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学 位 論 文 題 目	Removal of Quartz from Dickite by Oleate Flotation —Fundamental Study on Purification of Kaolin Minerals (オレイン酸浮選によるディッカイトからの石英の除去 —カオリン鉱物の精製に関する基礎的研究)
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論 文 内 容 要 旨

CHAPTER 1 : INTRODUCTION

In some fields, there is a requirement for high quality kaolin minerals. Raw kaolin minerals often contain pyrite, hematite, goethite, quartz, etc. as impurities. It is required to remove those impurities from kaolin minerals as much as possible.

As for the removal of quartz from kaolin minerals, cationic amine flotation in the acidic pH range has been proposed for the separation of quartz and kaolinite. But the separation of quartz and dickite, one of the kaolin minerals, by this method becomes difficult as the particle size decreases and impossible for the particles finer than 5 μ m, since heterocoagulation is inevitable in this pH range. Accordingly, it is desirable to explore a flotation method for removing fine quartz from kaolin minerals.

It is well known that, with continuously diminishing grades of ores, fines and ultrafines are invariably produced during the processing of ores. Many researches associated with fine particle flotation have been done in recent years and a variety of methods have been proposed. It has been pointed out that the best examples of ores that consist mostly of fine particles are those encountered in the kaolin industry, where the separation problems usually involve the

removal of impurity minerals from the desired kaolin. On the other hand, kaolin minerals are often contained in many ores. In treating these ores by flotation, kaolin mineral fine particles often play a very important role. Therefore, it is important to investigate the flotation properties of kaolin minerals in detail in order to develop a method for removing impurities from kaolin minerals, as well as to improve the flotation separation of ores containing kaolin minerals.

From the point of view, the flotation properties of dickite and the flotation separation from quartz were investigated using sodium oleate as a collector in the neutral and alkaline pH range. The reason why dickite was chosen as a sample is that the grain size sample is available and its particle size is desirably adjusted by comminution.

CHAPTER 2 : EFFECT OF DILUTED HCl PRECONDITIONING ON FLOTATION OF DICKITE FROM QUARTZ

Although natural dickite was almost not floated by oleate, it was found in this chapter that by preconditioning in $1 \times 10^{-3} \text{ kmol/m}^3$ HCl solution for 2 hours, dickite of $+10-20 \mu\text{m}$ size fraction can be floated from quartz of $+10-20 \mu\text{m}$ size fraction at pH around 7, clearly indicating that the floatability of dickite with oleate was greatly enhanced by preconditioning.

When dickite was preconditioned in diluted HCl solution, dissolution of dickite occurred, releasing aluminum and silicon species. Aluminum concentration was $4.5 \times 10^{-5} \text{ kmol/m}^3$ in $1 \times 10^{-3} \text{ kmol/m}^3$ HCl solution for two hours at which high flotation recovery of $+10-20 \mu\text{m}$ dickite was obtained. Therefore, it is considered that dickite is activated by aluminum species dissolved. However, when aluminum salt was added to the mixed suspension of dickite and quartz of $+10-20 \mu\text{m}$ size fraction, selective flotation of dickite from quartz did not occur. Accordingly, it is considered that one part of the decomposed aluminum is released to the solution and the other part remains in the dickite surface during preconditioning, the latter part may offer active sites for oleate adsorption and play an important role in selective activation of dickite.

The adsorption results of oleate on dickite showed that there were both physically adsorbed oleic acid and chemically adsorbed oleate species on dickite; the former can be extracted from the surface of dickite with ethyl alcohol. The amounts of oleate left on dickite surface after alcohol extraction were increased by preconditioning. Moreover, the relationship between the amounts of oleate left on the dickite surface after alcohol extraction and the equilibrium concentration fitted the Langmuir adsorption equation.

After preconditioning in $1 \times 10^{-3} \text{ kmol/m}^3$ HCl solution for 2 hours, dickite was separated from solution. After this treatment, the separated dickite was suspended in distilled water and oleate adsorption was measured at pH 7. The maximum chemisorption amount is shown

in Table 1, together with those for dickite with and without preconditioning.

Table 1. Maximum chemisorption amount of oleate
in different conditions ($\times 10^{-6}$ mol/m²)

Condition	Untreated	Separated	Preconditioned
M.C.A.	0.55	1.11	1.53

M.C.A. = Maximum chemisorption amount

The results above show apparently that one part of the decomposed aluminum remains on dickite surface during preconditioning and offers active sites for oleate adsorption.

By preconditioning in suitable HCl solution, good separation of dickite from quartz was achieved for the particles larger than 5 μ m. For the particles finer than 5 μ m, particularly finer than 2 μ m, however, the selectivity of flotation was lowered.

CHAPTER 3 : EFFECT OF INORGANIC ELECTROLYTE ON FLOTATION OF DICKITE FROM QUARTZ WITH DILUTED HCl PRECONDITIONING

In this chapter, the effects of calcium chloride and potassium chloride on the flotation of dickite from quartz preconditioned in diluted HCl solution were investigated. In the presence of CaCl₂, the dissolved aluminum was increased, especially in a short time. The dissolved aluminum was increased with an increase in CaCl₂ at the concentration below 8×10^{-4} kmol/m³. It was also found that the further increase was very slight at high concentration. The increase in dissolved aluminum was also found by adding 1×10^{-2} kmol/m³ KCl. The increase in dissolved aluminum concentration in the presence of inorganic electrolyte such as CaCl₂ and KCl may be caused by ion exchange reaction, which was supported by a fact that the maximum increment was about 1.8×10^{-5} kmol/m³ (0.43 meq/100 g), comparable to the cation exchange capacity (0.3 meq/100g) measured by Mukai et al..

It was found that in the neutral pH range, the sufficient flotation recovery was attained by preconditioning for 5 minutes in 5×10^{-4} kmol/m³ HCl solution containing 4×10^{-4} kmol/m³ CaCl₂ or 1×10^{-2} kmol/m³ KCl. Good separation was made for the particles coarser than 2 μ m, although the separation was still unsatisfactory for the particles finer than 2 μ m.

From the oleate adsorption results, it was noted that the enhancement in the flotation recovery of dickite with preconditioning was brought about by decomposition of dickite and the effect of electrolyte was to promote the decomposition of dickite structure in a short time by ion exchange reaction, resulting in shortening the preconditioning time required for obtaining sufficient flotation recovery.

CHAPTER 4 : IMPROVEMENT IN FLOTATION OF FINE DICKITE FROM QUARTZ BY SELECTIVE FLOCCULATION

In this chapter, in order to improve the flotation of dickite from quartz finer than $2 \mu\text{m}$, selective flocculation with polymer was introduced to the flotation process which includes preconditioning in diluted HCl solution containing CaCl_2 .

At first, the flocculation abilities of dickite and quartz were studied. Quartz particles remained dispersed in the pH range studied. Dickite particles were flocculated in the weakly acidic pH range, even in the absence of Separan AP30. Enhanced flocculation of dickite occurred by the addition of Separan AP30 at pH below 8. Separan AP30 containing amide and carboxyl groups may adsorb on dickite not only by hydrogen bonding, but also by electrostatic attraction between negative charge of carboxyl group and positive charge of the edge surface in the weakly acidic pH range.

The selective flocculation of dickite particles occurs in the addition of 1 to $2 \text{ g}/\text{m}^3$ of Separan AP30, irrespective of the addition order of Separan AP30 and sodium oleate. It was found that some extent of flocculation of quartz particles occurred in the mixed suspension, even though Separan AP30 was not added. This may be due to quartz-dickite retrofloculation which is caused by the bridging action with the aluminum species dissolved from dickite during preconditioning. However, when Separan AP30 was suitably added, the bridging action was diminished, because Separan AP30 was adsorbed on dickite in preference to quartz and its macromolecules covered dickite surface. This perhaps is a reason that excellent selective flocculation of dickite from quartz occurs by suitable addition of separan AP30.

It was found that the addition order of Separan AP30 and sodium oleate had a great influence on the flotation of dickite. Namely, the flotation recovery of dickite was remarkably decreased by the addition of Separan AP30 prior to sodium oleate, while it was increased by about 10% when $2 \text{ g}/\text{m}^3$ of Separan AP30 was added in the reverse order.

It was found that when Separan AP30 was added after sodium oleate, both total abstraction and chemical adsorption were almost not influenced by the addition of Separan AP30. Accordingly, the increase in the flotation recovery of dickite by the addition of Separan AP30 after sodium oleate may result from the increased collision efficiency between bubbles and particles, due to the aggregates formation. On the other hand, when Separan AP30 was added prior to sodium oleate, both total abstraction and chemical adsorption were decreased with increasing the addition of Separan AP30, corresponding to the decrease in the flotation recovery. The reason for this probably is that oleate becomes difficult to approach dickite surface which is covered with macromolecule of Separan AP30 charged negatively, owing to steric hindrance and electrostatic repulsion.

The separation result was very similar to the selective flocculation results. Therefore, it is

considered that the suitable addition of Separan AP30 not only increases the flotation recovery of dickite through the aggregate formation (i.e. the increased efficiency of bubble-particle collision), but also diminishes the bridging with hydrolyzed aluminum species between dickite and quartz, resulting in satisfactory selective flotation of dickite from quartz.

CHAPTER 5 : REVERSE FLOTATION OF FINE QUARTZ FROM DICKITE

In this chapter, the depressing action of corn starch on dickite and the possibility of reverse flotation of quartz from dickite were investigated.

The flotation recoveries of both minerals was increased with increasing pH and reached a maximum at about pH 12. In this case, the amount of sodium oleate necessary for obtaining good flotation recovery for dickite was much higher than that for quartz. The amount of calcium chloride required for good flotation recovery of dickite was about 5 times higher than that of quartz. It was expected from the single mineral flotation results that quartz could be selectively floated from dickite. But, not only quartz but also dickite were well floated in the absence of corn starch. It is considered that flotation of dickite perhaps results from the heteroflocculation with quartz, which may be caused by the formation of particle-particle linkage action through calcium hydroxy complex or calcium hydroxide, or the hydrophobic interaction between hydrocarbon chains of oleate adsorbed on both mineral surfaces. Corn starch depressed dickite in preference to quartz, so that quartz was selectively floated from dickite in the addition of $75\text{g}/\text{m}^3$. Whereas the adsorption of corn starch on quartz was very small and only about one fourth of that on dickite.

The negative zeta potential of dickite in the alkaline pH range was lower than that of quartz. Accordingly, large adsorption of corn starch on dickite, compared with quartz, may be explained by weaker electrostatic repulsive force between corn starch and dickite.

It was noted that dickite is selectively flocculated from quartz by adding $75\text{g}/\text{m}^3$ corn starch. Furthermore, it was observed that quartz particles were also flocculated by the addition of calcium chloride after corn starch at pH 12.0. This may be caused by the formation of particle-particle linkage action through polyvalent cation as mentioned above. In the present flotation experiments, the reagents were added in the order of corn starch, calcium chloride and sodium oleate. Accordingly, dickite and quartz was flocculated in the separate stage. Judging from the flotation results that fine quartz and dickite were well separated, there seems no mutual interaction between dickite flocs and quartz flocs. This may be very preferable in fine particle flotation.

CHAPTER 6 : CONCLUSION

This chapter is the general conclusions.

審 査 結 果 の 要 旨

カオリン鉱物資源化の大きな問題点はカオリン鉱物と石英の分離である。粗粒の石英は水簸により除去されているが、微粒の石英の分離は確立されていない。陽イオン捕収剤を用いた浮選でも、分離 pH 領域がカオリン鉱物と石英の表面電位が低い酸性領域に限られるため、10 μm 以下の粒子の分離は困難である。本論文はカオリン鉱物としてディッカイトを用いて、陰イオン性のオレイン酸ナトリウムを捕収剤とする浮選を検討し、微粒の石英を分離する2つの新しい方法を見出し、それらの機構を明らかにしたもので、全編六章よりなる。

第1章は緒論である。

第2章では、希薄な酸溶液で1～2時間前処理すると、ディッカイトの浮遊性が中性 pH 付近で増大することを見出し、5 μm 以上の粒子に対してはディッカイトと石英の浮選分離が可能となることを示している。その理由として、希薄酸溶液中で分解されたアルミニウムの一部は溶液中に溶出されるが、相当量のアルミニウムがディッカイト表面に留まり、これがオレイン酸イオンの吸着に活性なサイトを与え、ディッカイトの選択的疎水性化を可能にしていると推察している。これは著者が見出した注目すべき知見である。

第3章では、希薄酸溶液前処理における共存電解質の影響について検討している。塩化カルシウム、塩化カリウムのような電解質が共存すると、浮選分離に要する前処理時間を5～10分間に短縮できることを見出し、その機構を明らかにしている。

第4章では、2 μm 以下の微粒のディッカイトと石英を分離するために、陰イオン性高分子凝集剤、セパラン AP30 による選択凝集の効果を調べている。凝集剤を捕収剤であるオレイン酸ナトリウムの添加後に加えると、ディッカイトの浮遊率が増大し、かつディッカイトと石英のヘテロ凝集が妨げられ、良好な分離結果が得られることを示している。

第5章では、2 μm 以下の粒子を対象として、pH12程度のアルカリ性領域でのカルシウム活性を利用して、石英を浮遊させてディッカイトと分離する方法を検討している。この方法では、とうもろこし澱粉がディッカイトの抑制剤、凝集剤、カルシウム塩が石英の活性剤、凝集剤として作用し、両者を凝集体として良好に分離できることを見出している。これは注目すべき結果である。

第6章は結論である。

以上要するに本論文は、微粒のディッカイトと石英の浮選分離に関して検討し、新しい方法の提案を行ない、その機構を明らかにしたもので、資源工学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。