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Occurrence State of Iron and Titanium in Kaolinite

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The process mineralogy characteristics, such as chemical composition, mineral components and contents, the occurrence of the main mineral, the occurrence state of Ti and Fe, and the mineralogy factors affecting beneficiation indexes, were studied in detail with the methods of lens-below identification, scanning electron microscope, chemical elements analyses, and the chemical phase analyses. The results show that kaolinite mainly distributed in villform and hexagonal flake form, little distributed in tube form. The aggregate of kaolinite irregularly distributed, always in floc, rodlike and wormlike form. Hematite, limonite, anatase, and fine grain-sized detrital quartz were mingled in intergranular spaces, with the average content of Fe at 0.24%, TiO2 at 0.03%. The iron and Titanium were mainly distributed in hematite and anatase form in the ores, these two minerals could both be removed with beneficiation method, and the application value of kaolinite would be improved

1. Introduction

Kaolinite has already been widely used in applications of paper-making, fireproofing, rubber etc. (Saikia et al., 2003; Rodríguez-Quirós et al., 2015; Aroke et al., 2016). Whiteness as one of the key factors affecting the properties of the kaolinite continuously attracted the attentions from the clay researchers (Chandrasekhar et al., 2002; Hernández et al., 2013). As known, previous studies focused on the occurrence state of iron and titanium in the kaolinite since it was closely related to the whiteness and to the further applications (Xiao, 1997; Bertolinoa et al., 2010; Ortega-Cubillos et al., 2015). Research was conducted on technology of iron and titanium removal in order to improve the whiteness of the kaolinite (Camesselleet al., 2003; González et al., 2006; Lu et al., 2006; Cai et al., 2008; Aghaie et al., 2012; Platova et al., 2013; Sivakumar et al., 2015). The kaolinite ores in this study are gray-white colored and locally mingled with less irregular tawny and bronzing massive aggregates, the ores are very easy to get argillization when encountering water due primarily to their loose structure. The processing mineralogical parameters such as the occurrence state of the useful elements, the chemical composition of the ores, the liberation degree, and the disseminated characteristics of the kaolinite were clarified by conducting the processing mineralogical studies using scanning electron microscope (SEM) and mineral liberation analyzer (MLA). This study would discuss the occurrence state of iron and titanium from the point of process mineralogy and provide some feasible iron removal suggestions.

2. Experimental methods

2.1 Chemical phase analysis

The original ores were sent to Changsha Research Institute of Mining and Metallurgy, CO., LTD for chemical phase analysis. According to the differences in the lattice energy, density, hardness and solubility product of the ores, the specific chemical solvents and test methods were chosen to make the ores quantitatively and selectively dissolve, then all the minerals of the ores could be measured in the solvent respectively.

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2.2 Scanning electron microscope

SEM images were obtained using a FEI Quanta650 SEM instrument at Changsha Research Institute of Mining and Metallurgy, CO., LTD. Powdered kaolinite specimens were air-dried for ~24 hours. Several small pieces were then affixed onto a stainless-steel sub with carbon tape, taking care to observe sample orientation and direction. The specimens thus prepared were kept in a desiccator before analysis by SEM to avoid moisture absorption. All the specimens were coated by platinum to obtain a good image quality.

2.3 Mineral liberation analyzer

Mineral liberation analyzer (MLA) is the high-speed automatic mineral parameters quantitative analysis system. In this study, MLA was used to analyze the mineral contents, disseminated grain sizes, and liberation degree of the aimed minerals. The micrograph and relative percentage content of each mineral were observed by the energy dispersive spectrum (EDS) equipped with MLA. The MLA used in this study is MLA650, with Bruker Quantax200 EDS, and process mineralogical parameters automatic analysis software (MLA3.1).

3. Results and discussion

3.1 Chemical composition of the ores

The results of chemical elements analysis of the ores and chemical phase analysis of iron and titanium are shown in Tables 1, 2 and 3, respectively. The results indicate that the ores are mainly composed of SiO_2 and Al_2O_3, the contents are 63.6% and 23.7% respectively. The impurity components such as Fe and TiO_2 have contents at 0.7% and 0.8%, they mainly occurred in the form of hematite (limonite) and alataes, respectively, the distribution ratio for both are around 85% and the Fe, TiO_2 occurred in these forms would be easily to remove from the kaolinite through beneficiation methods.

Table 1: Chemical composition of the ores (%)

Component	Al_2O_3	SiO_2	TFe	TiO_2	CaO	MgO	Na_2O	K_2O	Ignition Lost
Content	23.7	63.6	0.7	0.8	0.2	0.1	0.1	0.5	8.29

Table 2: Chemical phase analysis of Fe (%)

Iron phase	Magnetite	Hematite (limonite)	Carbonate	Sulfide	Silicate	Total
Content	trace	0.51	0.02	trace	0.07	0.60
Distribution ratio	trace	85.00	3.33	trace	11.67	100.00

Table 3: Chemical phase analysis of Ti (%)

Iron phase	Ilmenite	Anatase	Silicate	Total
Content	0.02	0.77	0.11	0.90
Distribution ratio	2.22	85.56	12.22	100.00

3.2 Mineral composition and contents

As shown in Figure 1, the ores are mainly comprised of kaolinite and quartz, with some sericite as well as minor anatase, hematite (limonite), and ferruginous matters. The results of X-ray fluorescence indicate that the percentage contents for each mineral are kaolinite at 54.9%, quartz at 40.3%, anatase at 0.9%, ferruginou matters at 0.7%, sericite at 2.7%, others at 0.5%.

3.3 The occurrence of the main minerals

Kaolinite, the main aimed mineral enriched during beneficiation recovery, has very tiny crystal size and micro-crystalline texture, showing unapparent hazy formation under microscope. The crystals are shown in villiform or pseudoexagonal schistose form, the crystal plates are generally <0.15 μm, and locally aggregated in book-like form (Figure 2). Tetragonal tube-like crystals with diameter < 0.2μm could be observed occasionally (Figure 3). The ratio of schistose to tube-like kaolinite crystals is approximately 98:2 in the whole specimen. Due to the tiny particle size, high viscosity of kaolinite, the minerals are not easy to disperse, therefore villiform and schistose crystals always mixed inter-grew in irregular floc, rodlike or wormlike aggregates, some shows low-transparency ash black colour because of dying by the organic matters.

As shown in Figures 4 to 7, the impurities including micro-fine particle-sized detrital quartz, anatase, hematite, and limonite etc. dispersedly distributed in villiform kaolinite. The results of SEM-EDS indicate that the kaolinite averagely contained Al_2O_3 at 38.87%, SiO_2 at 46.80%, Fe_2O_3 at 0.34%, TiO_2 at 0.03% and H_2O at 13.96%.

Quartz, widely distributed in the ores, usually showed angular detrital form and mixed intergrew with kaolinite, some particle surfaces had tawny-bronzing color when impregnated by the ferruginous matters (Figure 4). In some incomplete weathering ores, basal cementation would be observed where kaolinite is the cement filling in the inter-particle space of detrital quartz, the particle size of quartz is generally fine at 0.01～0.06mm (Fig.5).
Iron minerals including hematite, limonite and ferruginous matters are main components in the ores. Hematite was partially in fine globular form and partially in irregular crumb form, the particle size of the crystals was usually <0.01 mm. Overall, the disseminated hematite in the ores unevenly embedded in kaolinite-quartz basement, the particle size of the aggregates can reach up to ~0.4mm (Figure 5). The results of SEM-EDS indicate that the hematite averagely contained Fe_2O_3 at 95.01％, TiO_2 at 1.5% and minor impurities such as SiO_2, Al_2O_3 and MgO. Ferruginous matters could be observed in irregular skinlike form and distributed along the edge and crack of kaolinite and quartz. Kaolinite and quartz showed shades of tawny-hazel color due to the unevenly disseminated by ferruginous matters, the close relationship between kaolinite and ferruginous matters may lead to the hard iron removal from kaolinite using mechanical beneficiation methods (Figure 6).
Limonite, occasionally observed, mainly irregularly embedded with kaolinite aggregates, having particle size generally at 0.005～0.04 mm.
Anatase is the main mineral occurrence state for titanium element. It was idiomorphic-hypidiomorphic granular and embedded in kaolinite aggregates in scattered disseminated form. The particle size was mostly smaller than 0.005 mm, while some can reach up to 0.03 mm (Figure 5 and 7).

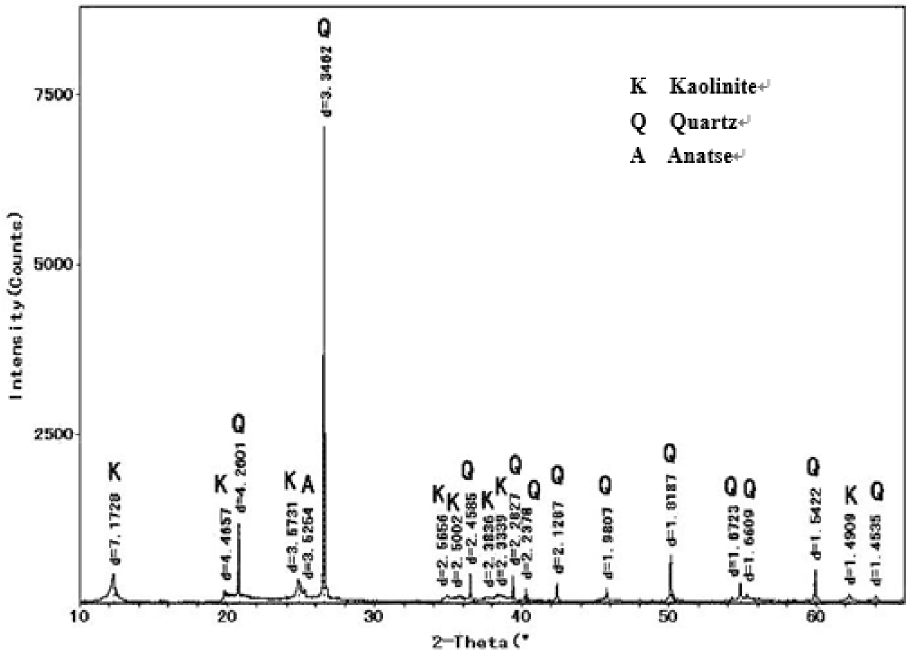

Figure 1: X-ray diffraction pattern of the ores

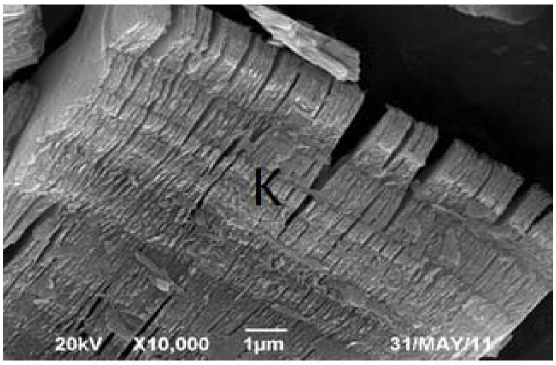

Figure 2: Tiny schistose kaolinite (K) aggregated in book-like form Secondary Electron Image

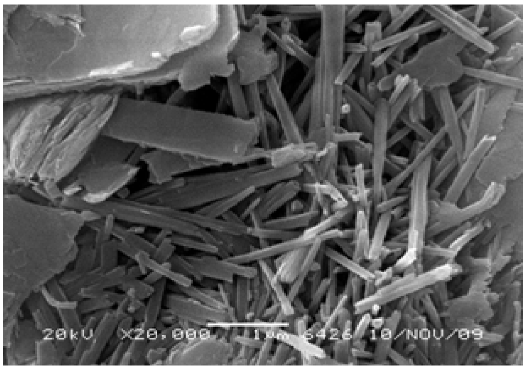

Figure 3: Kaolinite in micro-crystalline tube form Secondary Electron Image

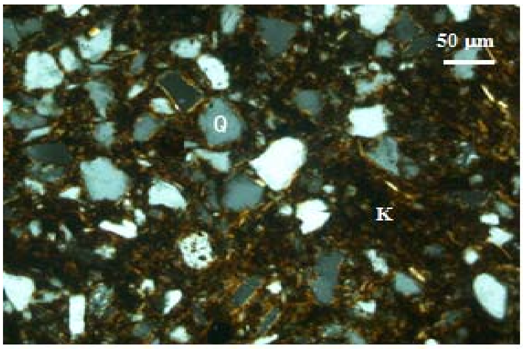

Figure 4: Fe- impregnated kaolinite (K) distributed along the edge of quartz (Q) Cross-polarized light

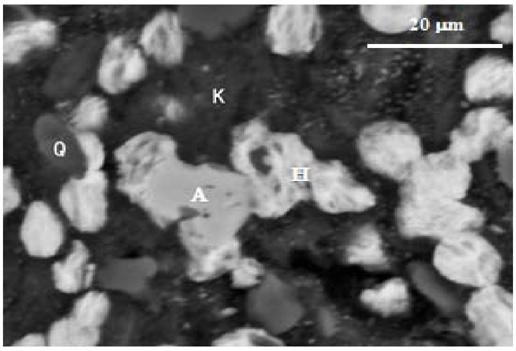

Figure 5: Hematite (H) scatteredly distributed in kaolinite (K), A-anatase, Q-quartz BSE

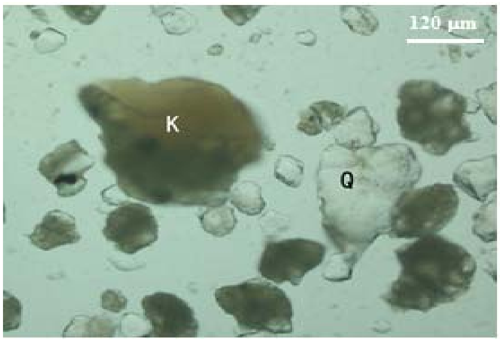

Figure 6: Skin-like Fe disseminated distribution along kaolinite (K), Q-quartz, plane-polarized light

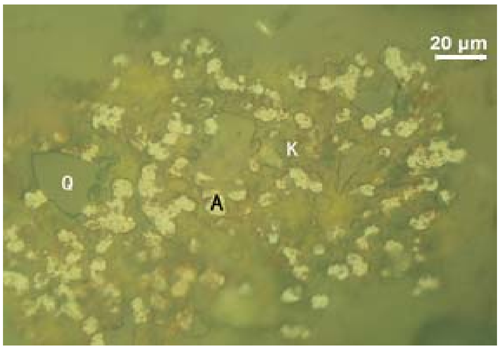

Figure 7: Fine grain-sized anatase (A) disseminated distribution in kaolinite (K), Q-quartz, reflective light

3.4 Occurrence state of iron and titanium

Distribution equilibrium calculation on Fe and TiO_2 in the ores was conducted based on the mineral composition and SEM-EDS analysis in order to find out their distribution characteristics, the results are presented in Table 4.As shown, the occurrence state of iron in the ores was hematite, the total distribution ratio of iron (including the iron in anatase) was 77%, which was the highest theoretical distribution ratio to remove the iron minerals form the ores during beneficiation, while iron in kaolinite was 21.54%. The occurrence state of titanium in the ores was relatively simple, mostly in anatase form (96.46%), only minor Ti substituted iron in hematite in a way of isomorphism.

Table 4: Distribution equilibrium calculation results of Ti and Fe in the ores (%)

Mineral	Content	Fe		TiO_2	
		Grade	Distribution ratio	Grade	Distribution ratio
Kaolinite	54.90	0.24	21.54	0.03	1.80
Quartz	40.30	-	-	-	-
Sericite	2.70	0.33	1.46	0.20	0.59
Anatase	0.90	0.66	0.97	98.02	96.46
Hematite	0.70	66.45	76.03	1.50	1.15
Others	0.50	-	-	-	-
Total	100.00	0.612	100.00	0.914	100.00
Raw ore		0.60		0.90	
Balance coefficient		1.02		1.01	

3.5 Analysis on the factors affecting beneficiation indexes

A slight of Fe and TiO_2 usually occurred in the kaolinite crystals as absorbed state or mechanical mixing materials, the Ti and Fe in these forms could not be disassociated effectively by using beneficiation methods, there would be 0.24% Fe and 0.03% TiO_2 in kaolinite ore concentrates.

Micro-fine particle-sized iron minerals and anatase in the ores were both scatteredly embedded in kaolinite, and closely intergrew with kaolinite. Hematite and anatase would mix into kaolinite ore concentrates inevitably even if conducting strong magnetic separation or gravity separation due to the tiny particle size, resulting high content of Fe and TiO_2 in kaolinite ore concentrates.

Skinlike ferruginous matters, observed along the edge of kaolinite, had faint boundary with kaolinite, which could not be removed entirely using beneficiation methods, which would affect the quality of kaolinite ore concentrates.

4. Conclusions

Kaolinite and quartz are the main minerals in the ores with minor sericite and some impurities including hematite, anatase, limonite, and disseminated ferruginous matters. Kaolinite is easily to get argillization, some monomers of hematite and anatase would appear when fully stirring under water, thus stir operation would be good for the mineral disassociation. The results indicate that the tiny particle size (<0.01 mm) of hematite and anatase embedded in kaolinite and the skinlike ferruginous matters observed along the edge of kaolinite could not be removed with the method of mechanical beneficiation, partially hematite and anatase would mix into the kaolinite ore concentrates. Methods besides mechanical beneficiation methods should be conducted in order to obtain better quality of ore concentrates.

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