was no measurable change in the zeta potential of ultrasonically treated quartz (No. 5) as a function of time, except in the alkaline pH range, changes in that of the nitric acid treated quartz (No. 2) were significant both in acid and alkaline range and persisted for as long as 30 hours. The error involved in these measurements is ±2% for consecutive readings using the same mineral plug and ±4.5% for values obtained using different plug preparations.
The most striking effect was observed for quartz treated with hydrofluoric acid solution followed by warm sodium hydroxide solution (No. 4) (see Fig. 5). In this test, the mineral was transferred immediately after pretreatment into the streaming cell, maintained at 35°C, for the electrokinetic measurements. An isoelectric point of 6.5 was obtained initially for this quartz. Upon aging the sample at a pH of 5.8 the zeta potential at that pH shifted gradually from +3 mV to -37 mV in about twenty-two hours. The isoelectric point (IEP) also decreased correspondingly from the initial value of 6.5. Thus different IEP values can be obtained on this mineral depending on the aging time after the hydrofluoric/sodium hydroxide treatment, which has been used in the past to clean quartz. This result also shows the rather unstable nature of the interface after such a treatment.

In the second set of experiments zeta potentials of quartz subjected to the different treatments were determined at a constant pH value of 4 as a function of aging time at two different ionic strengths. The results obtained are presented in Figs. 6 and 7. For the purpose of comparison, the values obtained for the sample subjected to treatment No. 2 are also plotted in each case as a reference. It can be seen that the deslimed quartz (treatment No. 1) exhibits a sharp initial decrease of zeta potential followed by a slow increase before attaining a steady value, which is lower than the initial value. The HNO₃-treated (No. 2) quartz does not exhibit such a change. The HF-treated (No. 3) quartz also does not show any time-dependent electrokinetic behavior, but it does yield a lower negative zeta potential at pH = 4 at both the ionic strengths. The HF/warm NAOH-treated (No. 4) quartz on the other hand exhibits time-dependence and has a lower negative zeta potential at pH = 4. It can be con-
Fig. 3. Zeta potential of HNO₃-treated (and aged at pH = 2.8 for 4 months) quartz as a function of pH without aging in between measurements, and at pH = 10.3 after 30 hours of aging; dotted curve is for equilibrium values obtained for HNO₃-treated (Treatment No. 2) quartz.

Fig. 4. Zeta potential of ultrasonically scrubbed (Treatment No. 5) quartz as a function of pH without aging, and at pH = 10.15 after 4 hours of aging; dotted curve is for equilibrium values obtained for HNO₃-treated (Treatment No. 2) quartz for comparison.

Included from the above observations that both the type of pretreatment and aging time do affect the zeta potential significantly. Previous work has shown that the nature of the zeta potential change obtained is markedly dependent on both pH and ionic strength of the solution in which the aging is conducted (4). Thus, whereas the zeta potential was found to continuously decrease upon aging a given quartz sample at pH = 4 and an ionic strength of 10⁻² N, an increase was obtained at pH = 9.1 under the same ionic strength conditions. A decrease in ionic strength below 10⁻³ N reversed the direction of the change at both pH values.

DISCUSSION

Quartz exists in the tetrahedral form with each silicon atom surrounded by four oxygen atoms each of which is in turn connected to two silicon atoms. This structure is a result of the mixed electrovalent and covalent character of the Si–O bond (Graham, 1969), nearly 50% of the bond being ionic (Pauling, 1969). When oxygen in the silica matrix is replaced by such elements as fluorine or chlorine, the ionic character of the bond, along with its ionization constant in aqueous solution, undergoes a change. It is known that oxygen can be spontaneously replaced from the lattice by fluorine. This can possibly be a reason for the observed severe effect of the HF treatment compared with the HNO₃ treatment. The dissolution of surface silica which is usually more
amorphous and more concentrated with respect to sodium as against silica in the subsurface region will also contribute significantly towards the alteration of the surface properties upon treatment with HF.

When quartz is contacted with aqueous solutions, hydrolysis of the surface species takes place generating silanol groups. This process continues with time giving successively $\equiv\text{Si(OH)}_2$, $\equiv\text{Si(OH)}_3$, and $\equiv\text{Si(OH)}_4$ at the surface and finally $\text{Si(OH)}_4$ in solution. The origin of surface charge is the result of the dissociation of surface species. The extent and rate of hydrolysis and ionization is dependent on pH as well as ionic strength. For example, the degree of ionization and therefore the surface charge will be larger in magnitude under high pH conditions than under low pH conditions. This has been discussed in an earlier paper (Kulkarni and Somasundaran, 1972). The number and type (isolated or interacting) of silanol groups present on the quartz surface and possibly even the related degree of hydration of the surface will be the major factors determining the electrokinetic properties of the particles. Thus, as the number of ionizable silanol groups per unit area of the surface increases, the zeta potential can be expected to become higher. Similarly, as the thickness of the adsorbed water layers on the surface increases, the shear plane can be expected to shift away from the surface thereby lowering the zeta potential. Any interference with the above interfacial processes or any contamination of the surface by pretreatments will result in changes in electrokinetic proper-
ties such as zeta potential. The severity of a pretreatment can be discussed in terms of the change in zeta potential owing to such a treatment as well as subsequent changes in it upon aging. In general, the higher the above change in zeta potential, the more severe is the pretreatment effect. Indeed, the changes produced upon treating a mineral that is precontaminated by surface active agents or specifically adsorbing inorganic species, must be interpreted by also considering any decontamination of surfaces.

Chemicals such as HF or NaOH will spontaneously react with quartz. Moreover, both F⁻ and Na⁺ are highly surface active for quartz (Meyer, 1968; Fowkes and Burgess, 1970). Thus, when quartz is leached with HF or NaOH solution, in addition to the dissolution of silanol groups and quartz from the surface, contamination of the surface with F⁻ or Na⁺ takes place. Meyer (1968) has pointed out that if silica is ever treated with HF or even if HF is used elsewhere in the laboratory building, fluoride can be found at significant levels on the quartz surface. Removal of Na⁺ or F⁻ is extremely difficult by washing with deionized water or even HCl solutions. It has also been indicated by Meyer that such HF treatments decrease the capacity of the silica surface to adsorb water. The HF treatment thus causes removal of hydroxylated silica surface species, contamination of the surface and a decrease in the hydration of the surface. All these changes will result in an alteration of the electrokinetic potential.

HF treatments have often been employed in the past (Zucker, 1959; Li and

![Graph](image_url)

**Fig. 7.** Variation of zeta potential of HF-treated (Treatment No. 3) and HF/NaOH-treated (Treatment No. 4) quartz as a function of aging time; dotted curves for equilibrium values obtained for HNO₃-treated (Treatment No. 2) quartz for comparison.
de Bruyn, 1966; Thiers, 1970) to free the quartz surface of amorphous silica. This treatment, in addition to contaminating the surface, also leads to a highly distorted surface. A NaOH treatment is usually given to remove such distorted quartz from the surface (Van Lier et al., 1960). The NaOH treatment does slowly dissolve the distorted quartz generating a much less severely treated surface. But this treatment results in the formation of sodium silicate and in the diffusion of sodium ions into the quartz lattice. When quartz subjected to the above treatment is contacted with fresh water free from sodium ions, a meta-stable equilibrium is set up with diffusion of Na\(^+\) ions from the surface to the bulk solution. A continuous removal of Na\(^+\) ions from the surface to the bulk solution will cause changes in the surface charge. Large continuous changes in zeta potential and a lowering of isoelectric point observed during the aging of quartz pretreated with HF and then with NaOH can be the result of such diffusional processes. Thus, even though HF or NaOH treatments can remove amorphous silica layers which have been generated during such preparatory techniques as grinding, they must be considered as highly undesirable due to the contaminating effects.

Dilute nitric acid does not appear to spontaneously dissolve quartz or distort the surface and therefore does not need any subsequent alkali treatment. However, it is safe to assume that it will remove any organic or inorganic species that are specifically adsorbed on quartz surface. Low pH conditions do not leave the mineral sufficiently negatively charged to retain the contaminants. Furthermore, nitrate ions, possibly due to their larger size, do not appear to specifically adsorb on the quartz surface to affect its surface properties permanently. For similar reasons, dilute perchloric acid solution also might be considered as a safe cleaning agent. Further surface analytical work is necessary to test these considerations.

It might also be noted at this point that contact of a mineral with hot solutions can cause significant changes in its surface properties. Previous studies (Somusundaran and Kulkarni, 1973) have shown zeta potentials of both aluminas and hematite to alter markedly upon subjecting the mineral/water system to a cycle of heating and cooling. It is not yet established whether the observed changes were the result of the contamination of the mineral surface with silicate species from the container walls, or from the mineral itself, or the result of actual changes in the type or activity of the surface species.

Minerals have to be often cleaned after their preparation particularly for the study of their interfacial properties. Selection of a cleaning procedure should actually depend upon the purpose and scope of the proposed study and no single universal pretreatment could be suggested. Mild pretreatments preferably with dilute nitric or perchloric acid are, however, considered to be safe for general use. In the light of the effects produced by various commonly used pretreatments such as boiling, acid leaching and alkali leaching, a certain amount of standardization of pretreatments used in mineral processing research appears essential.
SUMMARY AND CONCLUSIONS

Effects on the electrokinetic properties of quartz of various pretreatments such as (a) desliming, (b) ultrasonic irradiation, (c) leaching with nitric acid, and (d) leaching with hydrofluoric acid followed by cold or warm sodium hydroxide solutions were studied using streaming potential technique. Changes in zeta potential both due to the pretreatments and during the post pretreatment periods were monitored to determine the severity of the pretreatments and the instability of the resultant surfaces. Desliming, ultrasonic irradiation and leaching with dilute nitric acid were found to be mild treatments that did not produce marked changes in zeta potential.

Hydrofluoric acid contact resulted in a lower zeta potential of quartz. This treatment is considered to dissolve various surface silanol species, cause distortion of the surface and possibly contaminate the surface with silicon—fluoride complexes. Use of warm sodium hydroxide solution after the hydrofluoric acid treatment resulted in an increase in isoelectric point of quartz to about 6.5. Furthermore, the resultant surface was highly unstable as shown by the continuous shift in zeta potential towards more negative values during subsequent aging in water.

These observations along with the previous observation on the effect of the contact of minerals with hot water clearly suggest that such pretreatments commonly used in minerals research can result in literature data for surface properties that differ from each other significantly depending upon the treatment used and the duration of the post-treatment aging. Even though the type of pretreatment should depend mainly on the system and the aim of the study a general treatment cannot therefore be prescribed. Formulation of general guidelines for mineral preparation will certainly increase the utility of basic as well as applied mineral research.

From the present results, a mild pretreatment with dilute nitric acid or possibly perchloric acid seem appropriate for cleaning these oxide minerals.

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REFERENCES


