

Panzhuhua Titania Slag Transformation Dynamics

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Abstract—Titania slag is a high quality raw material containing titanium in the subsequent process of titanium pigment. The effects of cooling approaches of granulating, water cooling, and air cooling on chemical, phases, and acidolysis of Panzhuhua titania slag were investigated. Compared to the original slag which was prepared by the conventional processing route, the results show that the titania slag undergoes oxidation of Ti^{3+} during different cooling ways. The Ti_2O_3 content is 17.50% in the original slag, but it is 16.55% and 16.84% in water cooled and air-cooled slag, respectively. Especially, the Ti_2O_3 content in granulated slag is decreased about 27.6%. The content of Fe_2O_3 in granulated slag is approximately 2.86% also obviously higher than water (<0.5%) or air-cooled slag (<0.5%). Rutile in cooled titania slag was formed because of the oxidation of Ti^{3+} . The rutile phase without a noticeable change in water cooled and air-cooled slag after the titania slag was cooled, but increased significantly in the granulated slag. The rate of sulfuric acid acidolysis of cooled slag is less than the original slag. The rate of acidolysis is 90.61% and 92.46% to the water-cooled slag and air-cooled slag, respectively. However, the rate of acidolysis of the granulated slag is less than that of industry slag about 20%, only 74.72%.

Keywords—Cooling approaches, titania slag, granulating, sulfuric acid acidolysis,

I. INTRODUCTION

WITH rapid development of titanium industry chain, the high grade titania slag has become a superior quality raw material containing titanium in the following process of titania pigment [1], [2]. Titania slag is produced by carbothermic reduction of ilmenite in an electric arc furnace [3]. Titania slag of Panzhuhua typically contains about 8% FeO, 58% TiO_2 , and 14% Ti_2O_3 (with other impurities, such as SiO_2 , CaO, MgO, and Al_2O_3 , making up the balance) [4]. Panzhuhua titania slag is a typical high Ca (2%) and Mg (7%) slag which has a natural well sulfuric acid soluble property [5]. Therefore, Panzhuhua titania slag is mainly used in the sulfate process to produce white titanium dioxide pigment. The conventional processing route of titania slag is tapped into ingot moulds and usually takes five days to cool. However, the efficiency of current cooling approach of titania slag cannot meet the industrial production requirement due to the improvement of smelting technology of titania slag. Hence, a new cooling method of titania slag must be developed to increase the cooling efficiency.

In the conventional processing route, the liquid slag is cast into large blocks, which usually takes about five days to cool down before they can be crushed, milled to the final products [6]. The quality of titania slag can be remained stable using this processing route. Therefore, a few numbers of studies have reported on cooling of titania slag in the past decades. Bessinger et al. [7] and Kotze [8], [9] researched the granulation of titania slag using high-pressure water or compressed air, respectively. During

cooling, the high titania slags containing approximately 85% TiO_2 can decrepitate to a fine particulate material. Their results show that the disappearance of the M_3O_5 phase was linked to oxidation of the slag. From the Ti_2O_3 results, it is clear that some oxidation of the slag by water occurs, while chemical analyses of dry granulated slag indicated Ti_2O_3 content of less than 5%. They also concluded that the wet granulation of titania slag has the potential of successfully replacing the conventional block route for the treatment of titania slag. Bungu and Pistorius [6] concluded that water granulation is an attractive alternative sizing method since this avoids the long cooling times with large slag ingots and eliminates several crushing steps. But, a concern is that the granulated slag may react with oxygen of water during cooling processing.

Oxidation of titania slag can affect the chemical compositions and phases of titania slag, and further, it can affect the acidolysis of titania slag. Although a large number of studies have reported the phases of titania slag [10]-[15], the research on the acidolysis of titania slag is relatively rare. Wang et al. [16] reported the work on the sulfuric acid dissolution of the acid-soluble titanium slag. Their experimental results show that the acidolysis rate of titania slag was affected by the mass content of TiO_2 and rutile in titania slag. Lasheen et al. [17] investigated the effect of time, temperature, liquid/solid ratio, slag/ilmenite ratio, and acid concentration on the leach of titanium using concentrated sulfuric acid. The optimum conditions of titanium dioxide by the sulfuric acid process were determined. The acidolysis of titania slag which was treated by different cooling approaches is still less, especially for the Panzhuhua titania slag.

In this present work, the chemical components and phases of the cooled titania slag which was prepared different cooling approaches were studied. Sulfidation behaviour of cooled slag was studied in a laboratory equipment.

II. EXPERIMENTAL PROCEDURES

A. Raw Materials

The chemical composition of titania slag which was supplied by Panzhuhua Iron and Steel (Group) Co. is listed in Table I. The original titania slag was prepared by the conventional processing route (block-route slag). The X-ray diffraction patterns of titania slag showed that anatase and pseudobrookite were the principal minerals.

TABLE I
MAIN CHEMICAL COMPONENTS OF TITANIA SLAG /%

TiO ₂	Ti ₂ O ₃	TFe	FeO	CaO	SiO ₂	MgO	Al ₂ O ₃
75.81	17.50	6.40	7.49	1.60	5.25	7.24	2.57

B. Experimental Apparatus and Methods

1) Preparation of Cooling Titanium Slag

Cooling titania slag was prepared by different cooling approaches after melting of titania slag in an induction furnace. The cooling approaches of titania slag were granulated, water-cooled, and air-cooled. The schematic diagram of granulation device of titania slag is shown in Fig. 1. The molten slag from induction furnace was granulated with the granulated slag in the rotating turntable due to the centrifugal principle. The granulation machine was a laboratory scale made of graphite and stainless steel. The equipment is approximately 800 mm in diameter and 450 mm in high. Granulation was performed by graphite disc, which size is approximately 100 mm. The disc movement was controlled by adjusting the rotation speed. The rotation speed was set at 1000 rpm in each experiment. Individual granule particles produced from dry granulation were almost spherical, sometimes elliptical, and occasionally elongated and irregular. The surface morphology and particle size distribution of granulated slag are shown in Fig. 2 and Table II, respectively.

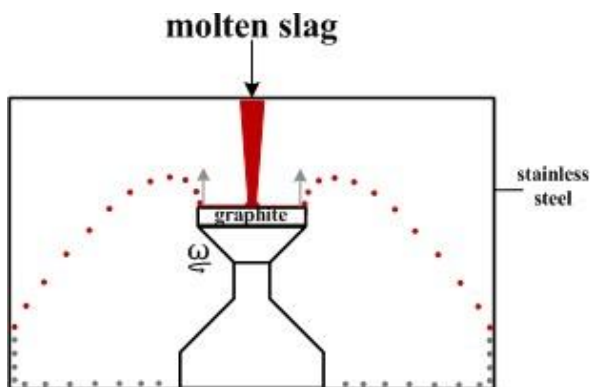
Fig. 1 Schematic diagram of granulation device of titania slag



Fig. 2 Particle morphology of granulated slag

TABLE II
PARTICLE SIZE DISTRIBUTION OF GRANULATED SLAG

Particle size	-0.42	+0.42~-0.5	+0.5~-0.88	+0.88~-1.7	+1.7~-3.35	+3.35
%	13.22	3.86	13.93	14.09	13.22	45.60



Molten titania slag was dumped in the cooling water to prepare the water-cooled slag. The water-cooled slag was dried at 393 K for 4h to remove the moisture. On the other hand, the molten slag was slowly cooled about 15h in the crucible to acquire the air-cooled slag.

After preparation, the chemical compositions, phases, and mineral compositions of all the cooled slag were then measured. The chemical composition was determined using wet chemical method. The phases of slags were characterized by X-ray diffraction (XRD, ZSXPrimus II, Japan) analysis using Co-K α radiation ($\lambda=1.789 \text{ \AA}$) at room temperature. A MLA mineral analyzer (MLA 650, USA) and a lithofacies and polarizing microscope (Olympus BX51, Japan) were employed to study the mineral compositions of titania slag.

2) Acidolysis of Cooled Titania Slag

The flow chart of acidolysis process of cooled slag is shown in Fig. 3. Before acidolysis, all the titania slag samples were

smashed to the particle size less than 45 microns (325 meshes). 200 g of cooled slag was mixed with 95.8% concentrated sulfuric acid according to 1:1.8 mass ratio in each experiment. The mixture was heated to induce the main reaction by electric heating jacker and then cured 2h at 458 K in a muffle furnace. The cured samples were added 400 ml water to obtain the slurry. The slurry was agitated at 338 K at 150 rpm in the thermostat water bath. At the end of each dissolution experiment, the slurry was filtrated and washed with distilled water to separate the titanium liquor and waste acidolysis sludge. The content of TiO₂ in titanium liquor and waste acidolysis sludge was determined using the chemical method, respectively. The ratio of acidolysis of cooled slag was defined as the following equation:

$$\omega = \frac{\text{TiO}_2 \text{ in titanium liquor}}{\text{TiO}_2 \text{ in titanium liquor} + \text{TiO}_2 \text{ in waste acidolysis sludge}} \times 100\% \quad (1)$$

TABLE III
CHEMICAL COMPONENTS OF THE COOLED TITANIA SLAG

Cooled slag	TiO ₂	Ti ₂ O ₃	TFe	Fe ₂ O ₃	CaO	SiO ₂	MgO	Al ₂ O ₃
Granulated slag/%	75.92	11.67	6.90	2.86	1.47	5.68	7.13	2.48
Water cooled slag/%	74.50	16.55	5.00	<0.50	1.56	5.37	7.54	2.45
Air cooled slag/%	74.71	16.84	5.00	<0.50	1.51	5.27	7.41	2.39

massive (or dense) particles occur. Meanwhile, some of the granules have been fused and sintered together. The granules consisted of a small amount of rutile, as identified by X-ray diffraction analyses. The rutile crystals can be clearly seen in Fig. 5, as well as the hollow nature of the particles.

Fig. 4 XRD Patterns of cooled slag and the original slag

Fig. 5 shows that some of the granules were entirely hollow, while porous particles were also common, and sometimes where ω is the ratio of acidolysis of cooled slags. M L and M S are the contents of TiO₂ in titanium liquor and waste acidolysis sludge, respectively.

approaches are given in Table III. Compared with the chemical composition of the original titania slag, the amount of Ti₂O₃ in cooled slag was decreased. The Ti₂O₃ content in granulated slag is less, and the reduced extent is about 27.6%. The decreased content of Ti₂O₃ was considered to increase the oxidation of Ti₂O₃ because the fine particles are exposed to air result in the Ti³⁺ is oxidized as Ti⁴⁺ during the granulate processing of titania slag. The large size particle is expected to cool more slowly than smaller particles because of their smaller specific area and larger thermal conduction resistance [19]. The Fe₂O₃ has the opposite trend with the Ti₂O₃. The oxidation is much more for granulated slag with some oxidation of the Fe²⁺ to Fe³⁺. Therefore, the titania slag of larger average particle size is less oxidized despite slower cooling. Table III also shows that titania slag would experience various degrees of oxidation during different cooling processing by compared Ti₂O₃ content. This result indicates that the slag contains a significant fraction of Ti₂O₃ (trivalent titanium) which is readily oxidized due to the reaction with oxygen during the cooling processing.

B. Phases of Cooled Slag

XRD results of cooled slag and original slag are shown in Fig. 4. Fig. 4 shows that the XRD spectra of the cooled slag detected both rutile and anatase in addition to (Fe Mg)_xTi_yO₅

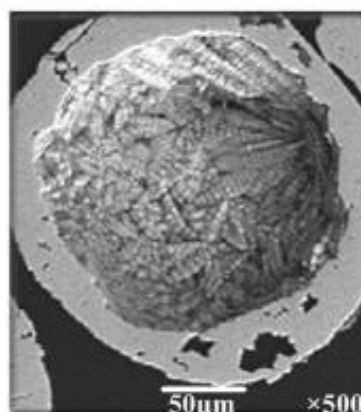


Fig. 5 Surface morphology of granulated slag (pseudobrookite) phase as indicated by the XRD pattern. However, the type of TiO₂ in the granulated slag is rutile, and the other one is anatase. It indicated that the rutile in the titania slag was formed because the oxidation of Ti³⁺.

The phases component of original slag or cooled slag at different cooling approaches is shown in Fig. 6. The hoary region is iron-anosovite, which clearly indicates that the shape of iron-anosovite has obvious difference under different cooling conditions. The white spots are metallic iron, which obviously means that most of metallic iron is discretely distributed in the contact with the anosovite solid solution and silicate phase. The dark grey area is the silicate phase, and the black region shows the pores. Figs. 6, (a), (b), and (d) are magnified 700 times, and in order to further clear observation, Fig. 6 (c) is magnified 2800 times. Fig. 6 shows that the surface of original slag is dense and without obvious crack. However, although the surface of cooled slag is also dense structure, a small amount of crack can be found in the surface of slag. The main mineral component of titania slag is iron-anosovite. The shape of iron-anosovite is the columnar collection of the original slags, the tabular in water cooled or air-cooled slag, and needle in granulated slag. Shapes of iron-anosovite in slag would be changed during the original slag cooling process. These results indicate that the original slag cooling treatment can reduce the crystalline grain size of the anosovite solid solution. The silicate phase in cooled titania slag was mainly distributed in the anosovite solid solution. Moreover, metallic iron was mostly distributed in the contact with the anosovite solid solution and silicate phase. Fig. 6 (d) shows that the silicate minerals distribution around the anosovite is less obvious. It indicated that titania slag cooling is helpful to separate

between anosovite solid solution and silicate phases. The metallic iron phase can be clearly observed in Figs. 6 (a), (b), (d) and without in Fig. 6 (c). This result suggests that the surface's metallic iron can likely be oxidized to metallic iron in the granulated slag because the higher particle surface area can result in more oxidation by contrast other cooled slag.

C. Ratio of Acidolysis

Panzhihua titania slag, which belongs to a typical high Ca and Mg titania slag and has a natural well sulfuric acid soluble property [5], is widely used in the titanium pigment of sulphuric acid method. The acidolysis ratio of the cooled or original slag is shown in Fig. 7. The ratio of acidolysis of original slag can reach 94.05%, higher than the other cooled slag. Moreover, the ratio of acidolysis of granulated slag was only 74.72%. The tapping temperature is about 1923 K during the processing of smelting titania slag. During the granulating cooling processing, such high temperature difference that some Ti_2O_3 was fast oxide to TiO_2 . Some anatase can be irreversibly translated to rutile when the temperature higher than 973 K; however, rutile TiO_2 is hardly soluble even in concentration sulfuric acid. The experimental results agree with the previous studies by the other researchers [18], [19]. Therefore, rutile content should be controlled under 5% to the acid-soluble titania slag. The cooling mode of air cooled slag is very similar with the original slag, and the rate of acidolysis of slag also has no significant differences. This suggests that rutile content in the titania slag can be efficiently

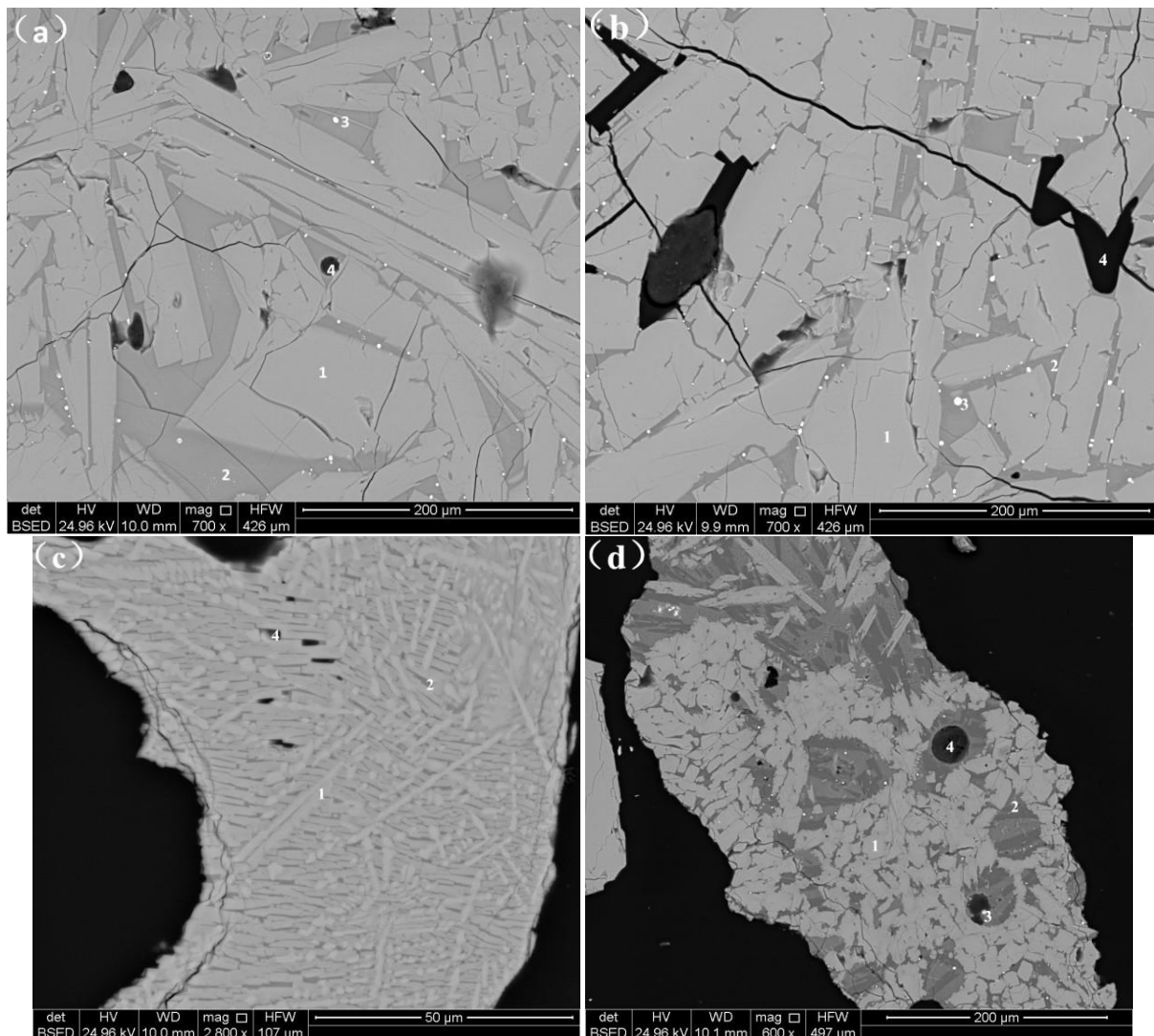


Fig. 6 Mineral micrograph of titania slag. (a), (b), (c), and (d) are water-cooled slag, air-cooled slag, granulated slag and industry slag, respectively; Numbers 1, 2, 3 and 4 are $M3O_5$ solid-solution phase, silicate phase, metallic iron and hole

controlled and improved the rate of acidolysis. Compared with the other cooled slag, the rate of acidolysis of granulated slag is the lowest. This result shows that the Ti_2O_3 content in granulated slag was easily oxidized during rapid cooling processing in air atmosphere. Moreover, the results of phases of titania slag indicate that the crystal of TiO_2 may be transformed during the cooling and oxide processing. Therefore, it controlled the cooling rate and improved the cooling environment of titania slag, which may be an effective method in order to increase the rate of acidolysis of granulated slag during granulating processing of titanium slag. However, taking the acidolysis rate of titania slag into account, the dry granulated slag may not be suitable for cooling titania slag, but water cooling treatment is relatively an attractive method to cool titania slag.

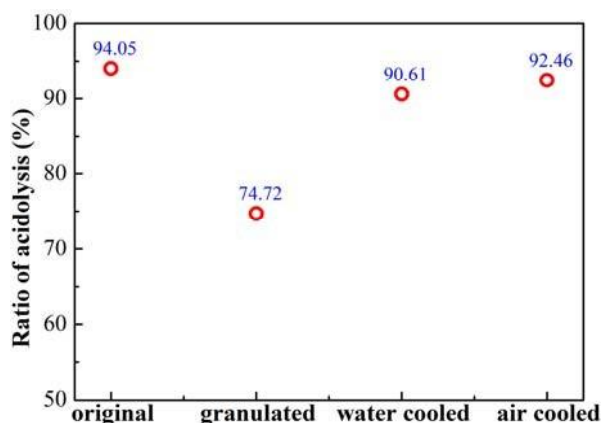


Fig. 7 Acidolysis ratio of cooled slag and the original slag

IV. CONCLUSIONS

This work studied the effect of cooling approaches on chemical compositions, phases, and acidolysis of titania slag. The conclusions can be summarized as following:

- (1) Titania slag undergoes oxidation of Ti^{3+} during cooling processing. The Ti_2O_3 content of all cooled slag was decreased in different degrees due to the different cooling approaches, especially in the granulated slag which reduced by about 27.6%.
- (2) XRD results show that the main phase of cooled slag and original slag is $(Fe\ Mg)_xTi_yO_5$ and TiO_2 . Type of TiO_2 is rutile in the granulated slag, and it is anatase in the other slag. The main mineral composition is iron-anosovite in cooled slag and original slag. The content of iron-anosovite in titania slag can be reduced by cooling treatment.
- (3) The acidolysis ratio of cooled slag is lower than the original slag, especially the acidolysis ratio of the granulated slag is only 74.72%, but original slag is 94.05%. Water cooling treatment may be relatively an attractive method to cool titania slag.

REFERENCES

- [1] S. Watson, D. Beydoun, J. Scott, and R. Amal. Preparation of nanosized crystalline TiO_2 particles at low temperature for photocatalysis. *Journal of Nanoparticle Research*. 2004, pp. 193-207.

- [2] S. Yang, Y. Liu, Y. Guo, J. Zhao. Preparation of rutile titania nanocrystals by liquid method at room temperature. *Materials Chemistry & Physics*. 2003, pp. 501-506.
- [3] D. Bessinger, J. M. A. Geldenhuys, P. C. Pistorius, A. Mulaba, and G. Hearne. The decrepitation of solidified high titania slags. *Journal of Non-Crystalline Solids*. 2001, pp. 132-142.
- [4] B. Song, X. W. Lv, J. Xu, H. J. Miao and K. X. Han. Effect of wet grinding on carbothermic reduction of ilmenite concentrate. *International Journal of Mineral processing*, 2015, pp. 101-106.
- [5] X. Wu, and J. Zhang. Geographical distribution and characteristics of titanium resources in chins. *Titanium Industry Progress*, 2006, pp. 8-12.
- [6] P. N. Bungu, and P. C. Pistorius. Mineralogy and initial chlorination of water granulated high titania slag. *Canadian Metallurgical Quarterly*. 2009, pp. 45-52.
- [7] D. Bessinger, P. Beukes, P. Glenwinke. Granulation of titania slag. The 6th International Heavy Minerals Conference 'Back to Basics', The Southern African Institute of Mining and Metallurgy, 2007, pp.159-162.
- [8] H. Kotze, P. C. Pistorius. A heat transfer model for high titania slag blocks. *The Journal of the Southern African Institute of Mining and Metallurgy*. 2007, pp.57-66.
- [9] H. Kotze. Investigation into the effect of cooling conditions on the particle size distribution of titania slag. University of Pretoria, 2007, pp. 90-95.
- [10] Y. R. Liu, J. L. Zhang, Z. J. Liu, and X. D. Xing. Phase transformation behavior of titanium during carbothermic reduction of titanomagnetite iron sand. *International Journal of Minerals, Metallurgy and Materials*. 2016, pp. 760-768.
- [11] T. Lei, J. R. Mi, L. Zhou, Y. H. Yang, and Y. L. Zhang. Study on Phase Compositions and Removal Impurities Mechanism of Electro-Titanium slag. *Chinese Journal Of Rare Metals*, 2007, pp. 93-97.
- [12] Y. H. Yang, T. Lei, J. R. Mi, L. Zhou. Studying on Phase Compositions and Formation Mechanism of Electro-Titanium slag. *Yunnan Metallurgy*, 2006, pp. 35-37.
- [13] F. C. Xu, Y. L. Liao, Y. Lei. Influence of modification on phase composition of titania slag. *Titanium Industry Progress*, 2011, pp. 21-24.
- [14] Y. J. Wang, S. M. Wen, and Q. C. Feng. Mineral phase reconstruction behavior of direct reduction and smelting titania slag at high temperature and slow cooling. *Rare Metals*. 2015, pp. 440-444.
- [15] W. Zhang. Selective separation of rutile phase in modified high titania slag. Northeastern University. 2010.
- [16] B. Wang, X. Z. Cheng, K. X. Han, X. H. Qin, and Y. Ma. Research of acidolysis performance of acid-soluble titania slag. *Iron Steel Vanadium Titanium*, 2003, pp. 39-45.
- [17] T. A. Lasheen, E. A. Saad, M. E. H. Shalabi, and W. M. Abo-Elhamd. New development in leaching of ilmenite ore and titania slag mixture using sulfate process. *Egyptian Journal of Pure and Applied Science*. 2015, pp. 18-21.
- [18] J. H. Guo, X. C. Shen, L. Y. Wu, W. J. Zheng. The accelerated crystal phase transition for rutile-titania. *Chinese Journal of Applied Chemistry*. 2003, pp. 647-650.
- [19] L. L. Sui, Y. C. Zhai, and L. H. Miao. Recovery of titania from high titania slag by roasting method using concentrated sulfuric acid. *Rare Metals*. 2015, pp. 895-900.