Preparation of Rutile Titanium Dioxide Pigment from Low-grade Titanium Slag pretreated by the NaOH Molten Salt Method

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Abstract: Low-grade titanium slag with a high accumulation of Mg, Al, Si, and the refractory structure of spinel, was sodiumized-oxidized to make it usable in the sulfate process for TiO₂ pigment production. In the sodiumized-oxidized process, the Ti₃O₅ and Mg₂SiO₄ transform into Na₂TiO₃ and Na₂MgSiO₄, respectively. From combined ICP-OES with XRD refinement of the molten NaOH intermediate, the ideal stoichiometric ratio of NaOH to slag was calculated to be 0.9:1. After acidolysis of the intermediate, the obtained TiOSO₄ solution, with Mg²⁺ and Al³⁺ impurities, was hydrolyzed to prepare metatitanic acid (H₂TiO₃) with a suitable particle size D(0.5) of 1.0–1.5 μm. The particle size D(0.5) of the hydrolyzed H₂TiO₃ decreased, while the concentration of Mg²⁺ and Al³⁺ increased. Finally, under optimal doping and calcination conditions, the rutile content of the prepared sample was 97.0%, and the achromic abilities of TCS and SCX were 1937 and 1.54, respectively.

Keywords: Pretreatment of low-grade titanium slag, NaOH molten salt method, Sulfate process, Hydrolysis with impurity, Rutile TiO₂ pigments

1. Introduction

Titanium dioxide (TiO₂) is one of the best known white pigments. It is widely used as filler for paint, plastic, paper, and cosmetics due to its high achromic ability, together with its chemical and heat stability [1]. The traditional commercial technologies for the manufacture of titanium dioxide are the sulfate and chloride processes. In the sulfate process, ilmenite

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(40–60% TiO_2) and titanium slag (70–80% TiO_2) are used as raw materials. In the chloride process, the raw materials used are rutile (natural or synthetic) and high-grade titanium slag (85–90% TiO_2) [2].

Panzhihua titanomagnetite minerals account for more than 90% of the titanium reserve in China [3]. At present, titanomagnetite concentrates are smelted in a blast furnace to produce cast iron and titanium slag. The titanium slag contains 22–25% TiO_2 existing as the perovskite structure (CaTiO_3) [4,5]. Due to the stability of the perovskite structure, the refinement of the titanium components is difficult [6]. Thus, in order to fully utilize the Panzhihua abundant titanium resources, the titanomagnetite concentrates were first reduced in a rotary hearth furnace (RHF) by direct reduction-electric furnace smelting, to produce cast iron and titanium slag. The titanium slag contains 42–45% TiO_2 existing as the active anosovite structure (Ti_3O_5 , FeTi_2O_5 , or MgTi_2O_5) [7,8]. However, plenty of impurities, such as Mg, Al, and Si, still exist in the titanium slag. Particularly, the high content of silicon (SiO_2 17–20 wt.%) prevents the acidolysis in TiO_2 production by the sulfate process.

Recently, Qi et al [8-11] proposed a NaOH molten salt decomposition process for the preparation of TiO_2 , to deal with the low grade titanium slag that is hard to use directly in the sulfate process. In this process, titanium slag (~75 wt.%) and high-grade titanium slag (~90 wt.%) were decomposed by NaOH molten salt, forming the intermediate product Na_2TiO_3 , with a NaCl-type crystal structure [12]. The obtained intermediate sample was washed with water to recycle the NaOH reaction medium and obtain the layered $\text{H}_{2-x}\text{Na}_x\text{TiO}_3$ intermediate. The obtained NaOH solution was recycled into the NaOH molten salt roasting process, after concentration and purification by the removal of Si, Al, and Mn. The NaOH molten salt decomposition process can be considered as a mineral activation process, making it suitable for use in the sulfate process for TiO_2 production.

Unlike the traditional sulfate process for TiO_2 production, the $\text{H}_{2-x}\text{Na}_x\text{TiO}_3$ intermediate can be easily converted into the TiOSO_4 solution (~240 g/L TiO_2 with < 10 g/L Fe^{2+}) at low-temperature and low-acidity in one step [13]. Hydrolysis of the titanyl sulfate solution to prepare the metatitanic acid (H_2TiO_3) is the essential step of the sulfate process, as the quality of the final TiO_2 pigment is directly affected by the properties of H_2TiO_3 . There are many research studies about the factors that affect the hydrolysis process, such as TiOSO_4

concentration, free H_2SO_4 , nuclei, stirrer speed, impurity, heating rate, etc. [14-19]. However, due to the high amount of impurities (especially Mg and Al) contained in the titanyl sulfate solution, low-grade titanium slag needs special consideration with respect to the effect of Mg and Al in the hydrolysis process.

After the calcination of H_2TiO_3 , the TiO_2 white pigment can be prepared. In order to improve the pigment performance of the TiO_2 white pigment products, the pigments are doped with additives such as K, P, and Zn salts, and rutile nuclei [11,20-23]. The K salt can improve the tinting strength and hiding power, and resist the sintering of titanium dioxide during calcination, but it has an inhibitory effect on the transition of TiO_2 from the anatase to the rutile phase. The Zn salt has the opposite properties of the K salt. For example, it can induce the anatase-to-rutile phase transition, and the sintering of titanium dioxide particles, at the same time. P compounds can improve whiteness and make the TiO_2 crystals grow into a regular shape. Meanwhile, the rutile nuclei are added with the aim to increase the transition of the rutile, and partially replace the addition of the Zn salt.

This study focuses on the mineralogical composition of titanium slag, the structural transformation in the alkali pretreatment process, the influence of Mg^{2+} and Al^{3+} impurities in the hydrolysis process, and the regulation of TiO_2 pigment quality.

2. Experimental and computational details

2.1. Experimental procedure

An alternative route for the production of TiO_2 white pigment by using high-silicon titanium slag was proposed, based on the NaOH molten salt decomposition process. A brief flow sheet of the novel process is shown in Fig. 1. The key steps are highlighted in yellow and discussed in this paper.

In this process, the titanium slag was first sodiumized and oxidized to invert it into activated titanium intermediate. The obtained intermediate sample was countercurrently washed with water to recycle the NaOH reaction medium. The washed solid was digested with 40% sulfuric acid at low temperature. To ensure high recovery of Ti, we employed three-level countercurrent washing after the acidolysis process. A titanyl sulfate solution with high impurity of Mg and Al was formed in the subsequent concentration/hydrolysis operation.

In the hydrolysis process, external-seeds were added to increase the hydrolysis rate and reduce the hydrolysis time. The precipitate H_2TiO_3 was then washed to remove soluble impurities and residual acid. Finally, the intermediate product was doped with K, P, Zn, and rutile nuclei, and calcined at the selected temperature to complete crystalline growth.

2.2. Experimental details

2.2.1. NaOH molten salt roasting process

The titanium slag used in this work was supported by Panzhihua iron and steel group (Sichuan, PR of China). The detailed chemical composition of the titanium slag was analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 5300DV, Perkin-Elmer, USA), as shown in Table 1. In order to detect the content of Ti_2O_3 , the titanium slag was first treated with 4.7 vol.% HCl to remove metallic iron, and then the solid residue was decomposed with 36 wt.% HCl in a homogeneous reactor at 130 °C. In the sulfate process the concentration of Ti(III) can be detected by $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2$ standard solution with NH_4SCN indicator. In this work, we used the same method to determine the concentration of Ti(III) and the content of TiO_2 and Ti_2O_3 .

Table 1. Chemical compositions of the titanium slag (wt.%)

Component	TiO_2	Ti_2O_3	MgO	Al_2O_3	SiO_2	CaO	MnO	$\sum\text{Fe}$
Content (wt.%)	31.13	12.56	14.36	17.55	17.77	4.49	0.9	1.24

The mineralogical analysis of the sample was investigated using X-ray diffraction (XRD, X'Pert PRO MPD, PANalytical, Netherlands) performed using Cu $K\alpha$ radiation ($\lambda = 1.5408 \text{ \AA}$). In order to obtain accurate crystalline information, we used the GSAS-expgui programs [24] to refine the XRD patterns. GSAS (General Structure Analysis System) [25] is a comprehensive system for the refinement of structural models to XRD data. The XRD analysis of the titanium slag (Fig. 2) indicates that the main titanium compositions are the anosovite structure (M_3O_5) and the spinel structure (M_3O_4), where the M_3O_4 or M_3O_5 is a solid solution with M sites occupied by Ti, Mg, Al, or Fe. In order to simplify the crystal structures

and to easily deal with the XRD refinement program, the structures of M_3O_5 and M_3O_4 are fixed as $MgTi_2O_5$ and $MgAl_2O_4$, respectively. The structures are shown in Table 2. All the atom sites in the unit cell have been obtained by ABINIT code (version 7.2.1) [26,27] with the GGA (PBE) pseudopotential of the Fritz-Haber-Institute (FHI) [28] provided on the web page of the ABINIT code at <http://www.abinit.org>. As the atom position is fixed, the values of R_w and R_{wp} (blank) can only be controlled at 5–12%. The mineralogical composition is shown in Fig. 2.

Table 2. Crystal structure optimized by ABINIT code

Chemical formula	Space group	Z	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	Optimized content
$MgTi_2O_5$	<i>Cmcm</i>	4	3.765	9.777	9.957	90	90	90	geometry
$MgAl_2O_4$	<i>Fd-3m</i>	8	8.117	8.117	8.117	90	90	90	geometry
Mg_2SiO_4	<i>Pnma</i>	4	4.775	10.191	5.976	90	90	90	geometry
Na_2MgSiO_4	<i>Pna21</i>	4	10.916	5.288	7.056	90	90	90	geometry
SiO_2	<i>P3121</i>	3	4.913	4.913	5.405	90	90	120	energy
Na_2O	<i>Fm-3m</i>	4	5.550	5.550	5.550	90	90	90	energy
Na_4SiO_4	<i>P-43m</i>	1	4.885	4.885	4.885	90	90	90	unit cell
Na_2SiO_3	<i>Cmc21</i>	4	10.480	6.070	4.820	90	90	90	geometry
MgO	<i>Fm-3m</i>	4	4.211	4.211	4.211	90	90	90	energy

Note: The crystal structure of Na_4SiO_4 that cannot be indexed from the inorganic crystal structure database (ICSD) is derived from the structure of Na_4CO_4 (ICSD #245406).

The titanium slag was dried, ground, and dry-sieved in order to prepare different narrow size fractions. The titanium slag used in this study was $< 74 \mu m$ (mass percent $> 80\%$). The experiments were performed with a muffle furnace and nickel crucibles. NaOH and titanium slag with a mass ratio of 1.1:1, was placed into the nickel crucibles, and heated in a muffle furnace at different temperatures for 2 h. The temperature of the muffle furnace was controlled using a programmable temperature controller.

The extent of the titanium conversion was calculated by dissolving the intermediate product in 4.7 vol. % HCl [29], since the unreacted titanium slag does not dissolve under such low acidity. The concentration of titanium in the filtrate was analyzed by ICP-OES.

2.2.2. Hydrolysis process

The typical composition of industrial titanyl sulfate ($TiOSO_4$) solution, taken from the sulfate process, was TiO_2 of 180–210 g/L, *F* value = (effective H_2SO_4)/ TiO_2 = 1.7–2.0,

$\text{Fe/TiO}_2 = 0.25\text{--}0.33$ (mass ratio), Ti^{3+} of about 2.0 g/L.

In this study, the titanium sulfate (TiOSO_4) solution, with a high content of Mg and Al, was obtained by dissolving the acid leaching solid with 40 wt.% H_2SO_4 at 60 °C. The composition is shown in Table 3. The elements of impurity were analyzed using ICP-OES. The concentrations of the total H_2SO_4 , free H_2SO_4 , and TiO_2 were determined by chemical titration.

The main components of the acid-insoluble substance were $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ colloid, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and the undecomposed spinel phase.

Table 3. Chemical compositions of the primary titanium sulfate solution (g/L)

Component	TH_2SO_4	FH_2SO_4	TiO_2	Na	Ca	Mg	Al	Si	Mn	Fe
TiOSO_4 solution (g/L)	208.3	190.1	92.3 /88.78	5.27	0.57	13.32	9.29	0.13	0.73	2.22

Note: TH_2SO_4 and FH_2SO_4 represent the total and free H_2SO_4 , respectively. The concentrations of TiO_2 were determined by chemical titration and ICP-OES analysis, respectively, and are divided by a slash.

In order to obtain an excellent white pigment property, it is important to prepare H_2TiO_3 in a suitable particle size. Thus, the concentration of TiOSO_4 , as one of the most important factors, was studied in this work. The TiOSO_4 solution was concentrated to 120, 150, 160, 170, 180, and 200 g/L, respectively. The titanyl sulfate solution was hydrolyzed at boiling temperature (105–107 °C) in a 500-mL four-necked round-bottomed flask at atmospheric pressure.

In order to investigate the effect of Mg and Al, $\text{Ti}(\text{SO}_4)_2$ with a certain amount of $\text{Al}_2(\text{SO}_4)_3$ and MgSO_4 were dissolved in water to simulate the real system. The simulated system was TiO_2 having a concentration of 180 g/L and an F value of 1.85 with concentrations of Mg and Al from 5 g/L to 30 g/L, respectively. Dilute H_2SO_4 solutions and NaOH were used to adjust the F value.

The particle size distribution was measured with a Mastersizer 2000 laser size analyzer (Malvern Instrument Ltd., UK) combined with a Hydro2000MU accessory.

2.2.3. Doping and calcination

The metatitanic acid (H_2TiO_3) cake was washed until most of the impurities were removed,

and then claimed at 950 °C, to obtain the titanium dioxide product. The chemical composition of the TiO₂ product, analyzed by X-ray fluorescence spectrometer (XRF, RIGAKU Simultix 12, Japan), is shown in Table 4. The product could be used as pigment after the doping treatment.

Table 4. The chemical composition of the titanium dioxide after calcination without dopant addition (wt.%).

TiO ₂	SO ₃	ZrO ₂	Al ₂ O ₃	SiO ₂	MgO	P ₂ O ₅	Fe ₂ O ₃	Na ₂ O	K ₂ O
99.35	0.314	0.171	0.055	0.045	0.042	0.012	0.0034	0.003	0.001

During the experiments, H₂TiO₃ suspension containing 30 wt.% of TiO₂ and the dopants (K₂O, P₂O₅, ZnO, and rutile nuclei) were introduced in the form of a solution into the H₂TiO₃ suspension. Potassium was doped as K₂SO₄, phosphate as H₃PO₄, and zinc as ZnCl₂. The rutile nuclei were obtained in the sulfate process in an industrial installation. The slurry obtained after thorough mixing (mechanical stirrer 500 min⁻¹ for 20 min) was filtered, and then inserted into a laboratory muffle furnace. After calcination, the obtained TiO₂ samples were milled in a power-driven agate mortar prior to powder characterization.

The mixture of pigment powder and standard black slurry was pressed into a film having a thickness of 250 μm. The tristimulus values of X, Y, and Z of the film were then measured by an integral ball spectrophotometer (SP60, X-Rite Corporation, USA), contrasting to that of the standard sample R258 (commercial titanium dioxide pigment produced by the sulfate process, Chongqing Titanium Industry Co. Ltd. of Pangang Group). The calculation methods of the reducing power index (TCS) and the blue phase index (SCX) are listed as follow:

$$TCS = TCS_{\text{standard}} + (Y - Y_{\text{standard}}) \times 100$$

$$SCX = SCX_{\text{standard}} + (X_{\text{standard}} - Z_{\text{standard}}) - (X - Z)$$

The mass fraction of rutile (W_R) in the samples was analyzed by Raman spectroscopy (Thermo Scientific DXR, Thermo Fisher, USA).

3. Results and Discussion

3.1. NaOH molten salt decomposition of the titanium slag

3.1.1. Effect of temperature and time

The effect of temperature on the titanium conversion was investigated at a temperature

range of 450–750 °C using a NaOH-to-slag mass ratio of 1.1:1. The results in Fig. 3 indicate that the temperature has significant influence on the titanium conversion. The titanium conversion ratio improved with increasing reaction temperatures, especially in the initial stage of the reaction. Temperatures between 550 and 700 °C had an insignificant effect on the conversion of titanium from titanium slag, and the titanium conversion ratio reached equilibrium within 60 min. When the roasting temperature reached 550 °C for 60 min, 92.2% titanium conversion was achieved. When the temperature increased to 750 °C, there was an expected increase in the conversion ratio and ~97% conversion was achieved. However, the product was caking at high-temperatures and needed the high acidity of H₂SO₄ to make it dissolve.

3.1.2. Phase transformation of the high-silicon titanium slag during the NaOH molten salt roasting process

The results show the presence of Na₂TiO₃, Na₂MgSiO₄, and MgAl₂O₄ peaks (Fig. 4). It can be considered that the titaniferous solid solutions of the anosovite-type (M₃O₅) and spinel-type structures (M₃O₄) are converted to NaCl-type Na₂TiO₃. Chen et al. reported the crystal transformation relationship of Ti₃O₅ and Na₂TiO₃ [30].

There is an overlap between the Na₂MgSiO₄ and NaAlO₂ peaks. Thus, to distinguish these two crystalline phases, the simulated XRD pattern is shown in the top left corner. As shown in Fig. 4, the main phases are Na₂TiO₃ (45.91%) and Na₂MgSiO₄ (28.46%) after the NaOH molten salt was pretreated.

In this paper, we focus on the investigation of the crystal transformation relationship of Mg₂SiO₄ and Na₂MgSiO₄. It is reported that the chemical reaction between Mg₂SiO₄ and Na₂MgSiO₄ can be described as follows [31]:

It is considered that Mg₂SiO₄ will invert into Na₄SiO₄ when NaOH is in great excess. However, the crystal structure of MgO does not exist in the XRD pattern. To explain the formation of the Na₂MgSiO₄ product without MgO being also formed, the energy change (ΔE) between is calculated by using the ABINIT code shown, as follows:

From the energy changes of these six chemical reaction equations, Eq. (3) and (8) seem to show more activity. It can be considered that in Eq. (3) the surface of quartz SiO_2 reacts with O^{2-} in a nucleophilic addition and a SiO_3^{2-} group is formed. Structurally, the crystal structure of Mg_2SiO_4 , with a *Pnma* space group, has two types of Mg^{2+} ions that are located at different sites in the unit cell. One is connected with the SiO_4 tetrahedron structure and exists in a layered $[\text{MgSiO}_4]^{2-}$ group, the other is inserted in the interlayer and has a high activate energy. Comparing with the $[\text{MgSiO}_4]^{2-}$ group from Mg_2SiO_4 , the crystal structure of $\text{Na}_2\text{MgSiO}_4$, with a space group *Pna21*, has a similar $[\text{MgSiO}_4]^{2-}$ group. We concluded that the activated Mg^{2+} ion exchanged by a Na^+ ion keeps the layered $[\text{MgSiO}_4]^{2-}$ structure at the low activation energy in Eq. (4). After the ion exchange reaction, the fresh Mg^{2+} and SiO_3^{2-} are combined with O^{2-} and the stable $[\text{MgSiO}_4]^{2-}$ structure is formed. Therefore, the existence of SiO_3^{2-} and O^{2-} inhibits the generation of MgO . This is consistent with the calculated results between Eq. (4) and (8).

3.1.3. The chemical equation of titanium slag with NaOH molten salt

The reaction of high-grade titanium slag (main component Ti_3O_5) with the alkali system yields Na_2TiO_3 and this can be described as follows, according to the high-grade titanium result [9]:

If 1 mol of Ti is fixed as 1 unit, the ICP-OES result of high-silicon titanium slag in Table 1 can be rewritten as shown in the second line in Table 5. The mol of Na is calculated with a NaOH and titanium slag mass ratio of 1.1:1. In the third line, the component of the raw material is obtained from the result of the XRD refinement, and the anosovite-type (M_3O_5) and spinel-type structures (M_3O_4) are simplified as MgTi_2O_5 and MgAl_2O_4 , respectively. Therefore, the contents of the titanium slag obtained by XRD are different from those

obtained by ICP-OES. In the fourth line, the component of the product is obtained from the result of the XRD refinement. Because the crystal structures of Na_2TiO_3 , $\text{Na}_2\text{MgSiO}_4$, and NaAlO_2 are not solid solutions, and the solid solution M_3O_4 (simplified as MgAl_2O_4) is only 4.64 wt.%, the components of the product obtained by XRD refinement are very close to the ICP-OES result. For example, the Si (0.525 units) and Mg (0.637 units) of the reactant (ICP-OES) are close to the Si (0.543 units) and Mg (0.645 units) of the product (XRD). By comparison with the content of Na, we conclude that the NaOH excess is 25.8%.

Table 5. The compositions of the titanium slag (molar ratio) obtained from ICP-OES and XRD refinement

Component (molar ratio)	Na	Ti(IV)	Ti(III)	Mg	Al	Si
Reactant (ICP+ chemical titration)	4.879	0.690	0.310	0.637	0.611	0.525
Titanium slag (XRD)	--	1	--	1.467	0.630	0.603
Product (XRD)	3.879	1	--	0.645	0.994	0.543

^a Note: The amount of Ti was set as 1 unit

According to the XRD and ICP results, the reaction of low-grade titanium should be described as follows:

From Eq. (10), Ti(III) is oxidized by O_2 and converted into Ti(IV). Abstract Eq. (11) is listed to obtain the content of Ti(III) that is about 32.8% of the component of Ti. This result is very close to the chemical titration result of 31.0%.

Based on the conclusion that the excess NaOH is about 25.8%, the NaOH-to-slag mass ratio of 0.9:1 should exactly meet the stoichiometric ratio. In order to reduce the addition of NaOH, mass ratios of 0.9:1, 1.0:1, and 1.1:1 were adopted to investigate the influence of NaOH-to-slag mass ratio on titanium conversion at 550 °C. The results in Fig. 4 show that the titanium conversion ratio improves with an increase in the NaOH-to-slag mass ratio. Therefore, excess sodium hydroxide was necessary to maintain the liquidity of the reactants and to ensure that sufficient reaction took place.

However, this result is quite different with titanium-enriched slag (~75 wt.%) and high-grade titanium slag (~90 wt.%). For these two kinds of slag, the titanium conversion ratio reached a minimum of 80% within 10 min at 550 °C [9,32], while in this work, the conversion ratio is only about 60%. We concluded that the high content of spinel-type M_3O_4 solid solution should be the main reason for this difference, since both the titanium-enriched slag and the high-grade titanium slag only have one mineral phase of anosovite. Wang et.al [10] considered that initially, the reaction is a chemical reaction controlled process, or a diffusion through the liquid boundary layer controlled process. As the reaction proceeds, it may be controlled by diffusion through the residue layer. In this system we concluded that the influence of the content of Ti(III) is a very important factor. Since the bond length of Ti(III)–O (2.0–2.2 Å) is longer than that of Ti(IV)–O (1.9–2.0 Å), it should be easily broken by O^{2-} to form new Ti–O ligands. Moreover, the influence of the content of M_3O_5 solid solution is another important factor, as M_3O_5 exhibits an anosovite structure that has an open-framework along the [0 0 1] direction. The O^{2-} anions can diffuse along the [0 0 1] direction. This is beneficial for this nucleophilic reaction. Thus, the reaction rate of M_3O_5 should be faster than that of the spinel-type M_3O_4 solid solution.

3.2. Hydrolysis with high impurity of Mg, Al

After concentrating the prime $TiOSO_4$ solution, the hydrolysis process was conducted at 150, 160, 170, 180, and 200 g/L concentrations of TiO_2 , and a selected F value of about 1.85. As expected, the average particle size of the meta-titanic acid samples decreased as the concentration of TiO_2 increased as shown in Fig. 6. It is well known that a higher concentration of TiO_2 with a higher acidity would inhibit the hydrolysis rate, decrease the initial hydrolysis nuclei number, and increase its radius. This would lead to a decrease in the second nucleation radius, thus eventually improving its pigment properties. According to the industrial sulfate process, a particle size of 1.384 μm for H_2TiO_3 , with a narrow particle size distribution, was beneficial to improve the pigment properties. For the experimental $TiOSO_4$ solution obtained from the titanium slag, the best concentration of TiO_2 was 180 g/L. Comparing this with the pure $Ti(SO_4)_2$ solution, the concentration of TiO_2 is required to be at least 230 g/L [33] to obtain a similar particle size. We consider that the Mg^{2+} and Al^{3+} ions

play an important role in the hydrolysis process.

Under the same TiO_2 F value and concentration, a series of TiOSO_4 solutions were prepared with different concentrations of Mg^{2+} and Al^{3+} . The particle sizes of H_2TiO_3 obtained by hydrolysis are shown in Fig. 7. Both the Mg^{2+} and Al^{3+} exhibit predicted effects on the particle size distribution of H_2TiO_3 . On increasing the concentration of Mg^{2+} , the particle size $D(0.5)$ of H_2TiO_3 is reduced from 6.059 μm for $\text{Mg}^{2+}=0$ to 0.993 μm for $\text{Mg}^{2+}=30$ g/L. Compared with the addition of Mg^{2+} , the addition of Al^{3+} had a similar result. We concluded that the positive charges (Mg^{2+} , Al^{3+} , and H^+) adsorbed on the surface, hinders the onset of coalescence and aggregation, resulting in smaller sizes of the H_2TiO_3 aggregates. Secondly, the addition of Mg and Al salts enhances the viscosity of the TiOSO_4 solution. This negatively affects the collision of the particles, resulting in smaller aggregates.

3.3. Doping and calcination

After doping and calcination of metatitanic acid, the uncoated pigments contain $\geq 98\%$ titanium dioxide. As shown in Table 4, the sample prepared in this work meets commercial requirements. It is clear that minor residues of Mg, Al, and Si existing in the product do not affect the pigment properties. We can prepare a suitable TiO_2 pigment by adding an appropriate doping agent. The dopant addition can be seen in Table 6. The TCS of sample 10 is about 1937 and is close to that of R258.

Due to the smaller microcrystal formation of H_2TiO_3 in this work, the sample is easier to sinter and requires further addition of K^+ . As shown in Table 6, the addition of K^+ (samples 1–3) and PO_4^{3-} (samples 4–6) significantly improved the achromic ability, but inhibited the transition from anatase to rutile. In order to improve the conversion of rutile, both the Zn^{2+} and rutile nuclei were added into the system. As shown in Table 6, the addition of Zn^{2+} seems to have a more remarkable effect (samples 1–3 compared with samples 10–12) than that of rutile nuclei.

The content of the rutile and the sample size distribution can strongly affect the TCS. It is well-known that the TCS of commercial rutile and anatase TiO_2 is about 1700 and 1250, respectively. Therefore, the rutile content plays the most important role in pigment properties. Another important factor is the particle size distribution of TiO_2 . The optimum particle size of

TiO₂ pigment is between 0.2–0.3 μm (half of the visible wavelength). Unfortunately, it is very difficult to control such a small particle size at the rutile transition temperature. Thus, the content of rutile should be controlled between 96.3 to 97.1 wt.% to obtain optimal pigment properties.

Table 6. Dopant addition and pigment properties for TiO₂

sample	Dopant addition (wt.%)				Temperature/°C	Time/min	Achromic ability index		
	K ₂ O	P ₂ O ₅	ZnO	Rutile nuclei			Rutile/wt. %	TCS	SCX
1	0.5	0.1	0.15	5	890	120	99.3	1760	0.15
2	0.6	0.1	0.15	5	890	120	97.3	1770	0.51
3	0.7	0.1	0.15	5	890	120	96.35	1821	0.91
4	0.6	0.1	--	6	930	30	100.00	1706	0.42
5	0.6	0.15	--	6	930	30	98.88	1718	0.39
6	0.6	0.2	--	6	930	30	94.49	1735	1.14
7	0.5	0.15	--	6	900	90	99.07	1751	1.05
8	0.6	0.15	--	6	900	90	97.44	1777	0.98
9	0.7	0.15	--	6	900	90	96.89	1802	0.95
10	0.5	0.15	0.1	6.5	900	60	97.07	1937	1.54
11	0.6	0.15	0.1	6.5	900	60	96.00	1807	1.20
12	0.7	0.15	0.1	6.5	900	60	94.49	1725	1.25
R258							97.22	1940	4.20

Table 7 gives the chemical composition of sample 10. This exhibits the best pigment properties. Before addition of K, P, and Zn, Fe impurities need to be removed from the mixed slurry of H₂TiO₃ and rutile nuclei. Therefore, the mixed slurry is washed using 10% H₂SO₄ and Ti(III) solution. As shown in Table 7, the main impurities in sample 10 were ZrO₂, SiO₂, and SO₃, while the Mg, Al, and Fe impurities (shown in Table 4) were completely removed. The dopant contents K₂O, P₂O₅, and ZnO were 0.185%, 0.160%, and 0.03%, respectively.

Table 7. The chemical composition of the sample 10 (wt.%).

TiO ₂	ZrO ₂	K ₂ O	P ₂ O ₅	SO ₃	SiO ₂	ZnO	Na ₂ O
99.29	0.186	0.185	0.160	0.091	0.058	0.030	0.005

4. Conclusion

Based on the NaOH pretreatment of titanium slag, acidolysis of pretreated low-grade titanium slag, hydrolysis of TiOSO₄ solution, and doping and calcination of meta-titanic acid, rutile TiO₂ white pigment with good pigment properties was prepared from low-grade

titanium slag.

In the NaOH molten salt pretreatment process, using a temperature of 550 °C, an alkali-to-titanium slag ratio of 1.1:1, and a reaction time of 90 min, a titanium conversion ratio > 92.2% was achieved, and the main phase of Ti_3O_5 and Mg_2SiO_4 transformed to Na_2TiO_3 and $\text{Na}_2\text{MgSiO}_4$, respectively. By using DFT calculations and XRD refinement, the crystal structures and the mass content of the indexed mineral phases from XRD patterns were optimized. Based on these results, and the mass content of elements from ICP-OES, the chemical equation of titanium slag with NaOH molten salt could be described as follows:

$$0.829 \text{ Mg}_x\text{Al}_y\text{Ti}_{3-x-y}\text{O}_5 (\text{anosovite}) + 0.520 \text{ Mg}_m\text{Al}_n\text{Ti}_{3-m-n}\text{O}_4 (\text{spinel}) + 0.541 \text{ Mg}_2\text{SiO}_4 + 0.459 \text{ SiO}_2 + 7.138 \text{ NaOH} + 0.151 \text{ O}_2 (\text{g}) \rightarrow 1.840 \text{ Na}_2\text{TiO}_3 + \text{Na}_2\text{MgSiO}_4 + 1.457 \text{ NaAlO}_2 + 0.186 \text{ Mg}_i\text{Al}_j\text{Ti}_{3-i-j}\text{O}_4 (\text{spinel}) + 3.569 \text{ H}_2\text{O} (\text{g})$$

In the hydrolysis process, H_2TiO_3 was prepared through the selected condition of $C_{\text{TiO}_2}=180 \text{ g/L}$ with a high content of Mg^{2+} and Al^{3+} . The increase in Mg^{2+} and Al^{3+} ions in the titanyl sulfate solution could clearly reduce the particle size of H_2TiO_3 . It was very beneficial for realizing the hydrolysis with unenriched titanyl sulfate solution.

In the doping and calcination processes, the TiO_2 rutile white pigment was prepared by doping K_2O (0.5 wt.%), P_2O_5 (0.15 wt.%), ZnO (0.1 wt.%), and rutile nuclei (6.5 wt.%), followed by calcination under 900 °C for 60 min. With this optimization of the preparation conditions, a TCS of 1937 and an SCX of 1.54 approached the commercial pigment standards of R258. The anatase-rutile phase transformation was enhanced by the addition of rutile nuclei and Zn, but inhibited by the addition of K and P. A 96.3–97.1% rutile content of TiO_2 produced the best pigment properties.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7a

Figure 7b