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Study on Occurrence of Titanium Element in Anatase Ores of Shazi, Qinglong, Guizhou Province

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Abstract

The tectonic position of anatase deposit in Shazi area, Qinglong, Guizhou Province is located at the transitional area between Yangtze Platform and the western part of South China orogenic belt. Three industrial ore bodies in this deposit are yielded above the limestone Karst unconformity of the Middle Permian Maokou Formation and at the bottom of Emeishan basalt. Genetic type of deposit is hot water -eluvium talus sedimentary which is related to the eruption of Emeishan basalt. Based on the analysis of chemistry, X-ray phase, electron probe and microscopic identification, etc., the data suggest that TiO2 in anatase ores are mainly present in the form of microgranular inclusions in silicate and quartz; secondly, Ti occurs as isomorphism in limonite; few are as independent minerals existing in the anatase with particle size greater than 0.04mm. According to the occurrence of Ti, it is determined that the anatase ores are extremely refractory, using conventional processing methods (heavy, magnetic, flotation) are not effective in enrichment anatase, but "roasting- acid leaching-alkaline leaching" beneficiation process works and obtain anatase with 42.32% TiO2. Extraction method can also enrich the associated element Sc, obtaining 99.99% scandium oxide products, and the leaching rate of Sc is 90%, which can produce iron oxide red and poly aluminum silicate salt (PSA) coagulant by-product. Mineral resources can be effectively developed and utilized without emission, which can obtain good environmental benefits.

Keywords*: We would like to encourage you to list your keywords in this section.*

1. Introduction

Titanium (Ti) is a transitional metal element of silver and white color, and in the fourth period and the group IVB of elements periodic table [1]. Its characteristics include light weight, high strength, having metal luster, and resistance to wet chlorine corrosion [2-4]. The chemical character of Ti is active, so there is no pure titanium in nature, and it is always associated with oxygen [5-6]. In minerals, Ti mainly exists in the forms of TiO2 and titanate, and often occurs with iron symbiosis. The main minerals of titanium include rutile, anatase, ilmenite, brookite, perovskite, ilmenite, titanite, pseudobrookite, titanomagnetite, and ilmenite, etc. [7]. Our study mainly focuses on the anatase deposit in Shazi area, Qinglong, Guizhou. Anatase one of the 14 strategic reserves of mineral resources heavily dependent on external resources, is the serious shortage of minerals in China [5-6, 8-9]. The theoretical research on newly discovered large anatase deposit at Shaizi, Qinglong just begins, and there are many aspects are still waiting for further work. Here we study the occurrence of anatase in the deposit, which has great significance to enrich the genetic theory of anatase deposit.

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Shazi anatase deposit is located at southeastern Guizhou, the tectonic position of which is at the transitional area between the southwest margin of Yangtze Platform and the western part of South China orogenic belt. It is in the east of Emeishan basalt rocks which are controlled by NS-trend Eastern Yunnan deep seated fault, NW-trend Yadu-Ziyun deep seated fault and WE-trend Nayong-Weng'an deep seated fault [10].

Shazi anatase deposit was a large residual slope type deposit, discovered by Professors Aiguo Nie, Ruzhu Zhang, and the author in 2007 at Qinglong County, Guizhou Province. General survey and detail investigations of this deposit had been worked during 2007~2011. The proved restores of the anatase deposit is 23060900 tons, quantity of TiO2 is 1024800 tons, and the average grade of TiO2 is 4.39% [10-12]. Previously, sedimentary metamorphic and hydrothermal modified-type anatase deposits were only discovered at Yangtizi Mountain- Moshi Mountain in Inner Mongolia [8-9]. Shazi anatase deposit is the first one discovered in the weathered residual slope soil of Emeishan basalt in Guizhou, and it is also the first large eluvium talus- type anatase deposit, which ended the history of Guizhou province without Titanium resources and has great practical significance for the reevaluation of the mineral resources in Southwest Guizhou.

Shazi anatase deposit mining area in Qinglong is located at the southwest limb of Bihenying dome-shaped anticline, and the exposed strata, in ascending order, includes Middle Permian Qixia and Maokou Formation; Upper Permian Emeishan Basalt Formation, Longtan Formation and Quaternary. There are three ascertain industrial ore bodies, `which are oriented in NESW, and they are numbered successively as①②③. The ore bodies are yielded above the limestone Karst unconformity of the Middle Permian Maokou Formation and at the bottom of Emeishan basalt [10-11].

2. Components of Ore

2.1 Ore Type

Ore type is oxidized ore, and generally can be divided into five types: clayey oxide ore, siliceous clayey oxide ore, siliceous tuffaceous clay oxidized ore, siliceous clay oxidized manganese oxide ore of iron and Kaolin siliceous oxide ore. Ores are mainly red and yellow clay and loam bearing anatase, and clay often contains breccias, which are dominated by basaltic pyroclastic rock, clay siliceous rock, iron manganese clay and tuff, *etc.* Gravel size ranges from 2mm to tens of centimeters.

2.2 Chemical Composition Characteristics of Ore

From the data of Tab. 1, the contents of Si, Al, Ti and Fe in Shazi anatase ores are greater than 1%, which is correspond with the result of Tab. 2; the main oxides in ores include SiO_2, Al_2O_3, Fe_2O_3 and TiO_2, and the content of them is 81.64-88.15% in total, which is close to the characters of modern laterite weathering crust and red clay type gold deposit in western Guizhou [13], but the content of TiO2 is higher than gold deposit. Iron in the ores occurs as Fe2O3, which reflects the strong weathering and completely oxidation of ores. Content of SiO_2 is less than 55%, indicating they are clay ores. Contents of TiO_2 and Fe_2O_3 are positively correlated, and the correlation coefficient is 91.06%, which suggests the relationship between the anatase and the iron minerals of the original rock is paragenesis. There is a positive correlation between LOSS and contents of TiO_2 and Al_2O_3, and the correlation coefficients are 86.21% and 66.36%, respectively, which indicates the relationship between anatase and clay minerals of original rocks is paragenesis.

Table 1. Spectrum Analysis Results of Shazi Anatase Ores

Element	Ba	Be	As	Si	Sb	Ge	Mn	Mg
Content %	0.02	<0.001	0.1	>5	<0.01	<0.001	<0.1	<1
Element	Pb	Sn	W	Ga	Cr	Bi	Al	Mo
Content %	<0.01	<0.01	0.01	<0.001	<0.01	<0.001	1	<0.001
Element	V	Ti	Li	Cd	Ca	Cu	Zn	Ni
Content %	0.04	1	<0.01	<0.001	<1	0.1	0.02	0.01
Element	Co	Fe	Y	Yb	La	Nb	Zr	Sr
Content %	0.01	>5	<0.01	<0.001	<0.003	<0.001	0.02	0.02
Element	K	Na	Ag	Sc	P	B	/	/
Content %	<1	<0.1	<0.0001	<0.001	<0.1	<0.1	/	/

Table 2. Analysis of Chemical Elements of Shazi Anatase Ore

Element	TiO_2	Fe	Cu	Co	Ta	Nb	Au(10^{-6})
Content %	4.00	14.92	0.014	0.008	<0.005	0.005	0.2
Element	Ni	CaO	MgO	Al_2O_3	SiO_2	Na_2O	K_2O
Content %	0.0057	0.17	0.33	20.20	40.33	0.13	1.36

2.3 Composition Characteristics of Ore Mineral

The results of the identification and X ray analysis show that main minerals in the ores include anatase, limonite, a small amount of magnetite, ilmenite, pyrite and arsenopyrite. Gangue minerals are dominated by kaolinite, sericite, chlorite and quartz, and also contain plagioclase, few zircons, tourmaline and epidote, etc. Ore composition is complexity, and minerals retained from the original rocks include limonite basalt, limonite siliceous rocks, clay siliceous rocks, clay basaltic pyroclastic rock interbedded with clay, etc.

Based on the analysis of X-ray phase, electron probe, artificial heavy concentrate and microscopic identification, etc., the data suggest that there are 14 kinds of minerals assigned to oxide, silicate and sulfide. Oxide accounts for about 38.7%, among which anatase accounts for 4.6%, quartz takes up 9%, and ilmenite is rare. Silicate accounts for about 61%, including 48% of kaolinite, 9% of sericite (muscovite), 3% of chlorite and less than 1% of plagioclase, other silicate minerals are only occasionally seen in the heavy fraction; sulfide occurs occasionally in ores.

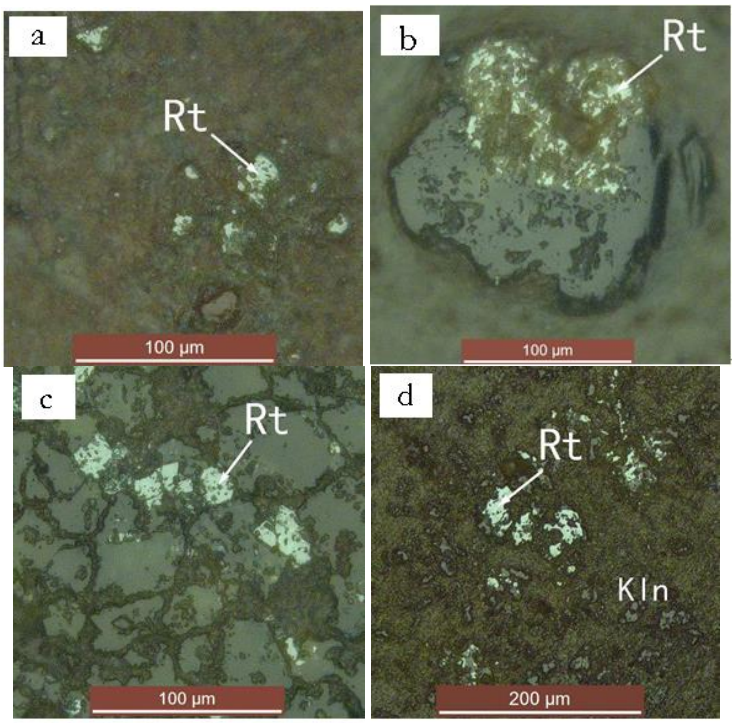
3. Titanium Independent Minerals and Carrier Minerals

3.1 Identification of Titanium Independent Minerals and Carrier Minerals

According to the analysis of electron probe, polarizing microscope and X-ray phase, the result suggests that the titanium independent minerals in Shazi anatase ores includes anatase and ilmenite, among which ilmenite occurs occasionally in ores. The carries minerals of titanium include limonite, quartz and silicate minerals (such as kaolinite, sericite (muscovite), chlorite and plagioclase, *etc*.).

Under polarizing microscope, anatase is mainly distributed in the seriously altered basalt in form of xenomorphic granular, dendritic and muddy and usually has intergrowth relationship with quartz, feldspar and kaolinite, etc. Some of anatase were wrapped in gangue minerals, or distributed in the cracks of quartz and feldspar, and sometimes associated with iron, which may result from the dark-colored mineral decomposition in the process of rock alteration, minerals grains are very fine (Fig. 1 a-e). In the artificial heavy concentrates, granular anatase are rare under stereomicroscope, which only accounts for 0.15%; (ore samples for artificial heavy concentrates are greater than 0.05mm), anatases under artificial heavy concentrates are green and yellowish-brown, adamantine luster, oily luster of fracture, quartet double cone-shaped and xenomorphic granular (Fig.1f). However, anatases with grains smaller than 47.2μm account for 96.35% under polarizing microscope, while the grains smaller than 23.6μm account for 75.37%, which reflects that the insetting grain size of anatase is small.

Through polarizing microscope investigation, the majority of limonite is disseminated in form of mud in clay minerals and the granularity is smaller than 0.004mm. A few occur as xenomorphic granular, mud and colloidal, xenomorphic granular limonite is distributed along the cracks of gangue and argillaceous. Colloidal limonite usually occurs among other minerals as cement, and mixed with clay minerals, less of them are present as granular particles, size ranges from 0.05mm to 0.3mm (Fig.1g, h).



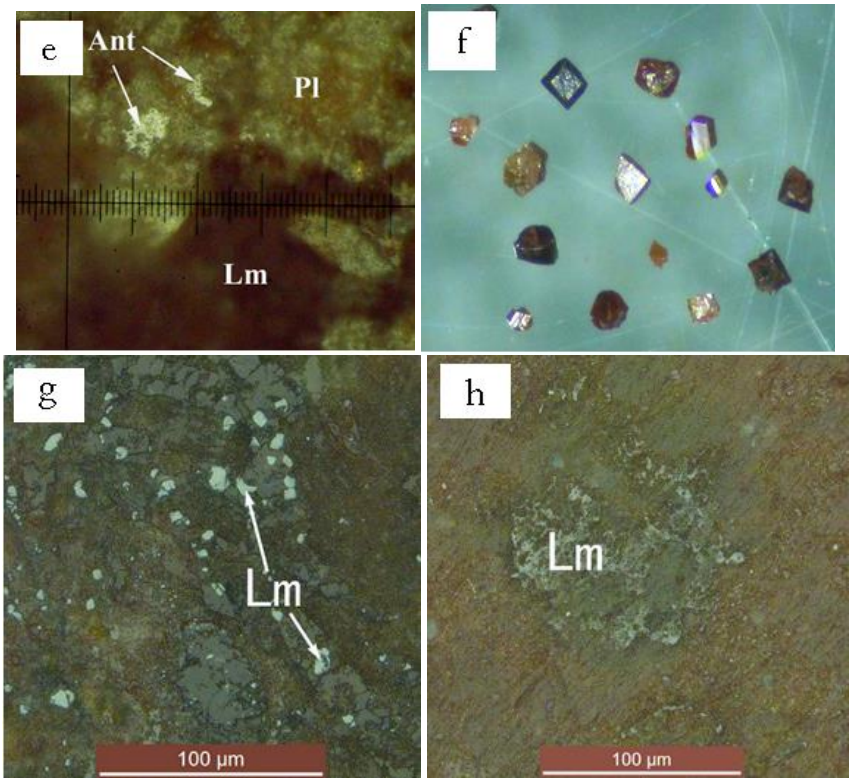


Figure 1. Micrographs

a, anatase associated with gangue, reflection single polarization; b, anatase associated with gangue, reflection single polarization; c, anatase distributed in the cracks of gangue, reflection single polarization; d, anatase associated with kaolinite, reflection single polarization; e, anatase wrapped in the plagioclase, reflection single polarization, every single lattice of scale =0.006mm; f, anatase in artificial heavy concentrate, observed under stereomicroscope; g, xenomorphic granular limonite, reflection single polarization; h, limonite disseminated other minerals, reflection single polarization. Rt, Ant: anatase; Kln: kaolinite; Pl: plagioclase; Lm: limonite.

3.2 Electronic Probe

According to the analysis of electron probe, polarizing microscope and polarizing microscope, minerals bearing Ti in ores can be divided into two types: independent minerals of titanium and the carrier of titanium minerals. According to the content of titanium in different minerals, the results of the electron probe analysis of the major titanium bearing minerals are as follows:

Anatase: molecular formula is TiO_2, the content is about 4.6%, which is the main recycle target in ores. Based on electron probe analysis, anatase contains 51.37% Ti, 47.72% O, and 0.91% Si (Fig. 2). The content of TiO2 in anatase minerals is uneven and ranges from 87% to 95%, which may be attributed by alteration. Besides, there are Sc and small amount of other elements in anatase, which is the main carrier of Sc, but the content of Sc2O3 is uneven, ranging from 0.1% to 0.03%. Backscattered electron images of anatase are shown in Fig.3, they are white and distributed in scattered shape.

Ilmenite: molecular formula is FeTiO3, it is rare in ores, and usually associated with kaolinite, granularity ranges from 0.01mm to 0.05mm. Based on electron probe analysis, ilmenite contains 34.50% Ti, 15.14% Fe, 46.54% O, 0.70% V and a small amount of Al, Si and As. Under stereomicroscope, ilmenite is black, submetallic luster, clintheriform and xenomorphic granular, occasionally occur in artificial heavy concentrate. Granularity ranges from 0.01-0.05mm. The content of TiO_2 in ilmenite is about 57%.

Limonite: molecular formula is FeOOH, he content is about 26%. Components of limonite include Fe (47.73%, 54.39%), O (42.75%, 39.22%), Ti (6.40%, 5.85%) and a little Si, Al and Ca. Average content of FeO in limonite is 70-80%, the iron content is not uniform, which may result from the uncertain content of moisture and mix of other minerals. Content of TiO_2 is 3.6-19%, which may come from the alteration of limonite. There are also some other components in limonite. The data indicate that Fe and Ti are negatively correlated.

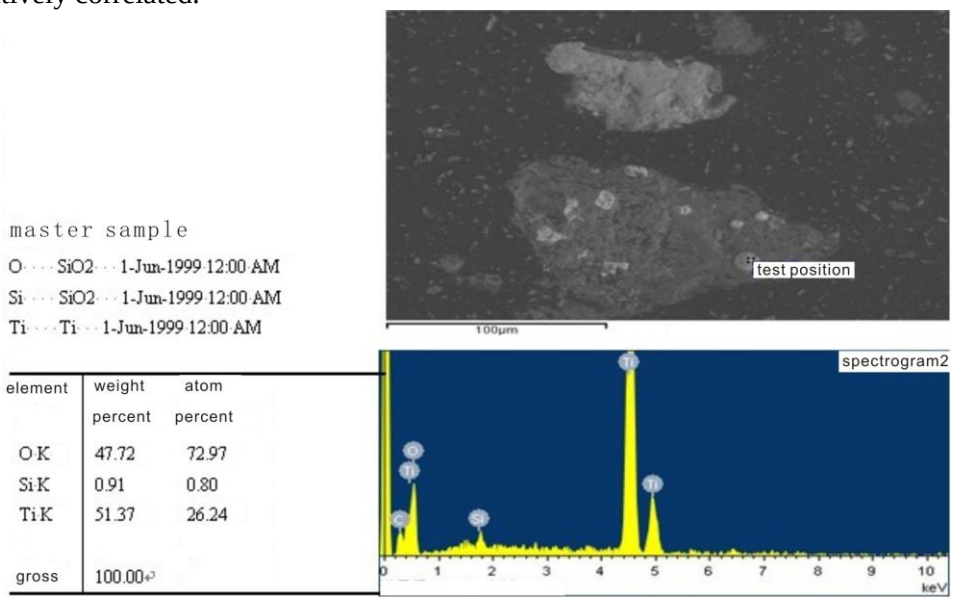


Figure 2. Electron Microprobe Analysis and Atlas of Anatase

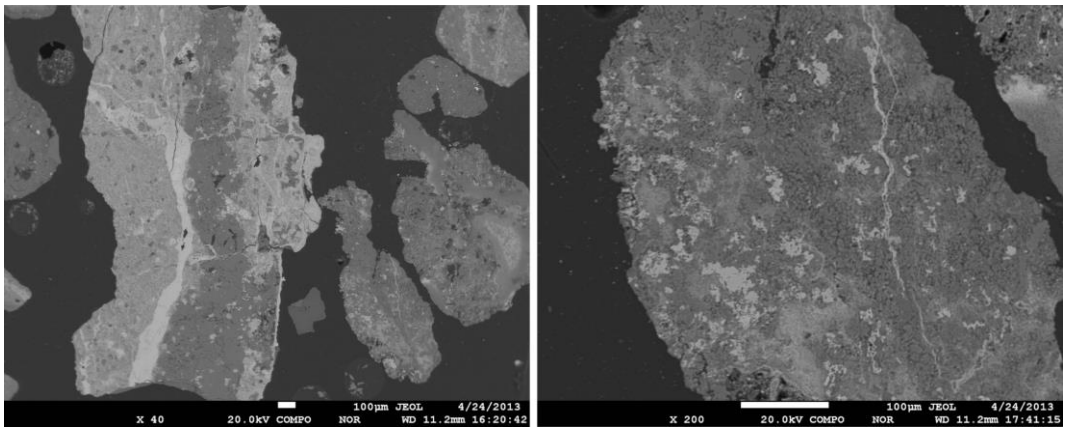


Figure 3. Backscattered Electron Image of Anatase

Kaolinite: molecular formula is $Al_4[Si_4O_{10}](OH)_8$, the content in ore is about 48%. It is the main gangue mineral, usually occurring as microscopic scales, mud and cryptocrystalline, and widely distributed in ores. Most of the kaolinites are disseminated to brown by iron, and the granularity is generally less than 0.004mm (Fig. 1d). Based on the analysis of electron probe, kaolinite contains 0.275%-0.426% of TiO2 and 0.01% of Sc_2O_3, which indicates that both Ti and Sc are common in this mineral, but the content of Sc is less than Ti.

4. Occurrence of Ti

The data of chemical analysis of ore samples collected from the studied area reveals that Ti mainly exists in the form of TiO_2, and the average content of TiO_2 is 4.0%.

According to the analysis of microscopic observation, X-ray phase, electron probe and single mineral chemistry, anatase (TiO_2) with grains smaller than 0.04mm usually occurs in the form of micro-fine inclusions in silicate and quartz. Multipoint electron probe of limonite shows that limonite may be the product of ilmenite alteration. The contents of Fe and Ti are negatively correlated, which proves part of Ti exists in the form of isomorphism in limonite. A small part of Ti exists in the form of independent mineral in anatase with granularity greater than 0.04mm.

TiO_2 is mainly in the form of micro-fine inclusions in silicate and quartz, and accounts for 77.38%. This part of the TiO_2 exists in the form of mud and fine anatase inclusions in gangue minerals, and is difficult to smelt. Even the particle size of grinded ore samples is smaller than 0.04mm for the isolation of single minerals, but there are still anatases in the gangue minerals. Ti is secondly in the form of isomorphism in limonite, which accounts for 18.97%. However, Ti in the form of independent mineral (TiO_2) in the anatase with granularity greater than 0.04mm only takes up 3.65%.

According to the above analysis, there are three kinds of occurrence of Ti in the ores: in the fine-grained independent anatase which is paragenesis or embedded with gangue minerals; in the form of anatase mineral wrapped in the silicate minerals and quartz; in the form of isomorphism in limonite. The occurrence of Ti suggests that the resource in the ores is extremely difficult to separate.

5. Discussion of Ore Beneficiability

According to the occurrence of Ti, it is determined that anatase ores are extremely difficult to process. The conventional mineral processing method (gravity, magnetic and flotation) cannot effectively enrich the anatase [12, 14]. However, the ore dressing process of "roasting-acid leaching -alkali leaching" can be applied to raw ores, and the selected ore grade of TiO_2 is 4.00%, which can obtain anatase with 42.32% TiO_2, recycle rate is 83.16%. Anatase with 42.32% TiO_2 can be sold as concentrates. Other elements dissolving out, e.g. Sc, Fe, Al and Si can be recycled. It can be received 99.9% of scandia product by extraction, and the leaching rate of Sc is 90%. Fe, Al and Si can be used to produce iron oxide red and by-product of polyalumicium silicate (PAS) coagulant [12]. According to the mineral processing test in Kunming University of Science and Technology, "roasting-acid leaching -alkali leaching" method works effectively for the extremely refractory ore, and obtains anatase with 42.32% TiO2, 99.9% of scandia product and iron oxide red and by-product of polyalumicium silicate (PAS) coagulant. Mineral resources without emission can be effectively utilized, and can get very good environmental benefits.

Application of anatase is extensive [13]. The high grade titanium dioxide (TiO2) is an important raw material for the production of coatings, plastics, ink, paper, chemical fiber, cosmetic, medicine, food and other industries[13,15]. Anatase with good photocatalytic properties [16], is better than rutile in the field of nano photocatalyst and is also applied to air pollution govern, degradation of organic matter in wastewater and car pigment, etc. [13]. The success of the experiment of the mineral processing of Shazi anatase deposit indicates that this ore can produce huge economic value to accelerate the construction of resource type city in southwestern Guizhou, to serve the economic construction of Guizhou Province, which has great social benefit and economic benefit.

6. Conclusions

From the data of above analysis, the following conclusions are drawn: (1) ore reserves of Shazi anatase deposit in Qinglong is 23060900t, resources quantity of TiO_2 is 1024800t; average grade of TiO_2 is 4.39%. (2) The titanium element in the anatase ore is mainly in the form of anatase inclusions with granularity less than 0.04mm in silicate and quartz minerals; secondly, it is in the form of isomorphism in limonite and a minority of

Ti exists in the form of independent mineral in the anatase with granularity greater than 0.04mm. (3) Ores are extremely refractory, as for the micro-fine anatase inclusions in silicate and quartz, even the particle size of grinded ore samples is smaller than 0.04mm for the isolation of single minerals, but there are still anatases in the gangue minerals. This part of anatase accounts for 77.38%. (4) According to the refractory characteristics, the ore dressing process of "roasting-acid leaching -alkali leaching" can obtain anatase containing 42.32% TiO_2 with recycle rate 83.16%. (5) The existing properties and recycling value of Fe, Sc, Al, Si and other beneficial elements in the anatase ore are still waiting for further work.

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