Effect of Alkalinity on Flotation Behavior of Quartz

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ABSTRACT: Alkalinity is defined as the capacity of a water to neutralize strong acids. In natural waters, this capacity is attributable to bases such as $HLU_{,}$, CO; and $OH"$ as well as to species often present in small concentrations such as silicates, borates, ammonia, phosphates and organic bases. Commonly, alkalinity originates from the total amount of carbonates in water. Since notation is a process dependent on the water chemistry, carbonate alkalinity which may change as a result of the seasonal climatic changes can be a plausible concern in flotation.

Effect of alkalinity on the notability of quartz with an amine type collector and with Na-oleate, in the presence of calcium ions al alkaline pH values were studied. It was observed that as the alkalinity of the process water is increased, the notability of quartz decreased both with an amine type collector and with Na-oleate.

I INTRODUCTION

Flotation is affected by a number of factors such as the electrical properties of the mineral surface, electrical charge of the collector, molecular weight of the collector, the solubility of the mineral, the interaction between the dissolved species and notation reagents, etc.. Many of these factors are related to the process water chemistry.

Carbonates are always present in natural waters, thus in the process waters in notation. When COi dissolves in water it forms a weak acid. This acid and its salts in solution constitutes the carbonic system which forms a buffer system that resists pH change. The pH of natural waters on land is controlled mainly by this system. Carbonic species in natural waters consist of dissolved $CO_{,}$, carbonic acid $1H, CU, j$, bicarbonate (HCO,) and carbonate CO; ions. The predominant carbonic species is pH dependent. Almost all carbonic species exists as H, CU, below $pH = b.J.$ as HLU, between $pH=6.3-10\sim25$ and as CO; above $pH=10.25$ (Stumm& Morgan, 1981). Alkalinity is the capacity of a water to neutralize strong acids. Alkalinity in natural waters derives mainly from the carbonate system and total alkalinity can be expressed as $HLO, +2CO; +OH - H$. Addition of bicarbonate and carbonate ions, and a strong base increase alkalinity, addition of a strong acid lowers the total alkalinity. Normally, dissolution of $CO_{,}$ does not change alkalinity. However, above $pH=4.5$, pH of the solution is lowered upon $CO_{,}$ dissolution. In order to keep the pH at a higher value than $pH=4.5$, a base has to be added to the solution. As a result in alkaline pH range, carbonate alkalinity of water continuously increases in the presence of CO_2 if the pH is to be kept constant (Snoeyink&Jenkins 1980).

It is known that the solubility of carbon dioxide in water is dependent on the partial pressure of carbon dioxide which is constant in the atmosphere at 10^{-15} atm and the temperature. Solubility increases with the decreasing temperature. For example, the amount of dissolved carbon dioxide in water at 5"C is nearly 2 times that in 25"C. Thus, alkalinity of waters at high pH values will be affected by temperature. Alkalinity of natural waters also varies depending on the ratios of source waters. Natural waters during rainy seasons are dominated by poorly buffered surficial runoff and have low alkalinity; on the contrary, during dry seasons, ground waters rich in weathered bedrock ions are dominant in the natural waters which will have higher alkalinity values (Howlandel.al2000.).

As climatic changes lead to the change in the process water chemistry especially in terms of alkalinity, mineral processing operations in general and notation in particular are expected to be affected by these changes. In fact, it has been reported, without deliniating the reasons, that seasonal climatic changes have a determining effect on grade and recovery (Lin 1988). A clear understanding of the effect of the carbonic system, i.e. alkalinity, on notation would provide a useful tool to improve the process efficiency.

In this study, the effect of alkalinity on notation behavior of quartz in the presence of both a cationic and anionic collector using EMDEE Microllot cell was investigated. Quartz was chosen on the basis of two reasons: Firstly, its flotation behavior is well defined and widely studied. Secondly, the cationic notation and the anionic flotation of quartz with an activator are both carried out at high pH values where the effect of alkalinity is more pronounced.

2 MATERIALS AND METHODS

Quartz sample used in the experiments was obtained from the Kalemaden Industrial Raw Materials Industry&Trade. As received sample was first ground by a roll crusher and then screened to obtain -140+200 mesh fraction for the tests. To remove the impurities from the sample, it was subjected to magnetic separation using a high intensity magnetic separator! Bateman Lab Permroll) followed by leaching with hot IN HCl solution several times. The leached quartz was washed with distilled water until free of chloride ions. The sample had a SiO_2 content of 99.21%.

All ol the flotation experiments were carried out by using the EMDEE Microtlot Agitator. The sample, weighing 0.5 g, was piaced in the flotation cell and filled up to 60 mL with water. After adding the collector and bringing the water level in the tube to 70 mL, the pulp in the tube was conditioned for 10 minutes using a two blade mixer tightly fitted to the tube by a stopper to prevent the interaction of the pulp with air. After conditioning, frother was added and the test tube was placed in the EMDEE Micro-Hot Agitator. Air pressure was adjusted to 250 kPa. The test tube was agitated for 20 cycles and then allowed a few seconds for drainage prior to froth removal with vacuum suction. All float and sink fractions were collected separately and filtered on tared filter papers which were dried at I05°C for 4 hours and weighed to determine the recovery.

Waters with different alkalinities at different pH values were prepared by dissolving NaHCOi in CO_2 free water (obtained by nitrogen Hushing at pH 4).As collectors, Flotigam Eda which is alkyl ether amine and Na-oleate were used for the notation tests. Flotanol D-14 which has a composition of alkyl polyglycol ether was used as a frother. NaOH and HCl were used for pH adjustment. $CaCl_2$ was used as an activator for quartz when Na-oleate was used as the colleclor.NaHCO.,, HCl. NaOH and CaCI; used in the tests were all reagent grade

3 RESULTS AND DISCUSSION

In order to investigate the effect of alkalinity on the flotation of quartz, the optimum flotation conditions

with both the cationic collector and the anionic collector with no carbonate alkalinity were determined first. As shown in Figures 1 and 2, the optimum collector concentrations and pH value for the cationic and the anionic notation were found to be 50 mg/L amine at pH 10 and $4*IO^a$ M Na-oleale in the presence of $4*10^*$ M Ca^{2+} at pH=!2, respectively.
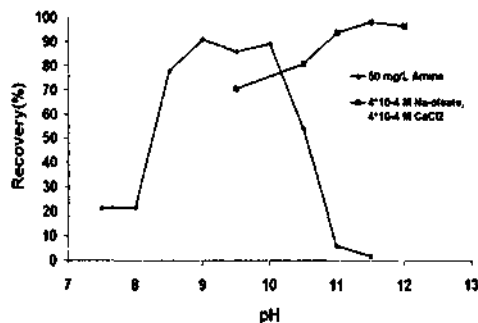

Figure I Flotation of quaitz with amine and Na-oleate as a function of pH at *lem* carbonate alkalinity; 100 ppm frotlier.
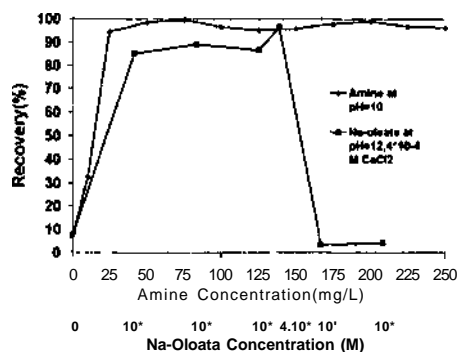

Figure 2. Flotation of quartz with amme and Na-oleate as a function of collector concentiation; 100 ppm frother.

The flotation mechanism of quartz with cationic and anionic collectors in the presence of an inorganic salt is well established and documented (Fuerstenau 1976,Uwadiale l992.Takedae4.Usui 1988, Iskra 1997a). In summary, the pzc of quartz occurs at pH 2. Therefore, quartz is negatively charged above this pH. Collector adsorption is due to the electrostatic interaction in cationic flotation and to chemisorption of oleate on calcium adsorbed on quartz (Iskra I997b, Sirkeci 2000,Ye&Matsuoka 1993). Ionization, micelle formation and hydrolysis of the collectors and activator ions play an important role in a successful notation operation. In addition, presence of other species may affect flotation. For example, Ba^{2+}, Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions have been reported to cause depression in the cationic flotation of quartz (Scott&Smith 1992.1993, Somasundaran 1974).

Flotation tests were carried out to determine the effect of carbonate alkalinity on the flotation of quartz. Alkalinity was adjusted by adding NaHCOj to the water. The carbonate alkalinity in waters equilibrated with atmosphere at or above pH 10 is in the form of (JO* and can exceed 10''' M (Stumin&Morgan 1981). Therefore, alkalinity of the test waters varied from zero to K)''' M CO; alkalinity. The flotation recoveries in the cationic and the anionic flotation as a function of alkalinity are given in Figure 3.
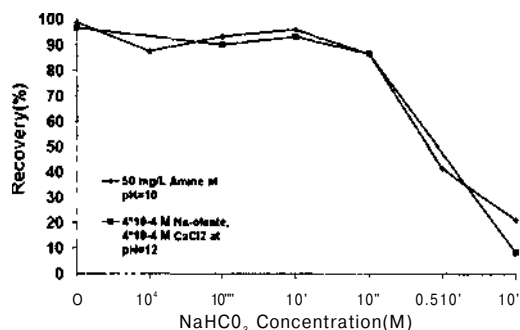

Figiue 3 Ettect of carbonate alkalinity on the flotation lecoveiy ot quartz with amine and Na-oleale: 100 ppm frother.

It is clear from the figure that as alkalinity increases from zero to 10''' M $W\backslash$, quartz is depressed as flotation recoveries sharply decrease from over 90% to 10% in both the calionic flotation using amine and in the anionic flotation using Na-oleale and Ca^{2+} as activators. In the case of cationic flotation, the depression of quartz might be related to the compression of the double layer caused by the higher ionic strength upon NaHCO^ addition(Vidyadhar et.al. 2002) or competetive adsorption of Na^+ and amine ions preventing the amine adsorption as reported earlier (Onada&Fucrstenau 1964, Iwasaki 2000). Another mechanism might be a reaction between amine and carbonate in the solution which would consume the collector and hinder flotation.

In the case of anionic flotation with Na-oleate, the mechanism of depression could be the replacement of $Ca(OH)^+$ ions on the quartz surface with Na^+ ions introduced by NaHCOi addition and pH adjustment with NaOH(Cooke&Digre 1949,Cooke 1949). $Ca(OH)^+$ ions which is thought to be responsible (Clark&Cooke 1968) for activation may react with CO; and precipitate on the quartz surface as CaCOi according to equation 1 :

$$CaOH + CO_3^- \rightarrow CaCO_3 + OH \qquad K = 10^{'''} \qquad (1)$$
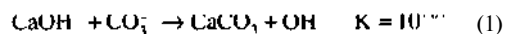
From the equilibrium constant of the reaction above, it is seen that CaCCh precipitation will strongly be favored at high pH values ihermodynamically. This

occurrence has been exploited in the precipitation of calcium ions in the selective floceulation of iron oxide from silica(Manukonda&lwasaki 1987). It can be speculated that in the anionic flotation of quartz, too, the activator calcium ions will react with the carbonate ions and precipitate. This freshly precipitated amorphous CaCO, is likely to be negatively charged at pH 12 (Rao&Forssberg 1991). The precipitates covering the surface of quartz will hinder the flotation of quartz with Na-oleate at high pH values in a similar manner to earlier studies (Aplan&Fuerstenau 1962). This phenomenon is probably more complex and requires further investigation.

Another series of flotation tests were conducted in order to investigate the effect of collector concentration on the flotation recovery at zero and 10''' M carbonate alkalinity. The latter value was chosen because of the noted effect. The results for amine and oleate are given in Figures 4 and 5, respectively.
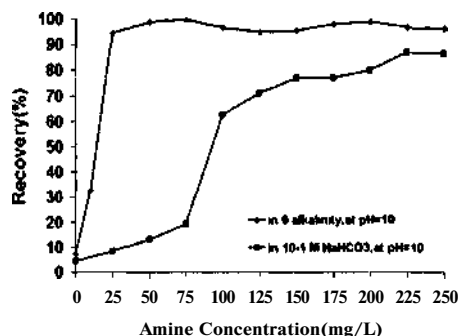

Figure 4. Effect of amine concentration on the flotation recovery of quartz at zero and l()''' M carbonate alkalinity; I00 ppm frother

It appears that increasing the amine concentration restored the recovery at I0''' M alkalinity tested. This behavior is in good agreement with earlier studies (Scott&Smith 1992,1993) where the effect of high ionic strength and calcium ions were reported to be remedied in the same way, that is by increasing the amine concentration. As the adsorption mechanism of amine on quartz is known to be electrostatic, adsorption equilibrium should be established as a result of ion exchange reaction according to equation 2:

Quartz'' - Amine* + Na* -> Quartz' - Na* + Amine* (2)
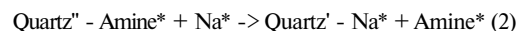
The equilibrium will shift in either direction depending on the relative abundance of Na^+ or amine in the solution. Excess amine ions will favor amine adsorption on quartz and vice versa. A similar cation exchange mechanism has been reported for the clay-amine adsorption system (Iwasaki 2000).

In the case ofoleate, a different flotation behavior was observed. Quartz, initially activated with calcium and then depressed with $10'''$ M carbonate alkalinity can not be floated effectively by increasing the oleate concentration, Figure 5.
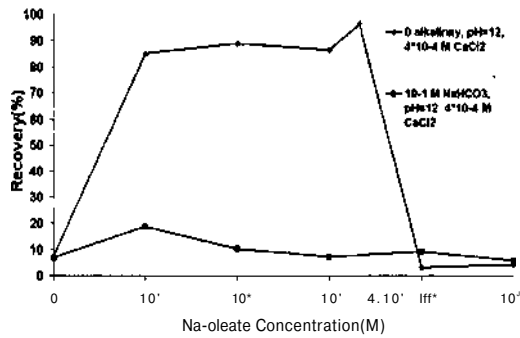

Figure 5. Na-oleate Concentration versus Recovery in different alkalinity values

This fact supports the postulation that Ca^{2+} ions precipitate on quartz and alter the nature of the surface. As an increase in the collector concentration does not effect the surface properties, in contrast with the cationic flotation explained above, quartz remain unfloatable. In this figure, the nonflotability of quartz with no added alkalinity beyond $10''$ M oleate concentration is related to the micelle formation (Antti&Forssberg 1989).

4 CONCLUSION

Carbonate alkalinity is an important characteristics of process waters open to atmosphere and can be as high as $10'''$ M. At this alkalinity level, both cationic and anionic flotation of quartz is adversely affected. Cationic flotation of quartz in the presence of $10'''$ M alkalinity can be improved upon increasing the amine addition. However, no improvements can be attained in the oleate flotation of quartz activated with calcium at the same alkalinity. As the carbonate alkalinity of the process water originates from either the dissolution of carbon dioxide in water or dissolution of carbonate minerals care must be taken to control both, so that flotation performance is not impaired.

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