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Flotation Properties of Silicon Carbide

I. Flotation of Silicon Carbide with Anionic and Cationic Collector

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Abstract: This article deals with the results of investigations on the flotation of silicon carbide by means of anionic and cationic collectors. On the basis of a wide range of physico-chemical and flotation tests, a mechanism explaining the effect of these reagents on the flotation of silicon carbide has been suggested. The deficient flotation of SiC in the presence of anionic reagents may be related to the negative charge occurring at the surface of silicon carbide in a wide region of pH (2.7–14), as has been proved by measurements of the electrokinetic potential. It was observed that in the presence of an anionic collector the negative charge increased at the surface of silicon carbide. This may be related to the adsorption of the anionic collector influenced by intermolecular forces between the hydrocarbon chain of the collector and the carbon atoms in the lattice of SiC.

Silicon carbide easily flotates by means of cationic collectors. The maximum flotation, when dodecylammonium chloride is being used as collector, occurs at pH = 9. Concentration of amine necessary for obtaining complete flotation recovery of SiC is two orders lower than in the case of quartz. The mechanism of amine action in the flotation of SiC consist in the adsorption of amine as a result of its electrostatic interaction with the negatively charged SiC surface. The negative charge of the surface originates from the silanol groups which are the oxidation product of SiC. © 1997 Elsevier Science Limited and Techna S.r.l.

Keywords: Silicon carbide, flotation, anionic collector, cationic collector, adsorption.

1 INTRODUCTION

Silicon carbide is rarely encountered in its natural state, usually it is produced artificially on a large scale. As a result of its peculiar physical properties, it has found wide application in numerous domains of technology. Its great hardness and resistance to high temperatures are responsible for its applications as an abrasive material and in the production of refractories. In electronics it is used as semiconductor.

Silicon carbide is one of the basic components of ceramic materials. There is much more information about the nature and surface properties like electrophoretic mobility, zeta potential and adsorption properties of oxide minerals[1–3] used for ceramic materials production. However, not much is known about non-oxide ceramic materials such as carbides, borides and nitrides. Silicon carbide belongs to them. In contrast, it is well known that a high degree of reliability can be achieved in processing of ceramic materials by optimizing the particle packing based on a knowledge of the interfacial chemistry of dispersed ceramic powders.[4–6]

Its main application, however, is the production of refractories and abrasives. Attention should be drawn to the fact that silicon carbide is not decomposed completely as a result of the use of these materials, so that much of it is left as unreacted solid wastes. If an adequate method of enrichment is applied, full-value silicon carbide can then be reclaimed from such waste material. Considerable amounts of waste are also obtained during the process of silicon carbide production.

The first stage of separating silicon carbide from the refractories is the liberation of SiC grains from the binding material and the products of decomposition, mainly SiO_2[7,8] by means of crushing and grinding. The liberated SiC grains which ought to be separated are very small, up to 0.5 mm, their mean size amounting to 0.2 mm at the most. For the separation of such fine grains, the process of flotation seems to be rather encouraging as far as the enrichment of silicon carbide is concerned.

Investigations have also been carried out concerning the recovery of silicon carbide from refractories making use of gravitational methods and applying dry flow separation based on the fluidized bed technique.[9] Because of the small difference of the specific gravities of the substances to be separated (SiC –3.15, SiO_2 –2.7 g/cm^3) only partial enrichment was achieved, the results being worst for grains smaller than 0.2 mm in diameter.

Utilizing the semi-conductivity of silicon carbide, attempts have been made to enrich it by means of electrostatic separation.[10] Very good results could be obtained when grains larger than 0.3 mm in diameter were being enriched. After multi-stage enrichment the concentrates then contained 95% SiC. For finer size grains the quality of the concentrates dropped considerably. The physicochemical properties of the silicon carbide surface present new problems for investigation. Foreman[11] has carried out investigations concerning the flotation of SiC with fatty acids, proving that in the low pH region differences occur in the intensity of adsorption of fatty acids on SiC and SiO_2, respectively, the adsorption being more intensive in the case of SiC.

2 MATERIALS AND MEASURING METHODS

Commercially available α-SiC was used throughout this work, after purification in order to remove the iron resulting from the process of grinding and classification. The purification was carried out first by means of washing with hot hydrochloric acid, then by rinsing with distilled water.

The composition of this purified SiC in weight percent was as follows:

SiC	Free C	Fe_2O_3	SiO_2
97.5	0.24	0.16	1.5

Spectral analysis indicated the presence of the following elements: silicon as the fundamental component, trace amounts of Al, Mg, B, Ca, Fe, Cu and Ag. The flotation tests were performed in a monobubble Hallimond tube. The 1.5 g sample of SiC having a grain size range of 0.075–0.15 mm was introduced in a 250 ml beaker and agitated in water for 10 min. Then the mixture was transferred to the Hallimond tube and floated with an air flow rate of 0.7 cm^3/s. For the adsorption tests, material of the same grain size was used. The specific surface area of the material was determined by means of the B.E.T. method and amounted to 0.02 m^2/g. The adsorption of oleate was determined by making use of the method suggested by Duncombe.[12] The adsorption of dodecylammonium chloride was measured by the method of scintillation counting using the amine labelled with ^{14}C. The contact angle was determined on well-shaped crystals making use of an apparatus manufactured by Kernco Instrument Co. This device, based on a goniometric microscope, allows to measure the contact angle of the drop placed on the mineral surface. The value of the electrokinetic potential was measured by means of the micro-electrophoretic method using Laser Zee^{TM} Meter Model 501 manufactered by Pen Kem, Inc. The apparatus consists of laser ultra-microscope for high contrast image, fatigue-free viewing of submicron particles, unique prism design permitting simultaneous measurement of many particles, silica/Teflon chamber and digital read-out of zeta potential. The suitable grain sizes of silicon carbide for electrokinetic potential determination were prepared by grinding and sedimentation. The ionic strength was 2×10^{-3} M. Distilled water was used in all experiments. Dodecylammonium chloride was analytical-grade. Sodium oleate was 90% pure and contained 5% of the long-chain fatty acid and 5% water.

3 RESULTS AND DISCUSSION

3.1 The flotation of silicon carbide with anionic collector

In order to find out the flotation properties of silicon carbide in the presence of an anionic collector, a series of flotation tests was carried out using a typical anionic collector such as sodium oleate. The results of these tests as a function of pH are shown in Fig. 1. As can be seen, silicon carbide displays some flotation activity in the presence of sodium oleate. This activity decreases at higher pH. If SiC flotation is compared to its natural floatability, we observe that oleate causes a slight increase of floatability in the acid pH range.

Therefore, no electrostatic effects should be expected which might give rise to an adsorption of the oleate, since silicon carbide displays a negative surface charge from pH = 3 upwards, as has been

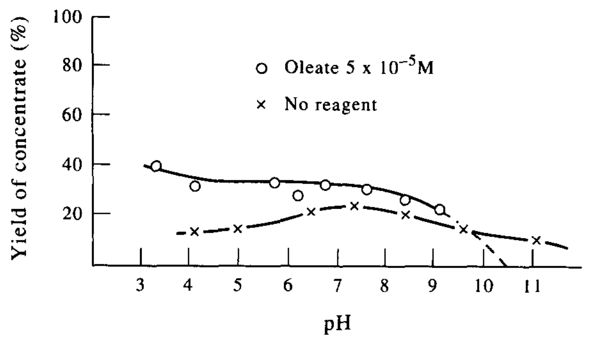

Fig. 1. Flotation of silicon carbide without and with sodium oleate vs pH.

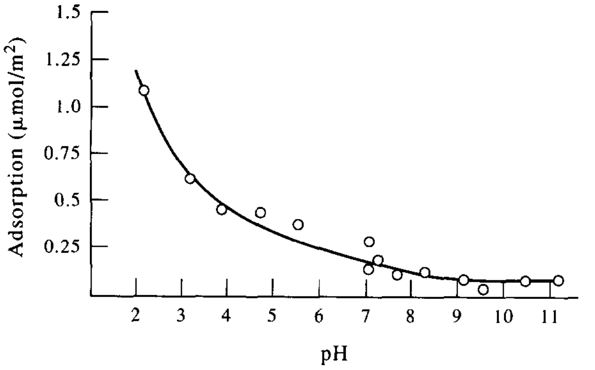

Fig. 3. Adsorption of sodium oleate from a 5×10^{-5} M solution on silicon carbide vs pH.

proved by measuring the electrokinetic potential (Fig. 2). It cannot be precluded, however, that oleate might be adsorbed on silicon carbide in the pH range where it has a negative surface charge in the presence of the activating effect of polyvalent metal cations. This is, however, a rather extensive problem which will be dealt with separately.

The slight increase of SiC flotation observed at acid pH may be accounted for by the adsorption of free oleic acid resulting from molecular interactions. Such adsorption has been observed, as may be seen from Fig. 3. This diagram indeed indicates a distinct increase of oleate adsorption on silicon carbide, at lower pH values. The highest adsorption is in fact achieved in the vicinity of the zero point of charge (ZPC), which in the case of silicon carbide amounts to about $\text{pH} = 2.7$. The mechanism is confirmed by the observations made by measuring the contact angle. The results of these measurements, depending on the pH value in the presence of sodium oleate, are presented in Fig. 4. They indicate some water-repellency of the surface of silicon carbide, as the result of the adsorption of oleic acid in the acid pH range with its maximum in the vicinity of ZPC. In order to explain the influence of the oleate at higher pH values, the electrokinetic potential was also measured in the pH range as shown in Fig. 2. As can be seen, the slight adsorption of oleate already observed in the alkaline range (Fig. 3) leads to an increase in the negative charge on the surface of SiC.

The adsorption cannot be related to electrostatic effects, because in the alkaline region silicon carbide is definitely negative. Moreover, the growth of the negative charge in the presence of oleate characterizes the kind of adsorption, in which the polar $-\text{COO}^-$ group carrying the charge, remains chemically unbounded. Thus, it might be assumed that the adsorption of the oleate was the result of interactions occurring between the hydrocarbon chain of the oleate and the carbon atoms in the crystallographic lattice of SiC, as well as the colloidal carbon on the SiC surface which has not undergone any reaction during the synthesis of SiC dispersed in its crystals. Such a mechanism of adsorption, in which the carboxyl groups continue to be active and chemically unbounded, may result in an increase of the negative charge at the surface, and hence also to a growth of the electrokinetic potential. Such an adsorption does not lead, either, to any hydrophobization of the surface, so that no increase in the floatability of silicon carbide could be observed in the presence of oleate at higher pH values. An increase of surface charge should rather

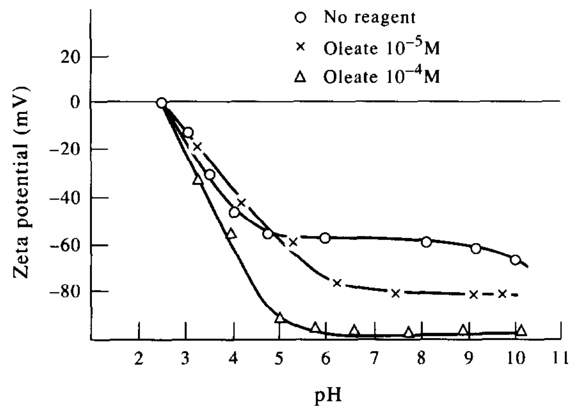

Fig. 2. Influence of sodium oleate concentration on electrokinetic potential of silicon carbide vs pH.

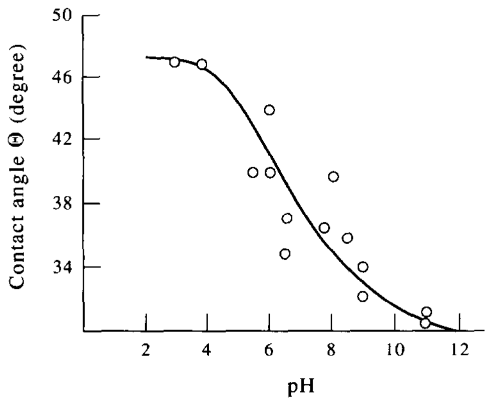

Fig. 4. Contact angle measurements on silicon carbide in the presence of 5×10^{-4} M sodium oleate, vs pH.

bring about the opposite effect, i.e. a hydrophilization of the surface. Such an effect has been in fact observed while measuring the influence of the concentration of oleate upon the value of the contact angle at pH = 9 (Fig. 5). Thus, the value of the contact angle of SiC decreases at higher concentration of the oleate in the solution, which indicates that the surface is becoming more hydrophilic. Since, however, at pH = 9 silicon carbide displays a better floatability in the presence of oleate than its natural floatability (cf. Fig. 1), it should not be forgotten that flotation is a kinetic process and that its effects need not coincide completely with the results of measurements of the contact angle, carried out at equilibrium conditions.

An additional negative charge will bring the oleate to the surface if its adsorption is assumed to take place as an interaction of the hydrocarbon chain of the oleate and the atoms of carbon present in the crystallographic lattice. This charge will vary depending on the concentration of the oleate at the value of pH which controls the dissociation of the oleate. Such changes of the charge are confirmed by measurements of the electrokinetic potential, as presented in Fig. 2. The introduction of oleate into the solution at a concentration of 10^{-5} M increases the negative value of the electrokinetic potential by 20 mV in the alkaline pH region. A further increase of the oleate concentration up to 10^{-4} M again results in an increase of the negative electrokinetic potential by 20 mV.

3.2 The flotation of silicon carbide with cationic reagents

There is some similarity between the flotation of silicon carbide and the flotation of quartz. In both cases a negative value of the electrokinetic potential has been observed in a wide range of pH. For this reason it is supposed that silicon carbide also could be floated with cationic reagents. For this purpose amine collectors were used with a hydrocarbon chain varying in length from C_6 to C_{18}. The results of these flotation tests are shown in Fig. 6. The influence of the length of the amine chain upon the results of flotation are obvious; the longer the hydrocarbon chain, the lower is the concentration necessary to warrant a complete flotation.

Similar results were obtained on quartz by Somasundaran.[13,14] The only difference is that in the case of silicon carbide a complete recovery is already obtained at concentrations of the respective amines by two orders lower than in the case of quartz. So, for instance, while quartz can be floated with amine containing 8 carbon atoms at a concentration of 10^{-2} M, silicon carbide is fully floated with the same amine, at a concentration of 10^{-4} M. The easier flotation of silicon carbide may be the result of its lower surface activity than that of quartz. In the crystallographic lattice of silicon carbide, besides silicon, there is inactive carbon. In addition to that, on the surface there may be found some unreacted colloidal carbon in the form of inclusions. In order to determine the effect of pH on the flotation of silicon carbide by means of amine, investigations have been carried out applying dodecylammonium chloride as the collector. It has been found that SiC floats in a wide range of pH with a maximum at about pH = 9 (Fig. 7). In order to find out the mechanism of the flotation of silicon carbide with amines, a series of additional tests was carried out, measuring the adsorption of dodecylammonium chloride (Fig. 8), the contact angle of SiC with dodecylammonium chloride (Fig. 9) and the electrokinetic potential of silicon carbide at various concentrations of dodecylammonium chloride and at various pH (Fig. 10). Both the adsorption of amine and the contact angle display a distinct maximum at pH = 9, which would account for the occurrence of the flotation maximum observed at the same pH value. At higher pH, a rapid drop of flotation connected with a decrease in the adsorption of dodecylammonium

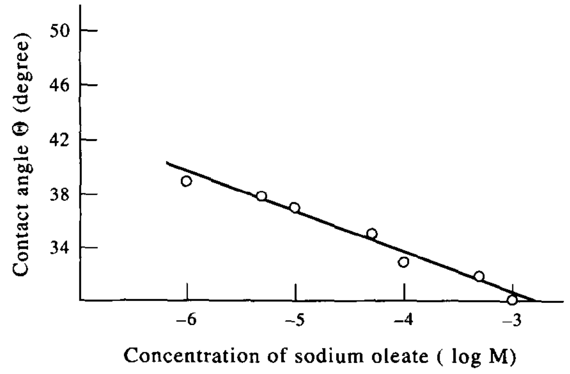

Fig. 5. Influence of sodium oleate concentration on the contact angle of silicon carbide at pH = 9.

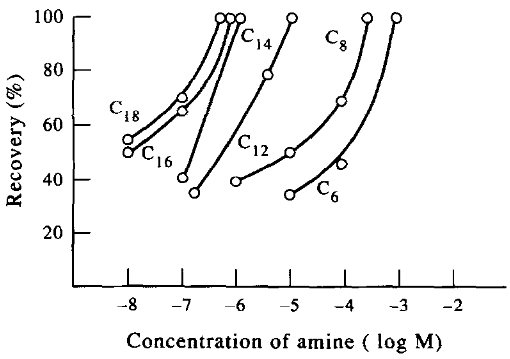

Fig. 6. Flotation of silicon carbide using amines with different chain lengths (C_6–C_{18}) and variable concentrations.

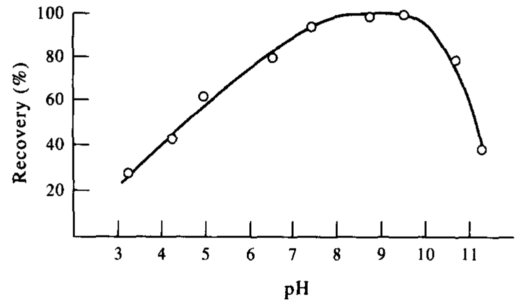

Fig. 7. Flotation of silicon carbide with 10^{-5} M dodecylammonium chloride vs pH.

chloride (Fig. 8), and hence also with a decrease of the contact angle (Fig. 9), may be observed.

According to Laskowski[15] these observations made in the alkaline pH range leading to a decrease of silicon carbide flotation by means of amine should not be related to the adsorption of amine on the mineral surface, but rather to the precipitation of the reagent.

The results presented in Fig. 10 show that dodecylamine is responsible for the considerable decrease of the negative value of the electrokinetic potential, and at a dodecylamine concentration of 5×10^{-4} M the double layer is overcharged and electrokinetic potential is changing its sign to a positive one. A similar effect for quartz has been observed by Gaudin and Fuerstenau.[16] The observed decrease of the electrokinetic potential, starting at pH = 10 (Fig. 10) is similar to that presented by Laskowski[15] and in fact concerns the electrokinetic potential of the precipitated amine itself. Based on what has been said above, it may be assumed that the mechanism of the effect of amines on the flotation of silicon carbide consists of the adsorption of amine as a result of its electrostatic interaction with the negatively charged surface. All the spots with a negative charge may become active points on the silicon carbide surface in the adsorption of amine molecules, i.e.:

- unreacted SiO_2
- Si with broken bonds
- the product of high-temperature oxidation of Si (SiO_2).

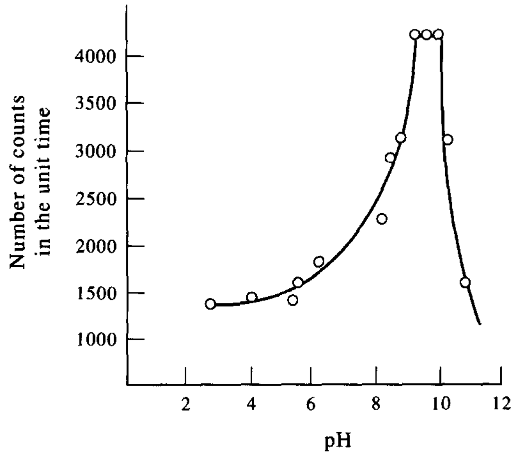

Fig. 8. Adsorption of dodecylammonium chloride labelled with ^{14}C on silicon carbide, vs pH. Initial concentration of dodecylammonium chloride was 10^{-5} M.

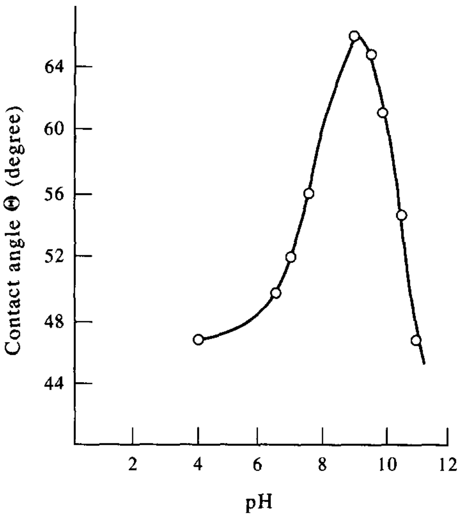

Fig. 9. Contact angle on silicon carbide with 5×10^{-4} M dodecylammonium chloride vs pH.

4 CONCLUSIONS

- Silicon carbide does not display any flotation activity when anionic collectors are used, due to its negative surface charge in nearly all the pH range (from pH 2.7 upwards).
- Silicon carbide floats well in the presence of amines, the maximum flotation occurring at pH 8–9.
- If amines of various lengths of chains are used, silicon carbide floats in a similar way to quartz, but the concentration of the collector needed to reach complete flotation is two orders lower than in the case of quartz.

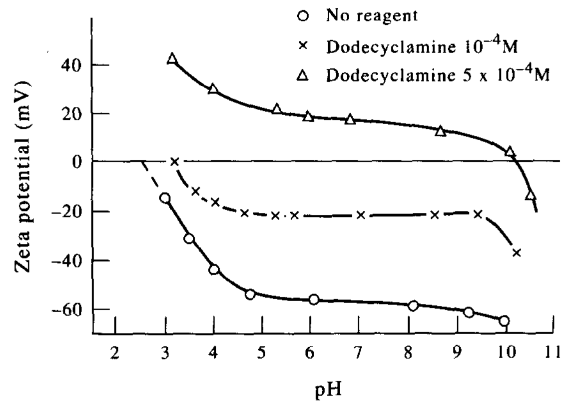

Fig. 10. Influence of dodecylammonium chloride concentration and pH on the electrokinetic potential of silicon carbide.

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