PII: S0272-8842(96)00039-9

*Ceramics International* **23** (1997) 343–348

0272-8842/97 $17.00 + 0.00

# Flotation Properties of Silicon Carbide

## II. On the Influence of Multivalent Cations on the Flotation of Silicon Carbide with Sodium Oleate

**J. Iskra**

Department of Mineral Processing and Waste Treatment, Mining Faculty, Silesian Technical University, ul. Akademicka 2,
44-101 Gliwice, Poland

(Received 15 November 1995; accepted 12 February 1996)

**Abstract:** This article presents the results of investigations concerning the influence of multivalent cations on the flotation of silicon carbide with sodium oleate as a collector.

These results show that there is great similarity of the effect of multivalent cations on the flotation of, respectively, silicon carbide and quartz, some oxides and silicates.

The influence of multivalent cations on the flotation of SiC with sodium oleate is manifested by the maxima recoveries observed at specific pH values for the different cations tested: $Fe^{+3}$, $Al^{+3}$, $Cu^{+2}$, $Mn^{+2}$. In order to interpret the mechanism of their activity, both measurements of adsorption and of electrokinetic potential were carried out.

The maxima recoveries observed are due to the presence of hydroxy complexes of the type $MeOH^+$, $MeOH^{+2}$, which were adsorbed on the negatively charged surface of the silicon carbide, as a result of which the adsorption of the anionic collector became possible. The flotation maxima occured in those pH ranges in which the hydroxy complexes reach the highest concentration in solution. This mechanism is similar to that explaining the phenomena observed in the case of quartz and some oxides and silicates. © 1997 Elsevier Science Limited and Techna S.r.l.

## 1 INTRODUCTION

Investigations concerning the flotation of silicon carbide by means of anionic and cationic collector,[1] have already displayed a great similarity in the respective flotation properties of SiC and quartz: both compounds do not float with sodium oleate, whereas their flotation with dodecylamine is very successful. Other investigations[1,2] have also proved a similar dependency of the electrokinetic potential of both compounds as a function of pH. Similarities of the surface characteristics were thus also expected as far as the effect of multivalent cations on flotation is concerned. In the case of quartz, such investigations have been carried out extensively by numerous authors showing maxima flotation recoveries at specific pH values for the respective cations. These maxima were shown to be related to the activating of $MeOH^+$, $MeOH^{+2}$ complexes, whose maximum concentration effect in solution occurs at these pH values. The similarity of silicon carbide properties to quartz accounts for the presence of a silica coating on its surface. The presence of these coatings on silicon carbide and silicon nitride has been observed by Whitman and Feke.[3]

Investigations concerning the infuence of multivalent cations on the flotation of silicon carbide are of great importance, in view of the possible introduction of some ions into the flotation system, e.g. as a result of the grinding process (Fe) or together with water (Fe, Ca, Mg). Technically obtained silicon carbide also contains certain amounts of Al, Cu and Fe.

## 2 INVESTIGATIONS CONCERNING THE INFLUENCE OF FERRIC IONS $Fe^{+3}$ ON THE FLOTATION OF SILICON CARBIDE WITH SODIUM OLEATE

Iron compounds belong to those materials which most probably may contaminate silicon carbide. This contamination may occur already in the process of the production of SiC, where iron oxides can be introduced together with the quartz sand. Further contamination may be the result of crushing and grinding.

In order to determine the influence of $Fe^{+3}$ ions on the flotation of SiC a series of tests were carried out, including flotation, adsorption measurement of $Fe^{+3}$ ions and determination of the electrokinetic potential in the presence of ferric ions. Materials and methods applied in the experiments are described in Part I of this article.[1]

Figure 1 is shows the results of the flotation of SiC in the presence of $5\times10^{-5}$ M sodium oleate and of various amounts of $Fe^{+3}$. A distinct flotation maximum occurs at pH = 3.5, which was not observed when SiC was floated with the oleate in the absence of $Fe^{+3}$ ions.[3] Measurements of the adsorption of $Fe^{+3}$ ions on silicon carbide show that adsorption takes place in the pH range 2–8 (Fig. 2). The electrokinetic potential of SiC was also measured in the presence of ferric ions. The results of these measurements are presented in Fig. 3. They show that because of the presence of ferric ions, the zero point of charge is shifted from pH = 2.5 to pH = 6, so that in this range the surface charge changes from a negative into a positive one. This change suggests that in this pH range some

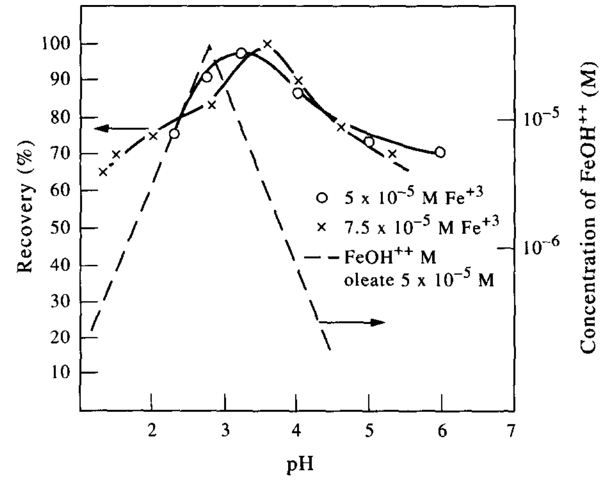

**Fig. 1.** Flotation of silicon carbide with sodium oleate $5\times10^{-5}$ M as a function of pH and various concentrations of $Fe^{+3}$. Dotted line is the concentration of the hydroxy complex $FeOH^{++}$ for $5\times10^{-4}$ M $Fe^{+3}$.

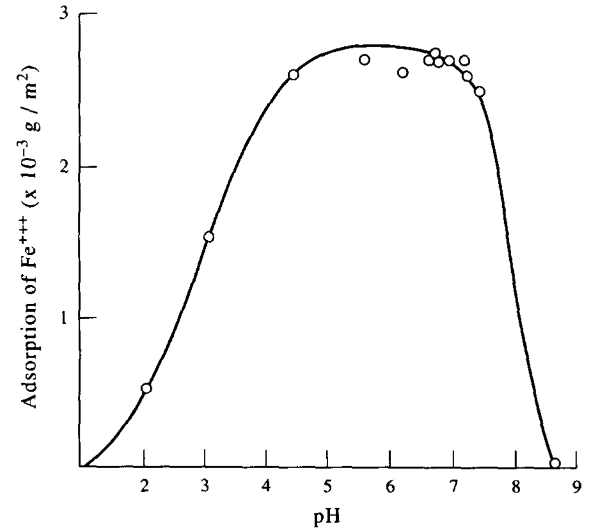

**Fig. 2.** Adsorption of ferric species on silicon carbide as a function of pH for $5\times10^{-4}$ M $FeCl_3$ concentration.

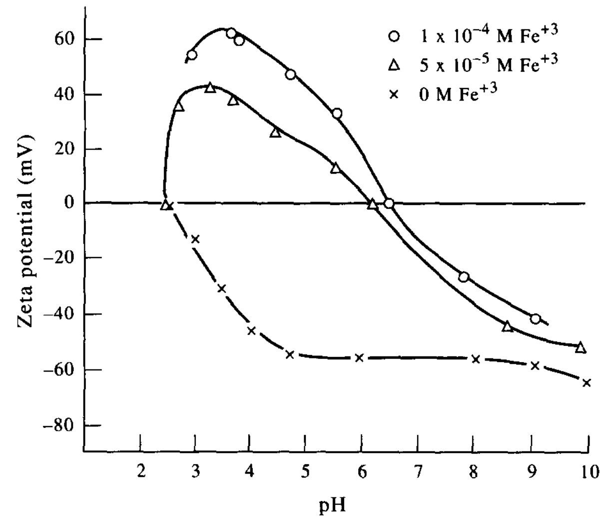

**Fig. 3.** Zeta potential of silicon carbide as a function of pH with various concentrations of $Fe^{+3}$.

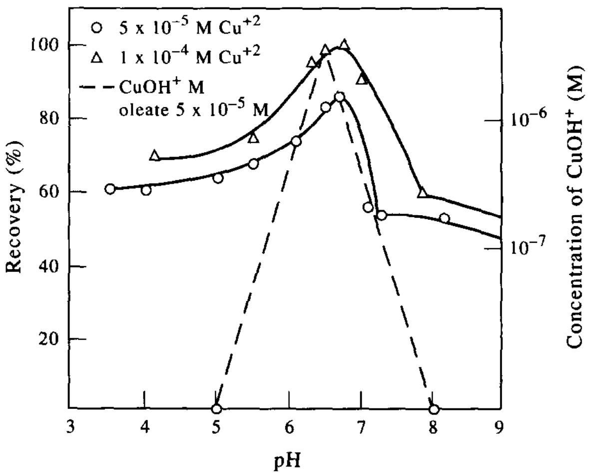

**Fig. 4.** Flotation of silicon carbide with sodium oleate $5\times10^{-5}$ M as a function of pH and various concentrations of $Cu^{+2}$. Dotted line is the concentration of the hydroxy complex $CuOH^{+}$ for $1\times10^{-4}$ M $Cu^{+2}$.

positive iron ions have been adsorbed in the double layer. Referring to the equilibrium diagram giving the occurrence (Fig. 4) of iron ions in a $1\times10^{-4}$ M $FeCl_3$ solution as a function of pH[4] it is seen that in the pH range concerned, where the sign of the zeta potential has changed from negative into positive, iron occurs in the form of a series of complexes, viz. $Fe_2(OH)_2^{+4}$, $Fe(OH)_2^{+}$ and $FeOH^{+2}$ with a maximum concentration of $2\times10^{-5}$ M at $pH=3.7$; at a concentration of $10^{-7}$ M they additionally comprise the pH range from 0 to 4.5. Thus it may be assumed that these complexes are responsible for the change of the sign of the zeta potential of silicon carbide in the pH range, being adsorbed in the double layer. The range of the occurrence of these complexes also falls within the range of the maximum flotation of SiC as shown in Fig. 1. It may thus be supposed that the flotation of silicon carbide is activated because of the presence of hydroxy complexes of iron.

## 3 INVESTIGATION ON THE INFLUENCE OF COPPER IONS $Cu^{++}$ ON THE FLOTATION OF SILICON CARBIDE WITH SODIUM OLEATE

In order to define the inflence of $Cu^{++}$ ions on silicon carbide, a series of flotation tests was carried out in the presence of copper ions, using sodium oleate as a collector. The results are shown in Fig. 4, which indicates a very distinct activation of the flotation of silicon carbide in the pH range 5–8. The presence of copper ions on the silicon carbide surface in this pH range was confirmed by adsorption tests, as may be seen in Fig. 5. Adsorption starts at $pH=4$ and then rapidly increases, reaching its maximum value at $pH=7$. In the pH range where activation of silicon carbide occurs two copper complexes, namely $Cu_2(OH)^{+2}$ and $CuOH^{+}$, may exist in solution, both of them reaching their maximum of concentration of $3\times10^{-6}$ M at $pH=6.5$.[5,6] It is therefore supposed that these complexes may be the cause of the activation of the silicon carbide flotation. The adsorption of these complexes in the double layer should then affect the value of the electrokinetic potential of silicon carbide. This was confirmed by measurement of the electrokinetic potential of SiC in the presence of copper ions. As seen in Fig. 6, in the pH range 6.5–9 there is a considerable change in the value of the zeta potential of SiC in the presence of copper ions. As can be seen from the figure, the zeta potential changes from a negative to a positive value. The adsorption of the copper complexes $CuOH^{+}$ has thus created the necessary conditions for the adsorption of the anionic reagent, making flotation of silicon carbide possible.

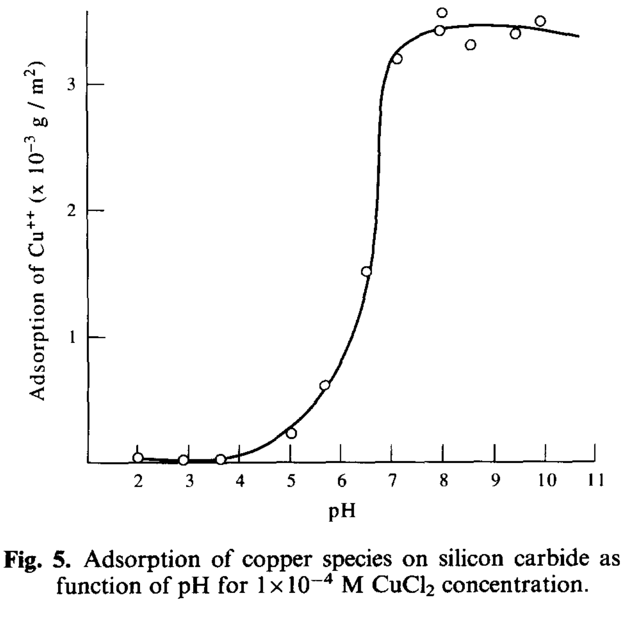

**Fig. 5.** Adsorption of copper species on silicon carbide as a function of pH for $1\times10^{-4}$ M $CuCl_2$ concentration.

## 4 THE INFLUENCE OF ALUMINIUM IONS $Al^{+3}$ ON THE FLOTATION OF SILICON CARBIDE WITH SODIUM OLEATE

Aluminium ions are probably not so widely used as activators as other ions, but their activating effect on quartz has been mentioned by some authors.[7] Moreover, at certain values aluminium ions yield complexes[8] similar to those of iron and copper.

The activating effect of aluminium ions on the flotation of silicon carbide is indicated by the flotation test results presented in Fig. 7. A distinct range of activation can be seen, which in the case of a $5\times10^{-5}$ M sodium oleate solution lies in the pH

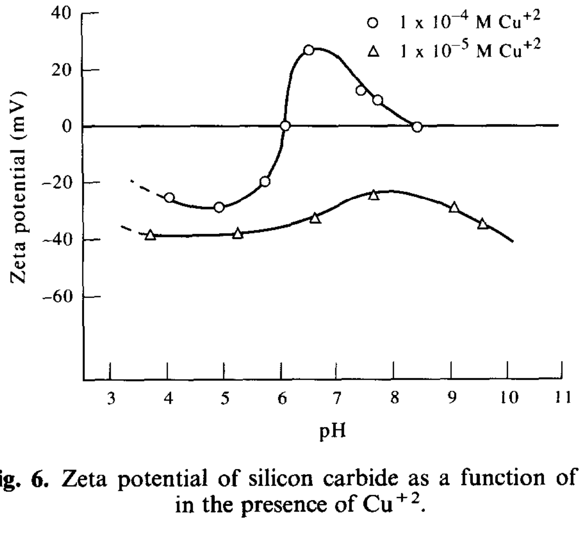

**Fig. 6.** Zeta potential of silicon carbide as a function of pH in the presence of $Cu^{+2}$.

range 3–5. The pH ranges in which the aluminium complexes $AlOH^{++}$ and $Al(OH)_2^{+}$ occur correspond to pH = 2–6 and pH = 3–8, respectively. This again coincides exactly with the range of the activation of silicon carbide flotation by means of aluminium ions.

The adsorption of aluminium ions on silicon carbide was confirmed by the adsorption measurements (Fig. 8) and the electrokinetic potential (Fig. 9). In this case, similarly as with other ions, a change in the value of the electrokinetic potential up to the change of the negative sign into the positive one can be observed. It can therefore be assumed that in this case the mechanism of the activation of silicon carbide flotation is also related to the presence of positive hydroxy complexes.

## 5 THE INFUENCE OF MANGANESE IONS $Mn^{+2}$ ON THE FLOTATION OF SILICON CARBIDE WITH SODIUM OLEATE

The effect of manganese ions was investigated in order to find out whether they comply with the rule observed in the case of metals forming complexes of the type $MeOH^{+}$. Manganese forms $MnOH^{+}$ in the pH range 7.5–11.5[9] with maximum concentration of $10^{-5}$ M at pH = 9.5. Flotation tests of silicon carbide in the presence of manganese ions (Fig. 10) indicate that activation occurs in the pH range 7–10. A similar activation was observed by Palmer[10] in the case of rhodonite $Mn_5(Si_5O_{15})$. Measurements of the electrokinetic potential (Fig. 11) indicate cation adsorption, because the negative charge decreases and at pH = 8 the value of the

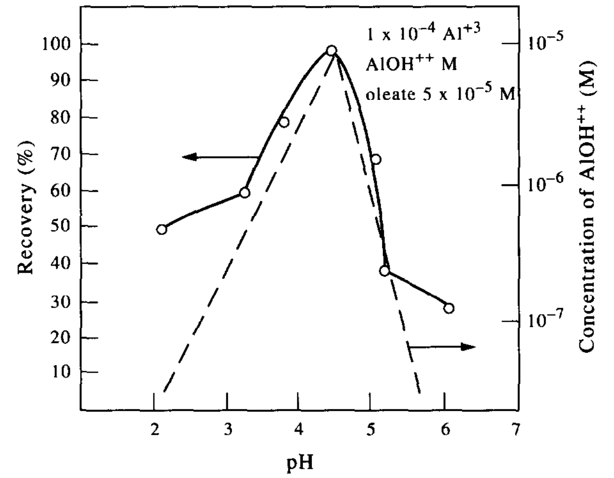

Fig. 7. Flotation of silicon carbide with sodium oleate $5\times10^{-5}$ M as a function of pH and aluminium ions concentration $10^{-4}$ M $Al^{+3}$. Dotted line is the concentration of the hydroxy complex $AlOH^{++}$ for $1\times10^{-4}$ M $Al^{+3}$.

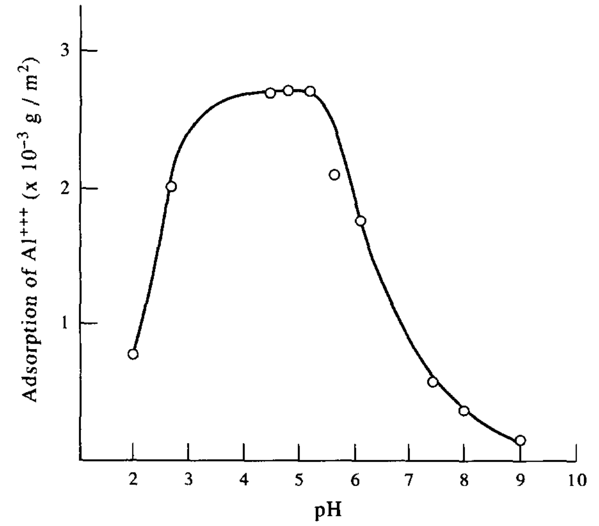

Fig. 8. Adsorption of aluminium species on silicon carbide as a function of pH for $1\times10^{-4}$ M $AlCl_3$ concentration.

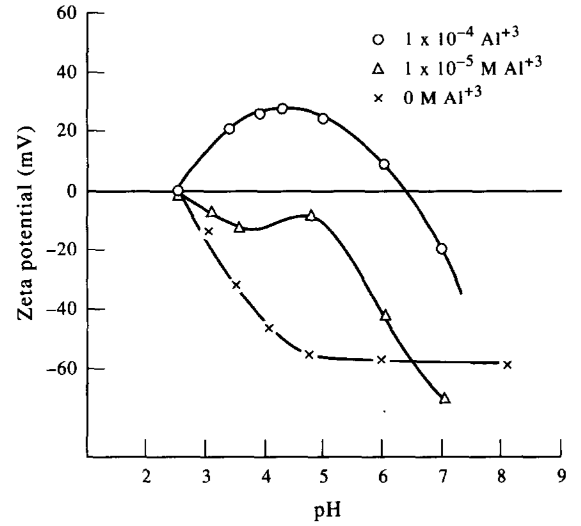

Fig. 9. Zeta potential of silicon carbide as a function of pH and two concentrations of $Al^{+3}$.

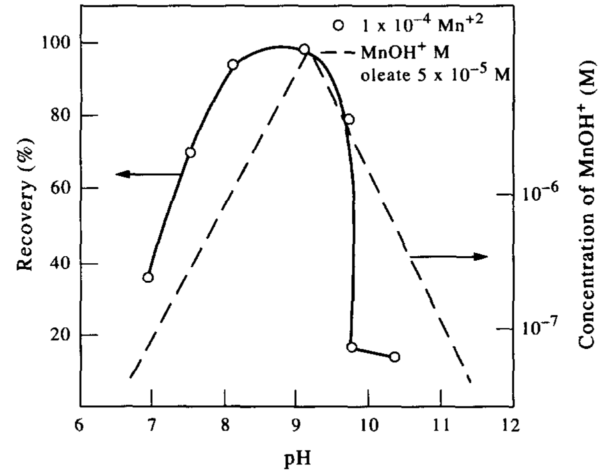

Fig. 10. Flotation of silicon carbide with sodium oleate $5\times10^{-4}$ M as a function of pH in the presence of $1\times10^{-4}$ M $Mn^{+2}$ ions. Dotted line is the concentration of the hydroxy complex $MnOH^{+}$ for $1\times10^{-4}$ M $Mn^{+2}$ vs pH.

zeta potential lies at about zero (or may be even slightly positive). The adsorption of manganese ions on silicon carbide was proved by direct adsorption measurements (Fig. 12). The results of these measurements indicate that adsorption takes place from pH = 7 upwards, i.e. in the range in which the flotation is activated.

The results seem to reinforce the earlier suggestion that $MnOH^+$ complexes also activate the flotation of silicon carbide.

## 6 DISCUSSION OF THE RESULTS OF INVESTIGATION CONCERNING THE EFFECT OF MULTIVALENT CATIONS ON THE FLOTATION OF SILICON CARBIDE WITH SODIUM OLEATE

In Fig. 13 the effect of the various cations studied on the flotation of silicon carbide has been plotted in those pH ranges where activation occurs. The pH ranges of the occurrence of the hydroxy complexes of the respective activating cations are also shown in this figure.

The results explicitly manifest the relation between the activation of SiC flotation and the occurrence of the hydroxy complexes of the type $MeOH^+$. The adsorption of metal ions in the ranges of activation is testified by the results of adsorption measurements. In these pH ranges also a change of the electrokinetic potential of silicon carbide towards positive values has been observed. Thus, an adsorption of $MeOH^+$ complexes in the double layer may be assumed.

Similar phenomena have been observed in the case of the anionic flotation of silicates and oxide minerals, such as augite with $FeOH^+$, $MgOH^+$ and $CaOH^+$[11] chrysocolla with $CuOH^+$,[12] pyrolusite,[13] rhodonite[10] and quartz.[14–18] The analysis of all these papers provides a similar view of the mechanism of activation as in the case of the minerals discussed earlier. The flotation of quartz with anionic collector occurs in those ranges in which the activating cations are present in the form of $MeOH^+$ complexes.

In the case of chrysocolla, augite and rhodonite the activating ions entered into the composition of the respective minerals, whereas in the case of quartz and silicon carbide proper conditions for their adsorption from a solution were required. On the newly exposed surface as a result of grinding there is reactive silicon, with broken bonds which will be able to annex OH-groups. Besides, there may occur some trace amounts of Si and $SiO_2$, which did not react during the process of synthesizing SiC. Finally, there still remain some products of high temperature oxidation of Si ($SiO_2$). Thus there are four kinds of active centres on the surface of silicon carbide which can produce hydroxyl groups. Thus the fixation of $MeOH^+$ complexes may take place by means of one of the described mechanisms.[19,20] In order to be able to be recovered by flotation, silicon carbide needs the presence of a collecting reagent at its surface. It is supposed that in this case a metallic organic complex was formed. This "compound" is probably precipitated either on the surface of the mineral or in the double layer, similarly as in the case of other systems.

The suggested mechanism of activating the flotation of silicon carbide with an oleate collector by addition of cations of multivalent metals consists of the adsorption of hydroxy complexes of these

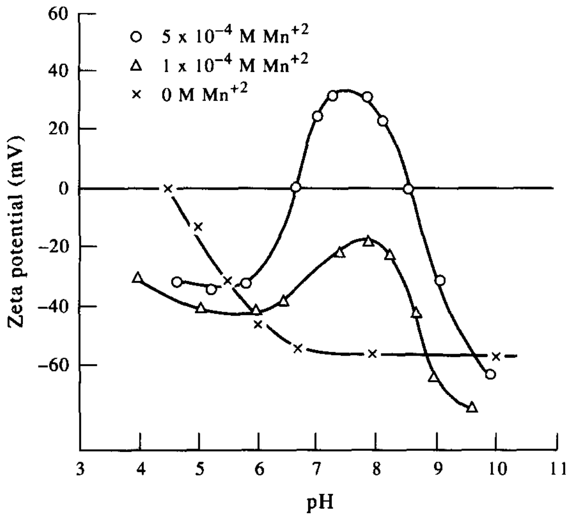

**Fig. 11.** Zeta potential of silcon carbide as a function of pH with various concentrations of $Mn^{+2}$ ions.

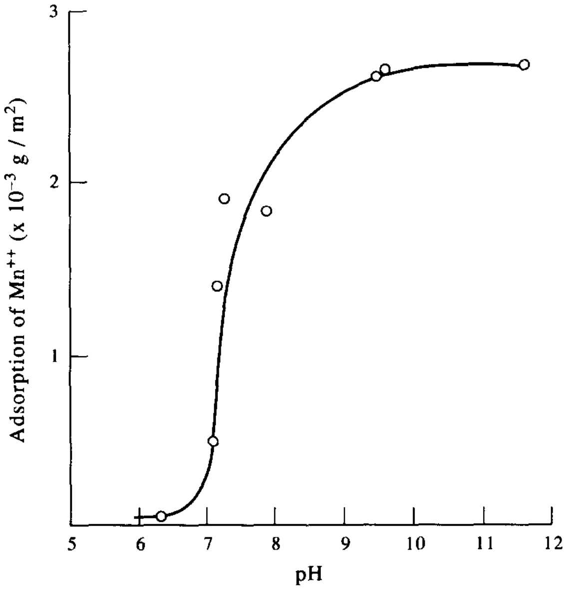

**Fig. 12.** Adsorption of manganese species on silicon carbide as a function of pH for $1 \times 10^{-4}$ M $MnCl_2$ concentration.

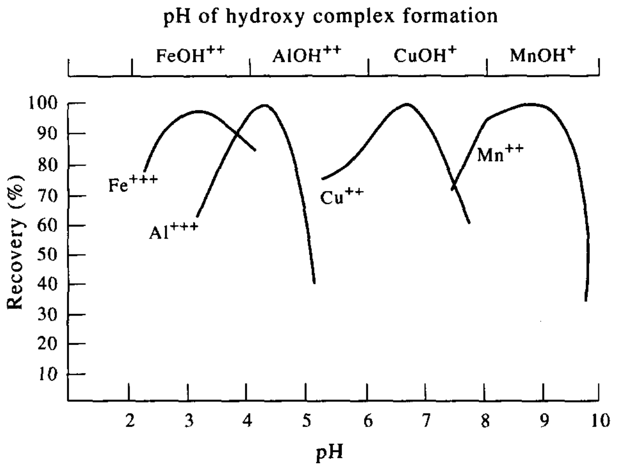

**Fig. 13.** Flotation of silicon carbide with $5\times10^{-5}$ M oleate as a function of pH and the pH of hydroxy complex formation.

metals in the form of $MeOH^+$, by which the surface of the silicon carbide becomes positively charged so that it becomes possible to fix the oleate.

The process of recognition of the products of the flotation reagents adsorbed on the surface of silicon carbide has been achieved by spectrophotometric investigations using the ATR technique. The results have also confirmed the proposed mechanism of SiC activation, since the absorption bands of OH groups coming most probably from the hydroxy complexes and spectra manifesting the oleate presence on the surface have also been observed.

## 7 CONCLUSION

The activation of the flotation of silicon carbide by means of multivalent cations is carried out in compliance with the mechanism of the formation of hydroxycomplexes of the type $MeOH^+$, which permit the adsorption of anionic collectors, similarly as in the case of quartz, some oxides and silicates.

## REFERENCES

1. ISKRA, J., Flotation properties of silicon carbide — I. Flotation of silicon carbide with anionic and cationic collectors. *Ceram. Int.*, **23**(4), (1997) 337.
2. FOREMAN, W. E., Electrokinetic studies on the $C_{18}$ fatty acid flotation of silicon carbide. Pennsylvania University, Disertation abstract, B27/3/776, F, 1966.
3. WHITMAN, P. K. & FEKE, D. L., *Adv. Ceram. Mater.*, **1**(4) (1986) 366.
4. BUTLER, J. N., *Ionic Equilibrium*. Addison-Wesley, Reading, MA, 1964, p. 287.
5. PEDERSEN, K. J., Danske Videnskat, Selskat., *Mat. Fys. Med.*, **20** (1943) 34.
6. LATIMER, W. M., *Oxidation Potentials*. Prentice-Hall, Englewood Cliffs, NJ, 1952, p. 187.
7. KRAEBER, L. & BOPPEL, A., *Metall und Erz*, **34** (1934) 412.
8. HEM, J. D. & ROBERTSON, C. E., Water Supply Paper 1827-A, US Geological Survey, 1967.
9. BUTLER, J. N., *Ionic Equilibrium*. Addison-Wesley, Reading, MA, 1964, p. 364.
10. PALMER, B. R., GUTTIERREZ, G. B. & FUERSTENAU, M. C., *Trans. AIME*, **258** (1975) 257.
11. FUERSTENAU, M. C., PALMER, B. R. & GUTTIERREZ, G. B., *Trans. AIME*, **262** (1977) 234.
12. PETERSON, H. D., FUERSTENAU, M. C., RICKARD, R. S. & MILLER, J. D., *Trans. AIME*, **232** (1965) 389.
13. FUERSTENAU, M. C. & RICE, D. A., *Trans. AIME*, **241** (1968) 453.
14. FUERSTENAU, M. C. & ATAK, S., *Trans. AIME*, **232** (1965) 24.
15. FUERSTENAU, M. C. & ELGILLANI, D. A., *Trans. AIME*, **235** (1966) 405.
16. COOKE, S. R. B. & DIGRE, M., *Trans. AIME*, **184** (1949) 299.
17. COOKE, S. R. B., IWASAKI, I. & CHOI, H. S., *Trans. AIME*, **217** (1960) 76.
18. CLEMMER, J. B. & CLEMMONS, B. H., US Bureau of Mines, RI, 1945, 3779.
19. FUERSTENAU, M. C., ELGILLANI, D. A. & MILLER, J. D., *Trans. AIME*, **247** (1970) 11.
20. JAMES, R. O. & HEALY, T. W., *J. Coll. Interface Sci.*, **40** (1972) 53.