QUANTUM CHEMISTRY ON FLOTATION BEHAVIOR OF KYANITE-GROUP POLYMERPHOUS MINERALS①

Dong, Hongjun Chen, Jin
Department of Mineral Engineering,
Central South University of Technology, Changsha 410083

ABSTRACT

The flotation role and behaviors of kyanite-group polymerphous minerals were studied in modified Hallimond tube in detail. Furthermore, the energy change of collector/mineral system before and after adsorption and the net charge densities of the atoms on the minerals surfaces were calculated by use of quantum chemistry. The flotabilities in minerals were successfully explained.

Key words: kyanite andalusite sillimanite flotation quantum chemistry calculation

1 INTRODUCTION

Kyanite-group minerals include kyanite, andalusite and sillimanite, which are polymerphous with the same chemical formula as $Al_2O_3 \cdot SiO_2$. After investigation on their flotabilities over sixty years, the main results obtained are as follows: (1) The adsorption of oleate on kyanite minerals is of chemical adsorption. (2) The adsorption of hydrocarbon sulfonate or sulfate is, however, of physical adsorption while the molecular weight is low and chemical adsorption occurs when the molecular weight is high. (3) The adsorption of alkylamine is of physical adsorpton as controlled by electrostatic charge.

The knowledge mentioned above is gained step by step through the investigations of interfacial electrokinetic properties of minerals, adsorption amount of collectors and infrared spectra. Some of them studied on the crystal structures of minerals[1], others dealt with the interaction mechanism between mineral and collector[2].

In short, these studies are based only on the level of molecule or atom neglecting the differences in electrostatic charge densities of atoms on the minerals. It is just the differences that are the key factors to determine the rules of the flotabilities of kyanite minerals.

The development of quantum chemistry and computer makes it possible to study the electron structure in the atoms of polymerphous minerals. Quantum chemistry has been applied to the study of mineralogy for only twenty years while to mineral flotation merely ten years or so.

In this paper, the parameters of atoms in quantum chemistry of kyanite-group polymerphous minerals and the energy change before and after the adsorption of collector on mineral are studied by use of quantum chemistry. The attempt is made to interpret the flotation rules of kyanite minerals from the electronic level.

The complete neglect of differential overlap (CNDO/2) of quantum chemistry was employed in this paper, which was a set of semiempirical calculation method established by Pople, J A *et al* with some small integrals neglected, other integrals which cannot be neglected are replaced by the parameters determined by experiments. It is said that CNDO/2 is particularly suitable for comparative calculation on homologous substances[3].

① Received Mar. 31, 1994

2 EXPERIMENTAL METHOD

2.1 *Flotation Test*

2.1.1 Ore Sample

Kyanite sample is obtained from Yinshan Kyanite Mine, Henan Province. Lump ore is crushed with sorting hammer. High grade ore is obtained by hand sorting and crushed by roll crusher, then ground in ceramic mill. Finally, the 100～200 mesh fraction is classified with Talyer standard sieve, then washed repeatedly with double distilled water, and air-dried and stored for use. The kyanite has a purity of 95%, as determined by optical miroscope and X-ray diffracton. Andalusite is obtained from Xixia Andalusite Mine, Henan Province, with a purity of 98%, sillmanite is however from Tuguiwula Sillmanite Mine, Neimenggu Province, with a purity of 90%. The procedure for the processing of andalusite and sillimanite is the same as that of kyanite.

2.1.2 Reagents

Sodium dodecyl sulfonate, sodium oleate and tetradecylamine are of chemical purity used as collectors, and hydrochloric acid with purity of C. P. and sodium hydroxide A. P. used as pH regulators.

2.1.3 Flotation Tests

The flotation tests on single mineral are carried out in a modefied Hallimond tube, take 1 gram mineral per test and 100 mL of total pulp volume. The procedure for pulp agitation is performed in electromagnetic agitator. The additions of distilled water (agitated 2 min), pH regulator (2 min.), and collector (3 min) are made respectively. The pH value of the pulp is measured after agitation. The pulp is then filled into Hallimond tube, agitated 2 min, switch on the nitrogen gas (35 mL per min), Flotation 3 min taking a measurement of the weight of ore floated and the recovery can be obtained.

2.2 *Quantum Chemistry Calculation*

The investigation of quantum chemistry calculation is generally carried out in four steps: (1) to establish the calculation model; (2) to choose the parameters; (3)to calculate by the computer, and (4) to analyze the calculation result. To establish the calculation model is the most important step. The quantum chemistry parameters needed for calculation can be chosen from references [4] and [5].

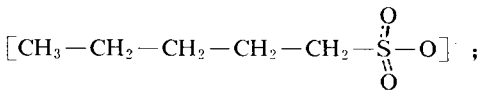
2.2.1 The Models of Minerals Crystalline

Generally speaking, it is possible to calculate with quantum chemistry only when the atom number of a system is limited. However, all the kyanite minerals are of silicate crystals with innumerable atoms. To solve the contradiction, it is necessary to select a molecular system with limited numerable atoms to simulate the silicate crystal with innumerable atoms. In other words, it is to say to establish model. For the periodicity of silcate crystal structure and the limited region where the electrons move, the molecular model which is a structure unit with few atoms usually can represent the real properties of the silicate minerals. For example, H_4SO_4 or $H_6Si_2O_7$ were chosen as molecular model to research on the bond length, bond angle and charge density of sillicate minerals, satisfactory results were obtained. But the simple model like this is impossible to show homogenous-isomerism. In order to investigate the changes in property of $AlAl[SiO_4]O$ resulting from different structures, the model must be chosen from the larger molecular systems. In this paper, their unit cells are chosen as their models of kyanite, andalusite and sillimanite respectively. Every mineral includes four Al_2SiO_5"molecule", and the arrangements of atoms in these models referred to reference [6]. In calculation, the suspended bonds are compensated by hydrogen ions[3].

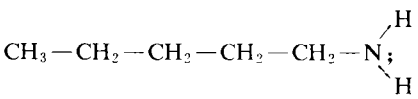
2.2.2 The Models of Collectors

All the collectors used in the test are of long chain surfactants. Their models are established through decreasing the number of $-CH_2-$, and are shown as follows:

the model of sodium dodecyl sulfonate is



the model of tetradecylamine is



the model of sodium oleate is

$$[CH_3-CH_2-CH=CH-CH_2-CH_2-C\overset{O}{\underset{O}{<}}]^-.$$

2.2.3 Model of Interacting Collector/Mineral

In kyanite minerals, the aluminium atoms have three coordination numbers 4, 5 and 6. Based on the calculation results of quantum chemistry, the aluminium atom with six coordination number, $Al^{(6)}$ has to be the active site for the collector adsorption. The models of collector/mineral are established by linking up the two models of mineral and collector through active sites.

The calculation of quantum chemistry are carried out on simons 7570c computer.

3 FLOTATION RESULT AND CALCULATION ANALYSIS OF QUANTUM CHEMISTRY

3.1 *Flotation Test Result*

Using sodium oleate, sodium dodecyl sulfonate and tetradecyl amine as collectors respectively, the recoveries of kyanite minerals as functions of pH are shown in Fig. 1.

It can be seen that there exist similarities and differences in their flotabilities of the three Al_2SiO_5 polymerphous minerals. Their flotabilities of the three minerals as a funcation of pH are of similarities: (1) When sodium oleate is used as collector, there are two peaks in the recovery curves, one of them is near pH=3, another at pH=8 or so. (2) Using anion collector, sodium dodecyl sulfonate, as the collector, the recovery decreases constantly when pH changes from low to high. In other words, at acid range, the minerals have better flotability. (3) Using cation collector, tetradecylamine, as the collector, the minerals have better flotability at the alkaline range. These similarities in flotability is determined by minerals "homogeneity", the internal origin. Although the flotabilities of kyanite minerals as functions of pH exist the same rule, their floating sequences varies when the collectors are different (after Fig. 1):

sodium oleate: sillimanite > andalusite > kyanite;
sodium dodecyl sulfonate: andalusite > sillimanite >kyanite; tetradecylamine:kyanite>sillimanite> andalusite.

These differences in flotability of the three polymerphous minerals resulted from the differences in their crystal structures. These different crystal strutures of minerals must lead to the change of electrostatic change distribution of atoms, thus influencing the flotabilities of kyanite

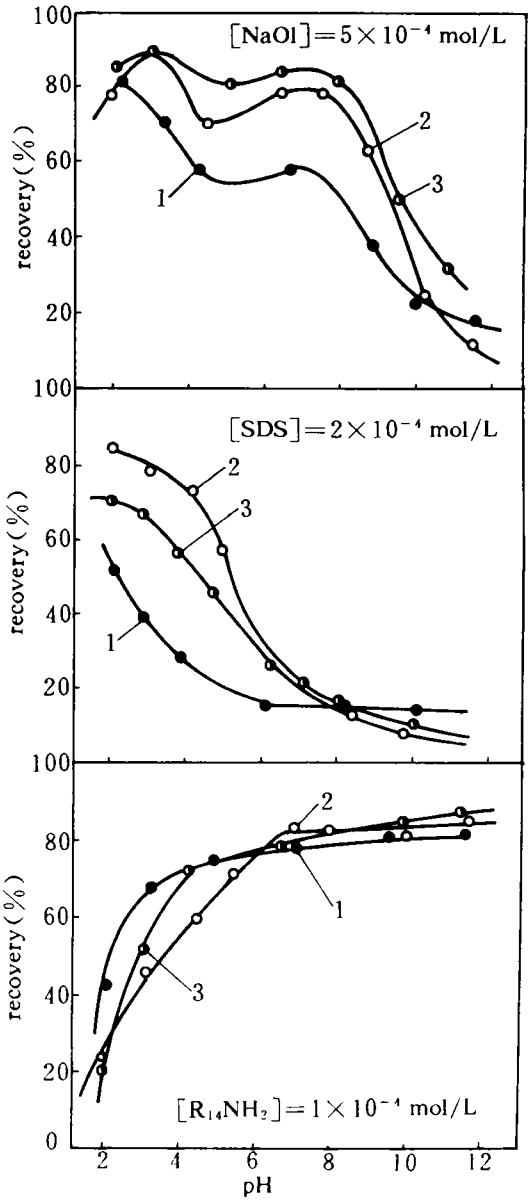


Fig. 1 Recoveries of kyanite minerals as function of pH

1—kyanite; 2—andalusite; 3—sillimanite

minerals. The influences of crystal structures of polymerphous minerals on their flotabilities are analyzed via the calculation of quantum chemistry.

3. 2 *Calculation Analysis of Quantum Chemistry*

3. 2. 1 The electrostatic charge distribution of atoms in minerals

A series of quantum chemistry parameters, such as total energy of a system, electron energy, molecular orbital energy, electrostatic charge density(Q), and bond order between atoms can be obtained by the calculation of quantum chemistry. These parameters play an important role in explanation of chemical properties, spectra properties and reaction ability of atoms or molecules. For the differences of the coordination number of aluminium, bond length and bond angle, their electrostatic charge density of each atoms in kyanite minerals are different from each other. The results of calculation of quantum chemistry are shown in Table 1. From Table 1, it can be seen that: (1) The electrostatic charge density of silicon atom in the three kinds of minerals is of little difference. The reason is that the silicon atom in silicate is always in the form of $[SiO_4]$, and its bond length and bond angle change very little. (2) When the coordination number of alumnium atom is different, the electrostatic charge density is also defferent. The electrostatic charge density of aluminium is in proportion to the square of its coordinaton number. In other words, the positive charge on six coordinative aluminium atoms is the most. When the interaction between collector and mineral is dominated by charge, the anion collector will select six coordinative aluminium atoms. So that, when the anion collectors are used in flotation, the floatability order of kyanite minerals predicted with charge amount of six coodinative aluminium atoms is as follows:

Table 1 Electrostatic charge density of atom in kyanite minerals (au)

Minerals	$Al^{(6)}$	Al	$Al^{(4)}$	Si	$O_{Si\,O\,Al}$	$O_{Al\,O\,Al}$
kyanite	1.802			0.797	-0.884	0.920
andalusite	1.833	1.130		0.727	-0.728	0.751
sillimanite	1.810		0.876	0.705	-0.616	0.725

au- atom unit; $Al^{(6)}$ means the coordination number of aluminium is 6.

kyanite>andalusite>sillimanite. For the same reason, when the cation collectors are taken for flotation, the floatability order of kyanite minerals predicted with the amount of negtive charge on oxygen atom is kyanite>andalusite>sillimanite.

The predicton mentioned above agrees in general with the flotation result. But the floatation order of andalusite and sillimanite sometimes disagree with the prediction above. This is because the interaction intensity between collector and mineral is related to not only the attractive force between the opposite charges, but also the repulsive force between the like electric charges, even related to the chemical interaction apart from electric interaction. Therefore, to determine the interaction intensity between collector and mineral, the general interaction energy must be taken into account comprehensively.

3. 2. 2 Calculation on energy change of interaction process of collector/mineral

In the process of adsorpation of collector on mineral surface exists energy change, and the amount of energy change determines the adsorption of collector on the mineral surface. This energy change can be obtained via the calculation of quantum chemistry accurately.

The adsorption process of collector on mineral surface can be expressed:

$$M_{(\text{mineral})} + L_{(\text{collector})} \rightleftharpoons ML,$$

Therefore, the energy change is approximately:

$$\Delta E = E_t^M + E_t^L - E_t^{ML}$$

where ΔE is equivalent to the amout of heat released in the adsorption process of collector on mineral. When ΔE is large, the collector can easily adsorb on mineral surface, on the contrary, ΔE is small, the adsorption process is difficult to proceed.

The energy change, ΔE of adsorption process of sodium oleate, sodium dodecyl sulfonate and tetradecylamine on kyanite minerals obtained by the calculation of CNDO/2 are shown in Table 2. The floatability orders predicated by ΔE are as follows. sodium oleate: sillimanite > andalusite > kyanite; sodium dodecyl sulfonate: andalusite > sillimanite > kyanite; tetradecylamine: kyanite > sillimanite > andalusite.

As motioned above, through the calculation of charge density of atoms on minerals surface and

Table 2 The energy change of the adsorption of three kinds of collectors on kyanite minerals(au)

minerals	sodium oleate	sodium dodecyl sulfonate	tetradecylamine
kyanite	0.2033	0.0651	0.1638
andalusite	0.2465	0.1837	0.0721
sillimanite	0.3451	0.1244	0.1270

the energy change in the process of collector adsorption, the flotation rule of kyanite-group polymerphous minerals may successfully be explained. It gets start only a short time that quantum chemistry is applied to study flotation mechanism. There are still a lot of intersting questions needed to investigate further. For example, what relationships exist between the electrostatic charge density of atoms on mineral surface and the point of zero charge of minerals? Can the influence of pH on the flotability of mineral be explained by the calculation of quantum chemistry? It is convinced that these problems will be taken into consideration by more reseachers and settled down step by step.

4 CONCLUSIONS

(1) Using sodium oleate, sodium dodecyl sulfonate, and tetradecylamine as the collector, the flotabilities of the three Al_2SiO_5 polymerphous minerals as function of pH display a similar rule. The foltability orders of kyanite minerals as demonstrated by single mineral test are as follows:
sodium oleate: sillimanite>andalusite>kyanite;
sodium doecyl sulfonate: andalusite>sillimanite>kyanite; tetradecylamine: kyanite>sillimanite>andalusite.

(2) The electrostatic charge density of atoms on minerals surface and the energy change before and after the adsorption of collector on mineral are calculated through quantum chemistry CNDO/2, and the flotation behaviors of kyanite minerals are fully explained with the calculation results.

REFERENCES

1 Yoon, R H; Salman. T; Donnay, G. Journal of Colloid and Interface Science, 1979, 70(3): 483—493.
2 Choi, H S; Oh, J H; Journal of Institute of Mining and Metallurgy of Japan, 1965, 81(927): 614—620.
3 Gao, Xiaohui. Journal of Inorganic Chemistry, 1987, 3(3): 58—68.
4 Weast, R C. CRC Handbook of Chemistry and Physics, 1990, 70th ed, Baca Raton, CRC Press Inc, F188—189.
5 Pople, J A; Beveridge, D L. Approximate Molecular Orbital Theory, London: McGraw-Hill, Rock-Forming Minerals, 1A, London: Longman House, 1982, 725—800.