Mechanism of Collector Adsorption on Monazite

By Hyung Sup Choi* and Ki Up Whang**

Monazite 界面上의 捕集劑 吸着機能에 關한 硏究

崔　亨　燮　·　黃　基　燁

(1963. 3. 7受理)

Abstract

The basic studies of adsorption characteristics of collector on monazite were made by electrophoretic measurement and by determination of the adsorption of some typical flotation collectors.

By above measurements made on monazite, it is concluded that H^+ and OH^- are identified to act as potential determining ions and thus the electrical properties of monazite is controlled by the pH of the solution.

Therefore, anionic collectors are adsorbed on positively charged surfaces and cationic collectors on negatively charged surfaces, which in turn controls the effective flotation condition with respective collectors for this mineral.

These results have been correlated with its flotation behavior obtained by Hallimond tube test.

要　約

浮選理論의 基礎的인 硏究는 從來 主로 接觸角, 臨界 pH 曲線, 吸着量의 測定等에 依해서 試藥이 鑛粒子表面에 吸着하는 機構를 解明하였다. 그러나 最近 界面電氣化學的인 考察이 通用되어 試藥類의 吸着의 理論的인 究明이 試圖되고 있다. 鑛粒子는 電氣泳動現象에서 보는 바와 같이 水中에서 荷電되어 있고 한편 捕集劑는 「이온」化되여 있는 故로 當然히 그 吸着에는 電氣的인 相互作用이 있다고 想像할 수 있다. 따라서 電氣二重層理論이 鑛粒子의 荷電原因, 그 制御方法 및 吸着에 있어서 相互作用의 定量化에 基礎가 될 수 있는 것이다.

本硏究에 있어서는 Monazite에 關하여 固相-液相界面에 있어서의 電氣化學的性質을 電氣泳動法으로 調査하고 한편 浮選捕集劑로 Dodecyl ammonium chloride(D.A.C. 라 略稱) 및 Sodium dodecyl sulfate(S.D.S. 라 略稱)를 使用하여 吸着量의 測定 및 浮遊度를 試驗한 結果 捕集劑 「이온」이 鑛物表面에 吸着하는데 있어서 電氣的인 相互作用이 重要한 役割을 하고 있다는 것이 實證되었다.

即 水溶液中에 있어서의 Monazite 表面의 電氣的 性質이 H^+ 及 OH^- 의 濃度(pH)에 따라 支配되는 것이고 電氣泳動法으로 測定한 Monazite의 等電點(Isoelectric point)은 pH 3.5이며 Monazite 表面은 pH 3.5 以上에서는 陰(—)으로 pH 3.5 以下에서는 陽(十)으로 荷電되어 있다는 것을 알 수 있다. 이와 같은 表面에 陰 「이온」系의 S.D.S. 或은 陽 「이온」系의 D.A.C.를 作用시키면 當然히 S.D.S. 는 pH 低下에 따라서 即 表面이 陽(十)이 되는데 따라 吸着量이 增加되고 한편 D.A.C. 때는 反對로 表面이 陰(—)이 되는데 따라 吸着量이 增加된다고 볼 수 있으며 實地로 吸着量의 測定은 이것을 立證하고 있다. 이와 아울러 炭素鎖 12의 陽「이온」 及 陰「이온」系 捕集劑 (即 D.A.C. 및 S.D.S.)를 使用하여 Hallimond tube 로 Monazite의 浮遊度를 測定한 結果를 보면 等電點을 中心으로 하여 左右로 거의 對稱的인 結果를 나타내고 있고 이것은 前述한 捕集劑의 吸着이 電氣的인 相互作用에 依한다는 事實을 뒷받침 하고 있는 것으로서 注目할만한 現象이다. 이러한 基礎的인 究明은 重砂에서 Monazite를 될 수 있는대로 品位가 높은 精鑛으로 選別回收하는데 基本方針을 提示하는 것이다.

* Atomic Energy Research Institute, Korea.
** Research Institute of Mining & Metallurgy, Korea.

Introduction

The heavy sands in Korea are chiefly composed of ilmenite, but also contain such minerals as monazite and zircon, which give additional importance. Therefore, the fundamental investigations of heavy sand beneficiation is urgently necessary. The monazite has been customarily separated by the physical methods from its associated minerals; however it is limited to upgrade the concentrate for the desired purity. Some other methods combined with above process may be necessary for further improvement.

When the flotation is considered as the effective beneficiation method, it is very important to study the adsorption characteristics of collector and floatability of the individual minerals.

Previous investigations on the surface properties and flotation characteristics of hematite[1], cummingtonite[2], and zircon[3] have demonstracted the electrical nature of the interaction of the collector with these oxide and silicate surfaces; anionic collectors are effective on positively charged surfaces and cationic collectors on negatively charged surfaces. Thus, from the differences in the surface properties of the above-named oxide and silicates, a theoretical basis has been provided for their separation by some typical collectors.

This article reports the findings on the general information of adsorption characteristics of collector on monazite investigated by measurements of the electropheretic mobility and the adsorption density of some typical flotation collectors. Its flotation characteristics was examined by simplified flotation tests using a Hallimond tube. The basic information thus gathered was shown to be directly applicable to the interpretation of the actual flotation behavior of monazite and such information is also practically significant in the beneficiation of the heavy sands.

Materials

Preparation of monazite sample:

The sample obtained from the Korea Rare Mineral Inc. was the concentrate of monazite which was separated from the heavy sand produced at Ku-Rea area, Jun-La-Nam-Do. The grade of this sample was 62 per cent for $R_2O_3+ThO_2$.

The sample was screened and the 100/150-mesh fraction was taken for the Hallimond tube flotation tests and for adsorption measurements. To obtaine purer material, the minor amount of non-magnetic materials in the sample was separated out with the induced roll type magnetic separator. Furthermore, a small amount of the other materials remained in the concentrate from magnetic separation was rejected by vanning, and followed by the sedimentation and decantation for the further purification of the sample. The purified sample was treated with 2N-HCl

Table 1 Composition of monazite samples

Sample*** No. (%) Composition	No. 1	No. 2	No. 3
ThO_2	6.32	6.18	5.92
Ce_2O_3	26.40	24.99	23.29
R_2O_3*	32.70	32.78	29.57
Fe_2O_3	0.45	0.91	1.55
Al_2O_3	1.43	1.65	2.28
TiO_2	0.21	0.23	0.91
ZrO_2	0.44	0.48	1.24
HfO_2	0.004	0.014	0.04
CaO	2.53	0.57	1.78
MgO	0.21	0.18	0.20
MnO	n.d.	n.d.	n.d.
PbO	0.20	0.45	0.37
U_3O_8	0.32	0.41	0.59
Na_2O	0.11	0.05	0.06
K_2O	0.07	0.02	0.02
$(Nb, Ta)_2O_5$	n.d.**	n.d.	n.d.
P_2O_5	25.19	28.19	26.02
SiO_2	3.17	2.32	5.18
CO_2	0.07	0.14	0.12
H_2O	0.32	0.52	0.43

*Total rare earth oxides excluding cerium oxide.
**n.d. = not detected.
***Sample No.1 : monazite produced from Ipchang
　　Sample No.2 : monazite produced from Koksung
　　Sample No.3 : monazite produced from Dukryung

solution for half an hour and then washed repeatedly with demineralized water. The cleaned sample was stored in demineralized water in a pyrex bottle.

Chemical analysis of monazite concentrate of Ku-Rea area is presented in Table 1[4].

For the electrophoretic mobility measurement, a small amount of the cleaned 100/150-mesh fraction was ground id an agate mortar and elutriated to minus 3 micron. The product was stored in demineralized water in a pyrex bottle.

Reagents:

The collectors used in this investigation were as follows:

$C_{12}H_{25}NH_3Cl$ — Dodecylammonium chloride
$C_{12}H_{25}SO_4Na$ — Sodium dodecyl sulfate
$C_{17}H_{33}COOH$ — Oleic acid
$C_{17}H_{31}COOH$ — Linoleic acid

Dodecylammonium chloride was obtained from Armour and Co. Highly purified sodium dodecyl sulfate was supplied by the Agricultural Research Service, U.S. Department of Agriculture, Philadelphia, Pa. Oleic and linoleic acids(purite 99 per cent) were obtained from the Hormel Institute, Minn. The water-insoluble fatty acids were converted to a water-soluble soap before use.

Experimental Procedure

Determination of the isoelectric point:

The electrokinetic properties of monazite were investigated by measuring the electrophoretic mobility of their aqueous suspensions as a function of pH. The apparatus used for the measurement was a flat-type, vertical microelectrophoretic cell constructed from microscope slides. The electrical condition at the solid-solution interface was determined by the direction of migration of the mineral particles, and the mobility was determined as an average value of at least dozen pairs of measurements.

Adsorption measurement:

Adsorption densities of dodecylammonium chloride and of sodium dodecyl sulfate on the 100/150-mesh fraction of monazite were measured as a function of pH. The samples filled with the test solutions in 100 ml. volumetric flask was conditioned by tumbling for 20 minutes. It was left for two hours after tumbling to attain the equilibrium before measurement, and then the residual concentration of the electrolyte in the solution was colorimetrically analyzed[5]. The surface area of the monazite sample used for the foregoing adsorption measurements was determined, at the temperature of liquid nitrogen, by the B.E.T. method with N_2 as an adsorbate. An average of four measurements gave 7,090 square centimeters per gram.

Simplified flotation tests:

The cleaned 100/150-mesh fraction of monazite was used for the simplified flotation tests, which was made in a modified Hallimond tube[6].

Purified nitrogen gas for areation was introduced into the flotation cell through a coarsepored fritted disk. The Hallimond tube flotation test was carried out with approximately 1 gram of the mineral sample at a gas flow of 35 ml. per minute. In the present work, the sample was conditioned by tumbling at a speed of 30 r. p.m. for 20 minutes in a 100 ml. volumetric flask, filled with the test solution, prior to flotation tests. The collectors used in these flotation tests were dodecylammonium chloride, sodium dodecyl sulfate, oleic acid, and linoleic acid, which were highly purified. The concentration of the all collectors used in this investigation was 10^{-4} moles per liter.

Results and Discussion

In order to observe the electrical condition at the solid-solution interface, the electrophoretic mobility of monazite was measured as a function of pH. The results are presented in Fig. 1. It shows that the isoelectric point of monazite occurs at about pH 3.5. This means, the monazite particles are positively charged below pH 3.5, and negatively charged above this pH.

In Fig. 2, the adsorption densities of dodecylammonium chloride and of sodium dodecyl sulfate (equilibrium concentration of 10^{-5}M.) are plotted

as a function of pH. It is obvious from the figure that an effective adsorption of cationic collector appears to be on a negatively charged surface of monazite and of anionic collector on a positively charged surface. From the above results, it clearly indicates that the adsorption of collector on the mineral surface is essentially due to the electrical interaction between the charged surface and collector ions, although the fact that the adsorption persists beyond the isoelectric point indicate that the affinity is not strictly electrostatic in nature. The collector necessary for monolayer surface coverage is 6.66 x 10^{-10} mol per sq. cm. It is calculated by assuming the cross sectional area of the hydrocarbon chain of the collectors to be 25Å².

According to Fig. 2 and Fig. 3, ten per cent flotation recovery occurs with an adsorption of collector amounting to 5.7 x 10^{-11} mol per sq. cm. This corresponds approximately to a surface coverage of 8.6 per cent of a monolayer.

In Fig. 3, the effect of pH on recovery of monazite with 10^{-4}M. of dodecylammonium chloride and of sodium dodecyl sulfate were plotted. This figure shows that the cationic collector is effective on monazite flotation above a pH of about 8, whereas the anionic collector is effective below a pH of about 3. It is interesting to note that the intersection of both curves occurs at the region corresponding approximately to the determined isoelectric point of monazite.

The floatability of monazite using 10^{-4}M. of oleic and linoleic acids are plotted as a function
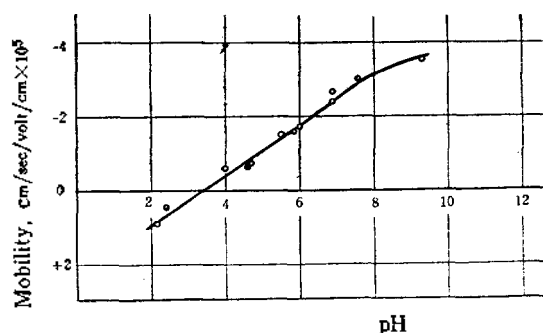

Fig. 1 Electrophoretic mobility of monazite as a function of pH.

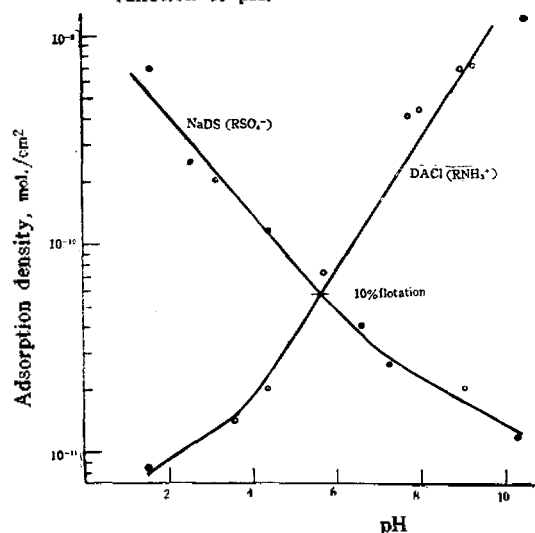
Fig. 2 Adsorption density of dodecyl ammonium chloride and of sodium dodecyl sulfate on monazite as a function of pH.

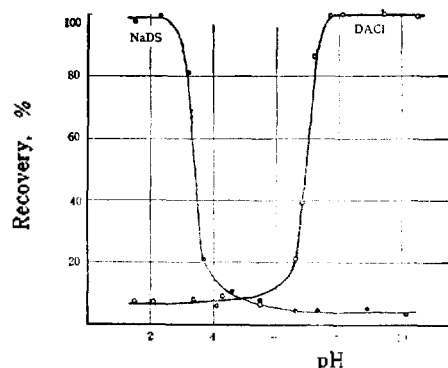

Fig. 3 Effect of pH on recovery of monazite (100/150 mesh) with 10^{-4}M. of dodecyl ammonium chloride, and of sodium dodecyl sulfate
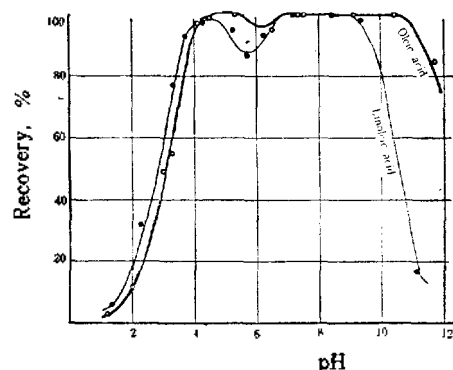

Fig. 4 Effect of pH on recovery of monazite (100/150 mesh) with 10^{-4}M. of oleic acid, and of linoleic acid.

of pH in Fig. 4. Comparison of the curves obtained with 18-carbon aliphatic acids with those for 12-carbon collectors shows that the flotation region at the same reagent concentration extends very widely into the adverse electrical condition of monazite surface.

This increased surface activity of the longer chained collectors indicates additional factors in the adsorption process. One such factor might be the "squeezing out effect"[7] of ions from water because of unfavourable ionic size with respect to the associated water structure, and subsequent lateral interaction between interfacial organic ions which have been squeezed out of solution. The lateral interaction is due to van der Waals forces between the hydrocarbon chains of adsorbed ions, which have a strong tendency to stay on the adsorbed mineral surface. The abrupt decline in the floatability with the fatty acid collectors below pH 4 may be attributed to the precipitation of free acids. There-fore, the effective pH range is pH 4 to 11 for oleic acid, and pH 4 to 9 for linoleic acid.

Conclusions

The basic flotation behaviors of monazite were investigated by the simplified flotation tests and results have been correlated with the adsorption characteristics of collectors. The results of this investigation have led to the following conclusions.

1. The isoelectric point of monazite occurs at pH 3.5. The monazite surface is positively charged at pH values lower than 3.5 and negatively charged at higher pH.

2. Anionic collector is effectively adsorbed on positively charged surface, and cationic collector is effective on negatively charged surface. The amount of adsorption of the anionic collector increases with increasing acidity. The converse is true for the cationic collector.

3. In the adsorption of collectors on monazite, a surface coverage of about 10 per cent of a monolayer is necessary for the minimum flotation requirement (about 10 per cent flotation).

4. The catonic collector, dodecylammonium chloride is an effective collector for negatively charged monazite, and the anionic collector, sodium dodecyl sulfate, for positively charged monazite.

5. The 18-carbon fatty acid collectors extend the flotation range of monazite to the alkaline side which is the adverse electrical condition of monazite surface. This may be due to the "squeezing out effect" of organic ions from water and subsequent lateral interaction of hydrocarbon chains of the adsorbed ions.

6. The optimum flotation of monazite occurs from pH 4 to 11 with 10^{-4}M. oleic acid, and from pH 4 to 9 with 10^{-4}M. linoleic acid.

Acknowledgements

References

1) I. Iwasaki, S.R B. Cooke and H.S. Choi, *A.I.M.E. Trans.*, 1960, Vol. **217**, pp. 237—244.

2) I. Iwasaki, S.R.B. Cooke, and H.S. Choi, *A.I.M.E.*, TN **60B** 213, 1960.

3) H.S. Choi and Ki Up Whang, "Surface Properties and Floatability of Zircon", submitted to the Journal of Canadian Institute of Mining & Metallurgy for publication, 1963.

4) Koo Soon Chung, "Development of Physico-chemical Methods for the Analysis of Mona-zites" Ph.D. Thesis, Univ. of Liverpool, 1962.

5) I. Iwasaki, S.R.B. Cooke, D.H. Harraway, and H.S. Choi, *A.I.M.E. Trans.*, 1962, Vol. **223**, pp. 97—108.

6) Fuerstenau D.W., Metzer P.H., and Seele G. D., *Eng. Min. Jour.*, Vol. **158**, March 1957.

7) D.C. Grahame, *Chem. Revs.*, **41**, 441(1947).