International Journal of Natural Sciences Research
2013 Vol. 1, No. 6, pp. 43-49
ISSN(e): 2311-4746
ISSN(p): 2311-7435

REVERSE FLOTATION OF TITANIUM CARBIDE FROM GARNET MINERAL USING CATIONIC SURFACTANTS

M.A. Abdel Khalek[1] --- B.K. Parekh[2]
[1]*Central Metallurgical R & D Institute, (CMRDI) Helwan, Cairo, Egypt*
[2]*FGX SepTech, LLC, Lexington, KY, USA*

ABSTRACT
For cutting garnet rocks Titanium carbide (TiC) blades are used, which produces a fine waste material, a mixture of garnet and a few percent of Titanium carbide. In the present study, a reverse flotation technique was developed to recover the valuable Titanium carbide as tailings from the waste mixture using cationic surfactants such as, DA-1618 (Diethyl Amine ether) or DDAB (Dioctyl Dimethyl Ammonium Bromide) and poly-propylenimine (PPI) as a depressant for Titanium carbide. The effect of collector dosage, pH and depressant on the flotation parameters was investigated. It was found that both surfactants provided good recovery and grade of TiC, however DDAB was little better surfactant along with 0.35 kg/t of PPI at pH 9.0 provided 94% recovery of TiC with a grade of 97%.
Keywords: Flotation, Cationic surfactant, Titanium carbide, Garnet.

1. INTRODUCTION

In the cutting operations of garnet rocks using Titanium carbide (TiC) blades a fine powder containing some TiC metal along with garnet is produced. Garnet is a group of minerals that have been used since the Bronze Age as gemstones and abrasives. Garnets are neo-silicates with a general formula $X_3Y_2(SiO_4)_3$. The X site is usually occupied by divalent cations (Ca^{2+}, Mg^{2+}, Fe^{2+}) and the Y site by trivalent cations (Al^{3+}, Fe^{3+}, Cr^{3+}) in an octahedral/ tetrahedral framework with $[SiO_4]^{4-}$ occupying the tetrahedral [1]. Garnet's light transmission properties can range from the gemstone-quality transparent specimens to the opaque varieties and used as abrasives [2].

Titanium is a valuable metal and Titanium carbide with a high Vickers hardness of N1450 [3] makes it an ideal tool for high temperature and high wear applications. Recovery of the TiC metal from the waste provides an economic avenue for the garnet industry.

The specific gravities of the garnet mineral and TiC are 3.7 and 4.9 gm/cm^3, respectively. Due to this close proximity and high densities of the two materials it will be difficult to separate them by any gravity separation technique.

Garnet as a silicate mineral can be floated with a primary long-chain alkyl amines or alkyl ammonium salts. These chemicals are the mostly used as flotation collectors primarily because of their relatively high solubility [4]. The adsorption of amines on silicates at a wide range of pH has been described in literature [5, 6]. The amine ions adsorb from a solution at well below the critical micelle concentration (CMC) onto a negatively charged silicate surface due to electrostatic attraction (physical adsorption) [7]. Recently, a model of successive two-dimensional and three-dimensional (3D) precipitation of the long-chain amines on silicate surface was suggested using spectroscopic studies [8, 9].

The aqueous processing of titanium carbide has received little attention to date, although it has been studied as far back as the mid 1960's [10]. Recently, studies have examined the use of both cationic polyalkylimine [11] and anionic ammonium salt of poly-methacrylate (PMA-NH_4) [12] dispersants to stabilize aqueous Titanium carbide suspensions.

This present work aimed to develop a process to separate TiC metal from the garnet using a reverse flotation technique utilizing different types of cationic surfactants in presence of a depressant for TiC, thus recovering it as flotation tailings.

2. EXPERIMENTAL

2.1. Characterization

The chemical composition of the sample was determined by the X-ray fluorescence (XRF) and the mineral composition of the waste sample was determined by the X-ray diffraction (XRD) method using a Rigaku-Giger Flex analyzer. Particle size analysis was conducted using the standard wet screening technique.

2.2. Reagents and Materials

Cationic collector, Dioctyl Dimethyl Ammonium Bromide (DDAB) of 99% purity was supplied by Merck. The Tomamines DA-1618 (1,3-Propane diamine, N-[3-(C10-16-alkyloxy) propyl]) of 95% was supplied by Air Products and Chemicals, Inc. Cationic poly propylenimine (PPI) of 90% purity was supplied by Aldrich Chemicals which was used as a depressant of titanium carbide. For base line studies samples of pure garnet and TiC were acquired from chemical suppliers.

2.3. Zeta-Potential Measurements

A "Zeta-meter system 3+ unit" was employed for measuring the zeta-potentials. For measuring the zeta potential about 1 g of –325 mesh size pure garnet or Titanium carbide was suspended in 100 cm^3 of 0.01 M NaCl solution. The pH of the suspension was adjusted using dilute solutions of NaOH and HCl.

2.4. Flotation

Flotation experiments were carried out using a "Denver D-12" flotation machine using a 1 liter stainless steel cell. In each flotation test, about 250 g of material was conditioned at desired pH using the flotation machine impeller speed of 2500 rpm for 5 minutes. For all the tests 25% solids suspension was used. The cationic collector was added to the pulp and conditioned for 5 minutes before opening the air valve. When depressant was used, it was added before addition of the collector and conditioned for 5 minutes. At the end of each flotation experiment, both the floated and non floated fractions were filtered, dried, weighed and analyzed..

3. RESULTS AND DISCUSSIONS

Table 1, shows the chemical composition of the waste sample. It shows that the waste material consisted of 4.95% Titanium carbide and about 95% garnet silicate minerals. The X-ray diffraction (XRD) shows that the mineral composition of the garnet is mainly Andradite mineral, calcium-iron silicate [$Ca_3Fe_2(SiO_4)_3$], which was also confirmed by the X-ray fluorescence technique (XRF). The particle size of the sample was mainly below 100 µm. The ultra fine fraction –34 µm (≈ 3%) which was mainly silicate, removed by desliming the slurry before flotation experiments.

The zeta potential of both Titanium carbide (TiC) and pure garnet mineral as a function of pH with and without PPI are shown in Figures 1 and 2, respectively. The zero point of charge (ZPC) for garnet mineral was 4.6. Addition of 0.1 mol/l propylenimine (PPI) did not alter the ZPC of the garnet and remained essentially unchanged over the entire pH range from 2 to 10.

Figure 2, shows that, the ZPC of Titanium carbide was 2.5. However, in the presence of 0.1 mol/l PPI it showed a positive charge on the surface at all the pH values, without showing any ZPC. These results show that that PPI which is positively charged surfactant completely coats the TiC surface making it positive at all pH values. The shift in the curve as a result of the PPI addition indicates that the steric component is more pronounced [13]

4. FLOTATION RESULTS

Figure 3 shows flotation data of the garnet using the two cationic collectors with respect to pH. It shows that using 0.6 mole/l of collector DA-1618 about 77% of garnet floated in acidic medium (~ pH 3), however, with the DDAB highest (> 94%) floatability was obtained in alkaline pH of 9.0. The difference in the flotation behavior of the collectors could be explained that, with DA-1618 in alkaline medium, hydrophobic aggregation between the planes of silicate particles induced by the surfactants exposes the hydrophilic plane. In acidic solutions, the self-aggregation between the negatively charged planes and the positively charged edge planes occurs and the hydrophobic silica planes are exposed, resulting in good floatability in acidic solutions [14]. With dioctyl dimethyl ammonium bromide (DDAB), in the acidic region, the interactions of the garnet surface with the collector were mainly electrostatic, but in the alkaline region, the interactions could be due to hydrogen bonding [7]. The maximum flotation recovery of silicate minerals at about pH 9 could be due to association between neutral molecules and ions resulting in dimers $(RNH_3)_2^{2+}$ and iono-molecular species $(RNH_2RNH_3)^+$ [15]. Decrease in the floatability above pH 9 is due to the bulk precipitation of molecular amine [16].

The effect of surfactant concentration on the floatability of garnet with two different cationic surfactants is shown in Figure 4. The floatability of garnet with DA-1618 and DDAB surfactants were carried out at pH of 4 and 9, respectively. The flotation of garnet increased with increasing surfactant concentration and reached maximum at 0.5 and 0.8 mole/l for DDAB and DA-1618, respectively.

The effect of DA-1618 dosage on the recovery and grade of titanium carbide at pH 4 without the use of PPI depressant is shown in Figure 5. It show that increasing collector dosage the weight percent of unfloated fraction (tailings) decreased from 94%to 1.5%, and titanium recovery from 94.9% to 23.1%. However, the titanium carbide grade increases from 5 to 76.2%. A low recovery of TiC in the tailings may be due to poor selectivity of the collector which allows TiC to report in the float fraction.

Figure 6 shows the effect of depressant PPI dosage on recovery and grade of the TiC at pH 4 using 1.2 kg/t of the DA-1618 collector. Increasing PPI depressant to 0.35 kg/t increased the amount recovered in tailings from 1.5% to 4.4%; TiC grade increased from 76.2% to 91.2% and recovery from 23.1% to 81.1%.

Figure 7 shows the effect of DDAB dosage on the recovery and grade of TiC pH 9 without using the PPI depressant. It shows that increasing collector dosage the weight percent of unfloated fraction (tailings) decreased from 89% to 1%, and titanium recovery from 91.7% to 17.5%. However, the titanium carbide grade increased from 5.1 to 86.62%. The flotation behavior of this collector for TiC was very similar to the DA-1618 collector.

Figure 8 shows the effect of PPI depressant dose on the recovery and grade of the TiC at pH 9 using the DDAB collector dosage of 1 kg/t. It show that using 0.35kg/t of the depressant increased amount recovered in tailings from 1% to 4.8%; TiC grade increased from 86.6% to 97% and recovery from 17.5% to 94%. These data showed that using PPI as depressant and a cationic collector an excellent grade and recovery of the TiC could be obtained.

5. CONCLUSIONS

Separation of Titanium carbide from a waste mixture of garnet could be achieved by reverse flotation process recovering TiC as the final product in the flotation tailings. It was found that using about 0.35 kg/t of the polypropylenimine (PPI) and 1.2 kg/t of the DA-1618 (*Diethyl Amine ether)* collector at pH 4 provided 80% recovery of TiC with a grade of 90%. Similarly, using 0.35 kg/t of the PPI along with 1 kg/t of the DDAB (Dioctyl Dimethyl Ammonium Bromide) at pH 9.0, a TiC recovery of 94% with a grade of 97% was obtained. Thus, it appears that the DDAB provided little better results than DA-1618.

REFERENCES

[1] Wikipedia, 2013. "Garnet." Available: http://en.wikipedia.org/wiki/Garnet.

[2] J. Briggs. *The abrasives industry in Europe and North America*, Materials Technology Publications. ISBN 1-871677-52-1, 2004.

[3] D. Miracle and H. Lipsitt, "Mechanical properties of fine-grained substoichiometric titanium carbide," *J Am Ceram Soc.*, vol. 66, pp. 592-7, 1983.

[4] J. Leja, *Surface chemistry of froth flotation*, Plenum Press, New York: 1982.

[5] A. A. Sirkeci, "The flotation behavior of N-(3-aminopropyl)-dodecane amide on three alumino silicates," *J Min. Eng.*, vol. 16, pp. 1391-1395, 2003.

[6] Y. Wang, P. Hu and G. G. He, "Reverse flotation for removal of silicates from diasporic-bauxite," *J Min. Eng.*, vol. 17, pp. 63-68, 2004.

[7] P. Somasundaran and D. W. Fuerstenau, "Mechanisms of Alkyl sulfonate Adsorption at the Alumina-Water Interface," *The Journal of Physical Chemistry*, vol. 70, pp. 90-97, 1970.

[8] I. V. Chernyshova, K. Hanumantha Rao and A. Vidyadhar, "Mechanism of adsorption on silicates. A spectroscopic study," *1-Quartz. Langmuir*, vol. 16, pp. 8071-8084, 2000.

[9] I. V. Chernyshova, K. Hanumantha Rao and A. Vidyadhar, "Mechanism of Adsorption on Silicates," *1-Quartz. Langmuir*, 2001.

[10] A. Dobrovol'skii, "Slip casting of titanium carbide components," *Powder Metall Met Ceram*, vol. 4, p. 751, 1965.

[11] J. Zhang, D. Jiang, S. Tan, L. Gui and M. Ruan, "Aqueous processing of titanium carbide green sheets," *J Am Ceram Soc.*, vol. 84, pp. 2537-41, 2001.

[12] C. Yeh and M. Hon, "Dispersion and stabilization of aqueous TIC suspension," *Ceram Int.*, vol. 21, pp. 65–8, 1995.

[13] R. Meszaros, L. Thompson, M. Bos and P. de Groot, "Adsorption and electrokinetic properties of polyethylenimine on silica surfaces," *Langmuir*, vol. 18, pp. 6164–9, 2002.

[14] J. L. Scott and R. W. Smith, "Ionic strength effects in diamine flotation of quartz and magnetite," *Miner. Eng.*, vol. 5, pp. 1287–1294, 1992.

[15] B. E. Novich and T. A. Ring, "A predictive model for the aakylamine-quartz flotation system," *Langmuir*, vol. 1, pp. 701-708, 1985.

[16] S. Prabhakar, R. K. Hanumantha and F. Willis, "Flotation and Surface Interaction of Wollatonite/ Dodecylamine System," In: *Proceedings of the 22nd International Mineral Processing Congress (IMPC) 29 Sept., Cape Town, South Africa*, 2003.

Table-1. Chemical Composition of the Garnet-TiC Waste Sample

Constituent	%
SiO_2	32.23
CaO	31.84
Fe_2O_3	30.21
Al_2O_3	0.43
MgO	0.21
Na_2O	0.07
K_2O	0.05
TiC	4.95
Total	99.98

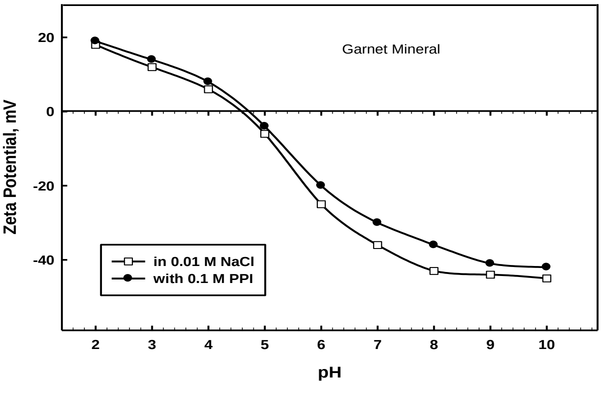

Fig.1. Zeta-potential of Garnet Mineral with and without PPI

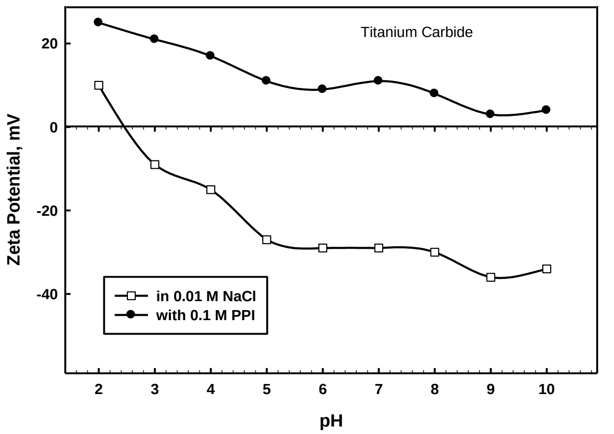

Fig.2. Zeta-potential of Titanium carbid with and without PPI

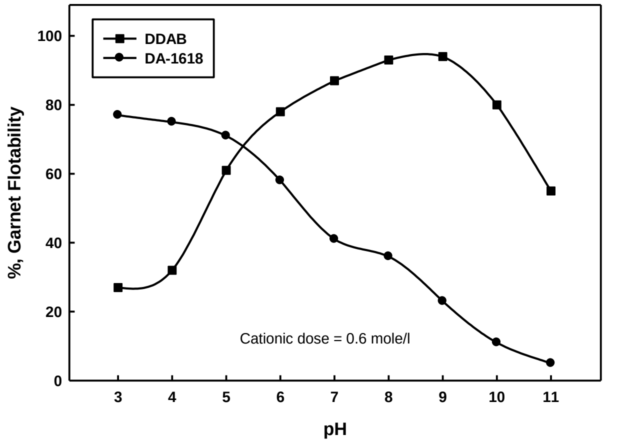

Fig.3. Effect of pH on the Floatability of Garnet with Cationic Collectors4.

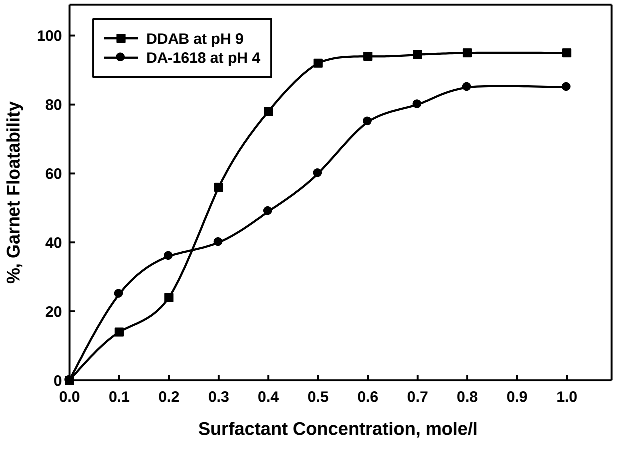

Fig.4. Effect of Surfactant Concentration on the Floatability of Garnet

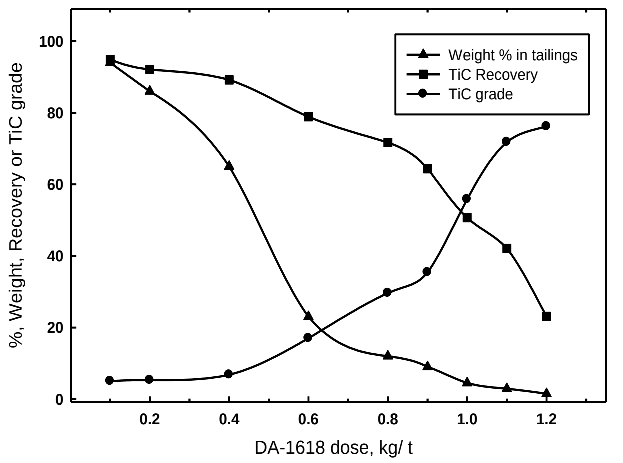

Fig.5. Effect of DA-1618 Collector Dosage on Recovery and TiC grade (pH = 4.0 ; without depressant)

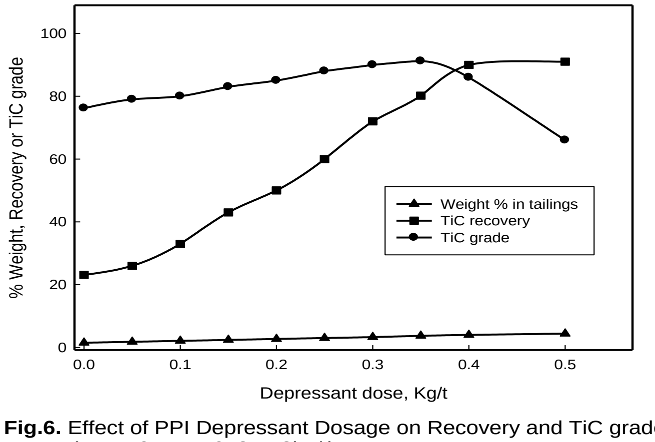

Fig.6. Effect of PPI Depressant Dosage on Recovery and TiC grade (pH=4.0; DA-1618=1.2kg/t)

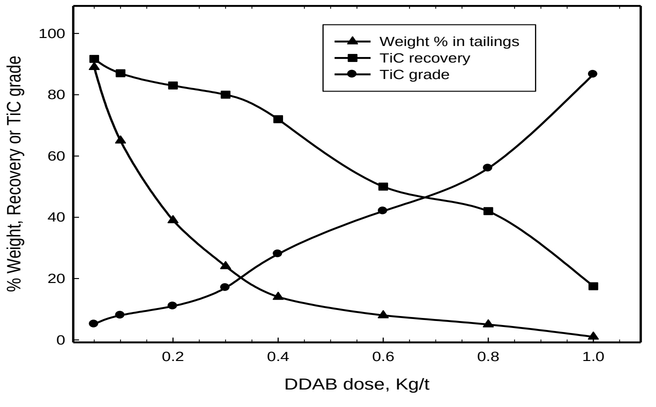

Fig.7. Effect of DDAB Collector Dosage on Recovery and TiC grade (pH=9.0; without depressant)

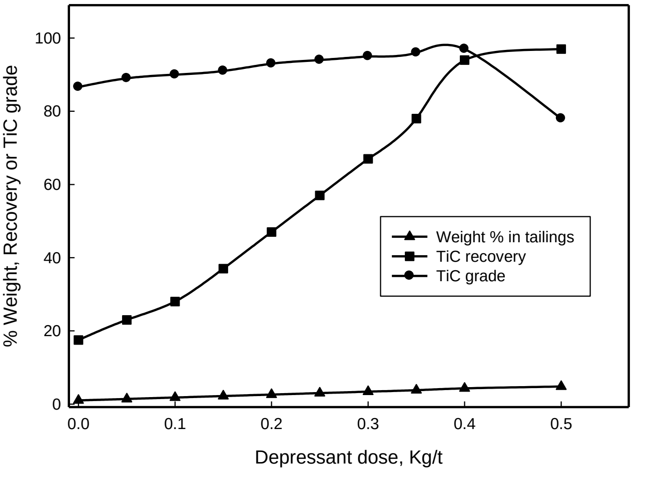

Fig.8. Effect of PPI Depressant Dosage on Recovery and TiC grade (pH=9.0; DDAB= 1kg/t)