Desilication of Highly Acidic Titanyl Chloride Solution for the Production of High-Purity Titania Pigment from a Spent Selective Catalytic Reduction Catalyst

Gyeonghye Moon^{1,4}, Yeon-Chul Cho^{1,2}, Jin-Young Lee^{1,3} and Jungshin Kang^{1,3,*}

¹Strategic Minerals Utilization Research Department, Korea Institute of Geoscience and Mineral Resources, 124 Gwahak-ro Yuseong-gu, Daejeon 34132, Korea

²Department of Advanced Materials Science and Engineering, Daejin University, 1007 Hoguk-ro, Pocheon-si, Gyeonggi-do 11159, Korea

³Department of Resources Recycling, Korea University of Science and Technology, 217 Gajeong-ro Yuseong-gu, Daejeon 34113, Korea

⁴HANNAE For T CO., LTD, 156 Munpyeongdong-ro, 48 Beon-gil, Daedeok-gu, Daejeon 34301, Korea

An effective desilication method for a titanyl chloride (TiOCl_2) solution obtained by dissolving sodium titanate using concentrated hydrochloric acid was investigated in order to increase the purity of titania pigment and the productivity of the process. When the TiOCl_2 solution obtained by HCl leaching was used without desilication, clogging of the filtration system or precipitation of silica occurs. To overcome these disadvantages using a simple and efficient desilication method, the acidity, preservation temperature, and time elapsed after the preservation of TiOCl_2 solution were controlled. In the experiments, TiOCl_2 solutions produced using 5–7 M HCl solution were preserved at 274–313 K for 5 days. When the acidity, preservation temperature, and time elapsed after preservation were increased, the removal efficiency of silica increased. The conditions for the concentration of silica below 1 mg/L and the removal of silica by gelation were determined. When the purified TiOCl_2 solution was hydrolyzed at 363 K, titanium dioxide with a purity of 99.6–99.9% was obtained. Therefore, the results of this study demonstrated a straightforward and effective desilication method for highly acidic TiOCl_2 solution. [doi:10.2320/matertrans.M2019045]

(Received February 19, 2019; Accepted April 2, 2019; Published May 25, 2019)

Keywords: selective catalytic reduction (SCR) catalyst, titania pigment, removal of silicon, desilication

1. Introduction

Pigments can change the color of a material, for example, by coating. Titania is widely used as a white pigment because it has superior properties such as high opaqueness due to its high refractive index, high brightness, chemical stability, and nontoxicity.¹⁾ Owing to its excellent properties, titania is mainly used for coatings, polymers, and paper.

Titania is commercially produced by the sulfate or chloride process. The sulfate process uses low-grade titanium (Ti) ore or titania slag as a feedstock. Digestion of the feedstock is conducted using 80–98% sulfuric acid (H_2SO_4) at 443–493 K.²⁾ As a result, titanium (Ti) and iron (Fe) are transformed to titanyl sulfate (TiOSO_4) and iron sulfate (FeSO_4), respectively. FeSO_4 is removed from the leach liquor through crystallization by decreasing the temperature to 283–303 K.^{3,4)} Afterward, hydrolysis of the TiOSO_4 solution and calcination are carried out to produce the titania pigment. The technological difficulty is not high and the capital cost is low.⁵⁾ In addition, low-grade Ti ore can be used as feedstock. However, large amounts of FeSO_4 waste and acid waste solution are generated.^{5,6)} Furthermore, the quality of titania pigment, such as particle size and impurities, is difficult to control.⁷⁾

In the chloride process, high-grade titanium dioxide (TiO_2) with a purity of above 95% is used as feedstock in order to reduce the chlorine loss and prevent the clogging of pipes in carbo-chlorination step.⁸⁾ The high-grade TiO_2 is chlorinated using chlorine (Cl_2) gas in the presence of carbon at 1273 K to produce crude titanium tetrachloride (TiCl_4).⁹⁾ The high-purity TiCl_4 obtained by distillation is oxidized to produce high-purity TiO_2 under an oxidative atmosphere at 1173–1873 K.^{2,10)} The chloride process is a semi-continuous

process, and the particle size and the impurities affecting the whiteness of the titania pigment are easy to control.⁷⁾ However, the use of Cl_2 gas has safety and environmental issues.¹¹⁾ In addition, there are few effective methods for recycling the chloride waste produced, although the amount of chloride waste is not large because of the use of high-grade TiO_2 .

Owing to the disadvantages of the current titania pigment production processes, several hydrometallurgical processes have been investigated.^{3,4,12,13)} One promising method involves a combination of alkaline roasting of titania slag, water leaching, hydrochloric acid (HCl) leaching, solvent extraction, hydrolysis, and calcination.¹³⁾ During HCl leaching in this process, Ti in sodium titanate, which is obtained after roasting and water leaching, is dissolved and siliceous components in the feed are formed as monosilicic acid ($\text{Si}(\text{OH})_4$) at initial and particles after polymerization of $\text{Si}(\text{OH})_4$.¹⁴⁾ In addition, even after filtration, the silica remains in the TiOCl_2 solution depending on the conditions of the HCl leaching and the subsequent treatment of the solution. The remaining silica in the TiOCl_2 solution tends to co-precipitate with TiO_2 during hydrolysis.¹⁴⁾ As a result, the purity of the titania pigment produced is decreased.

The silica in the TiOCl_2 solution also decreases the productivity of the process owing to filtration problems by the authors' preliminary study. Figure 1 shows the general theory of polymerization of silica.¹⁵⁾ The monosilicic acid condenses and forms cyclic oligomers.^{14,15)} The nanosized particles grown by the polymerization of cyclic oligomers eventually aggregate into 3-dimensional gel networks when the pH of the solution is low.^{15,16)} In addition, it was reported that the $\text{Si}(\text{OH})_4$ in the 2–8 M HCl solution is polymerized to form primary particles of diameter approximately 5 nm.¹⁷⁾ Then, these primary particles flocculate. During the growth of $\text{Si}(\text{OH})_4$ in the acidic solution, silicic acid and/or

*Corresponding author, E-mail: jskang@kigam.re.kr, jskang@ust.ac.kr

Fig. 1 Polymerization behavior of silica in basic or acid solution.¹⁵⁾

nanoprecipitates, with sizes are larger than the filtration limit of $0.20\text{ }\mu\text{m}$, block the filtration of the TiOCl_2 solution. Therefore, silica in the TiOCl_2 solution must be removed before the hydrolysis in order to increase the purity of titania pigment and the productivity of the process.

A few studies have been conducted for understanding the mechanism and the effect of processing variables for the precipitation of silicon (Si) in a highly acidic solution.^{14,17)} Gorrepati reported that polymerization and particle flocculation increased when the concentration of the HCl solution was increased in 2–8 M HCl solution.¹⁷⁾ In addition, the effects of salts such as AlCl_3 , CaCl_2 , MgCl_2 , and NaCl on the particle formation and growth rate were evaluated. The existence of these salts increased particle formation and growth rate. Lefler also reported the effects of acid concentration, temperature, and selected ionic species on the behavior of Si in 1–8 M HCl solution.¹⁴⁾ In addition, silica-gel was used as a seed for the adsorption of Si in the TiOCl_2 solution, and the concentration of Si decreased to $<20\text{ mg/L}$. Based on these results, it can be summarized that the important variables for the removal of Si in an acidic solution are acid concentration, temperature, and ionic species in the solution.

Figure 2 shows the process flowchart for the production of high-purity titania pigment from a spent selective catalytic reduction (SCR) catalyst investigated in the Korea Institute of Geoscience and Mineral Resources (KIGAM). The spent SCR catalyst reacts with sodium carbonate (Na_2CO_3) at 1273 K. In the water leaching, tungsten (W) and vanadium (V) in the soda-melted catalyst dissolve in water, and sodium titanate is obtained as a residue. Afterward, sodium titanate was dissolved using a concentrated HCl solution to produce the TiOCl_2 solution. However, difficulty in the filtration of the TiOCl_2 solution or/and the decrease of titania pigment purity obtained after hydrolysis were occurred owing to the remaining silica in the TiOCl_2 solution by the author's preliminary study.

Fig. 2 Flowchart of titania pigment production process, as investigated in the Korea Institute of Geoscience and Mineral Resources.

In this study, the influence of the preservation temperature of the TiOCl_2 solution, acidity of the HCl solution used, and the elapsed time after the preservation of the TiOCl_2 solution on the removal of silica was investigated in order to increase the purity of the titania pigment and the productivity of the process. The removal of silica from the TiOCl_2 solution obtained by HCl leaching of the soda-melted spent SCR catalyst has not been reported in the past. In addition, the influence of elapsed time on the silica behavior in the TiOCl_2 solution after HCl leaching has not been investigated. Therefore, the results of this study can be utilized when the practical process employs a combination of alkaline roasting, water leaching, HCl leaching, hydrolysis, and calcination.

2. Experimental

2.1 Preparation of titanyl chloride solution feed for the removal of silica

Table 1 lists the composition of the spent SCR catalyst, the residues obtained after soda-melting of the spent catalyst, and the residues obtained after deionized (DI) water leaching. The feedstock of the soda-melting reactions was the spent SCR

Table 1 Analytical results of the spent SCR catalyst, the residues obtained after soda-melting of the SCR catalyst, and the residues obtained after DI water leaching of the soda-melted SCR catalyst.

	Concentration of element i , C_i (mass%) ^a							
	TiO ₂	WO ₃	V ₂ O ₅	Al ₂ O ₃	Fe ₂ O ₃	CaO	SiO ₂	Na ₂ O
Feed (SCR catalyst)	67.2	7.49	3.23	1.59	0.33	1.80	7.15	N.A
Residues after soda-melting	34.3	4.35	1.88	1.23	0.36	0.77	4.71	39.3
Residues after DI water leaching	60.4	0.06	0.03	1.68	0.63	1.41	3.36	19.0

a: Determined by ICP-OES analysis except SiO₂. SiO₂ was analyzed by wet analysis (gravimetric analysis). N.A: Not Analyzed.

catalyst installed in a combined heat and power plant in South Korea. The dust inside the catalyst was blown out before pulverization.

The spent SCR catalyst was reacted with Na₂CO₃ (purity = 99.0%) at 1273 K for 1 h using a crucible made of Inconel 600 under atmospheric conditions. The weight ratio of Na₂CO₃ to the spent SCR catalyst was 1.2, and during the reactions, fused salt was stirred using an impeller, as shown in Fig. 3.

The soda-melted spent SCR catalyst was pulverized and particles in the range of under 75 μ m were leached using DI water in a polyethylene crucible at room temperature (297 ± 2 K) for 1 h under 20% solid/liquid (S/L) ratio (w/v , weight of feed (g) $\times$ 100/volume of solution (ml)). The solution was stirred at 500 rpm. After the leaching was complete, the leach liquor was settled for 1 h, and filtered (pore size: 0.2 μ m). Subsequently, washing of the residue using DI water with stirring at 300 rpm for 10 min., sonication for 20 min., and centrifugation with 4000 rpm for 10 min. (model No.: Combi 408, Hanil Science Industrial Co., Ltd.) were conducted four times. After the final centrifugation was carried out, the residues obtained were dried at 378 K for 24 h.

Fig. 3 Photograph of the electric furnace used for the soda-melting of the spent SCR catalyst.

HCl leaching of the residues obtained after water leaching was conducted using a double-jacketed reactor, as shown in Fig. 4. The residues in a range of under 105 μ m were dissolved in 5, 6, and 7 M HCl solutions at 333 K for 3 h under 10% S/L ratio (w/v). The solution was stirred at

Fig. 4 (a) Schematic and (b) photograph of the experimental apparatus used for HCl leaching.

300 rpm. The leaching temperature was controlled using a bath circulator (model No.: CW3-10, JEIO TECH Co., Ltd.). To prevent the evaporation of the contents in the reactor, a condenser was used. When the HCl leaching was complete, the leach liquor was placed in a polyethylene bottle without solid/liquid separation. Subsequently and immediately, the whole liquor was shaken and placed in the three polyethylene bottles uniformly.

2.2 Removal of silica from the titanyl chloride solution

Desilication from the TiOCl_2 solution prepared by HCl leaching was conducted at three different temperatures. Each TiOCl_2 solution in the polyethylene bottle was placed in a water bath (model No.: BS-21, JEIO TECH Co., Ltd.) set at 313 K, a refrigerator set at 274 K, and a fume hood at room temperature (297 ± 2 K) without stirring for 5 days. During the desilication, 2 ml of the solution was taken from the bottles at every 24 h, following which the sample was filtered using a syringe filter unit (pore size: $0.20 \mu\text{m}$, ADVANTEC®) for the analysis. After 5 days, the TiOCl_2 solution in the bottle was centrifuged at 3500 rpm for 15 min to separate the liquid from the leach liquor, and the liquid was filtered (pore size: $0.20 \mu\text{m}$).

2.3 Hydrolysis of the purified titanyl chloride solution

The purified TiOCl_2 solution obtained after desilication was hydrolyzed at 363 K for 3 h using a double-jacketed reactor. Figure 5 shows the schematic of the experimental apparatus used for hydrolysis. The solution was stirred at 300 rpm using a magnetic bar. The temperature was controlled using a bath circulator, and a condenser was used to prevent the evaporation of the contents in the reactor. After the reactions were completed, the contents of the reactor were filtered (pore size: $0.20 \mu\text{m}$). In addition, the residues obtained after the hydrolysis were rinsed thrice using 5 M HCl solution at room temperature for 5 min, and five times using DI water for 5 min. Afterward, the residues were dried at 378 K. The dried residues were calcined at 973 K for 1 h using a muffle furnace.

2.4 Analysis

The concentration of the elements in the samples was analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES: Perkin Elmer, Optima 5300DV). The crystalline phases of the residues obtained were identified by X-ray diffraction (XRD: Rigaku, SmartLab, Cu-K α radiation). In addition, the composition and surface of the samples were analyzed using field emission scanning

Fig. 5 Schematic of the experimental apparatus used for hydrolysis.

electron microscopy/energy dispersive X-ray spectroscopy (FE-SEM/EDS: Merlin Compact, Carl Zeiss AG/AZTEC, OXFORD INSTRUMENTS).

3. Results and Discussion

3.1 Salts present in the titanyl chloride solution obtained after HCl leaching

Table 2 shows the concentration of elements in the TiOCl_2 solution feed obtained after HCl leaching. As shown in Table 2, the major elements dissolved in the TiOCl_2 solution are Ti and sodium (Na) because the residue obtained after water leaching was sodium titanate. Besides Ti and Na, aluminum (Al), Fe, and calcium (Ca) are also dissolved by the HCl leaching.

Gorrepati reported that the particle formation and growth rate of silica increased when salts were present in the HCl solution.¹⁷⁾ When 1 M of salt was dissolved in 4 M HCl solution, the influence on the polymerization of silica according to each type of salt was as follows: $\text{AlCl}_3 > \text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl}$. These results show that ionic strength by salts of the solution affects flocculation rate.¹⁷⁾ Unfortunately, the influence of Ti in the solution on the polymerization of Si was not reported by Gorrepati.

Table 2 Concentration of elements in the titanyl chloride solution feed obtained after HCl leaching for the removal of silica.

Molarity of HCl solution used for HCl leaching (mol/L)	Concentration of element <i>i</i> , C_i (mg/L) ^a						
	Ti	W	V	Al	Fe	Ca	Na
5	28733	26	13	671	382	291	15200
6	28733	27	12	664	383	302	14767
7	29200	28	13	665	363	309	10433

a: Determined by ICP-OES analysis.

Average value of the concentration of the elements in the titanyl chloride solution contained in three bottles.

The influence of the acidity of the HCl solution on the polymerization of silica was also examined.^{14,17)} The flocculation rate of silica was increased by two orders of magnitude when the molarity of HCl solution was increased from 2 to 8 M.¹⁷⁾ These results indicate that the increase of molarity of the HCl solution can be the dominant factor for the polymerization of silica when the concentration difference of ionic species present among HCl solutions is not large.

As shown in Table 2, the concentration of Al, Fe, and Ca in the three TiOCl_2 solutions is significantly lower than that of Ti and Na. In addition, the concentration difference of Al, Fe, Ca, and Ti among the three TiOCl_2 solutions is small. Meanwhile, the concentration of Na in the TiOCl_2 solutions using 5 and 6 M HCl solutions was higher than that of Na in the TiOCl_2 solution using 7 M HCl solution by approximately 4300–4750 mg/L. The solubility of NaCl in the HCl solution decreases when the molarity of the HCl solution is increased.¹⁸⁾ As a result, the concentration of Na in the TiOCl_2 solution using 7 M HCl solution was lower than that in the other two solutions. However, the influence of the concentration difference of Na in the TiOCl_2 solutions on the polymerization of silica is expected to be limited by comparison with the influence of the molarity of HCl solution on the polymerization of silica. This is because the concentration difference of HCl solution among three TiOCl_2 solutions is significantly larger than the concentration difference of Na among the TiOCl_2 solutions. Therefore, it is expected that the silica in the TiOCl_2 solution prepared using 7 M HCl solution better promotes aggregation than the silica in the TiOCl_2 solution prepared using 5 or 6 M HCl solution.

3.2 Influence of acidity of HCl solution, preservation temperature, and time elapsed after preservation for the removal of silica

Figure 6 shows the influence of preservation temperature and acidity of the HCl solution used on the concentration change of silica in liquor as days elapsed after the HCl leaching. As shown in Fig. 6(a), there is no concentration change of silica in the liquor prepared using 5 M HCl solution when the TiOCl_2 solution is preserved at 274–297 K. However, when the TiOCl_2 solution is preserved at 313 K, the concentration of silica in the liquor dramatically decreases after 3 days, and the concentration of silica is below 1 mg/L after 5 days.

In addition, when the TiOCl_2 solution prepared using 6 M HCl solution was used, the concentration of silica did not change when the solution was preserved at 274 K. However, the concentration of silica was below 1 mg/L after 3 and 2 days had elapsed when the solution was preserved at 297 K and 313 K, respectively. Furthermore, when the sodium titanate was dissolved using 7 M HCl solution and the TiOCl_2 solution was preserved at 274–313 K, the concentration of silica was below 1 mg/L after 1 day had elapsed.

These results indicate that the removal efficiency of silica in the TiOCl_2 solution prepared using 5–7 M HCl solution by dissolving sodium titanate with 10% S/L ratio increased when the preservation temperature was increased in a range of 274–313 K. It is worth noting that the concentration of silica in the TiOCl_2 solution below 1 mg/L implies that the growth of silica has occurred, and that the size of particles,

Fig. 6 Influence of the preservation temperature on the concentration change of Si in liquor as days elapsed when (a) 5 M, (b) 6 M, and (c) 7 M HCl solution were used.

nanoprecipitates, and/or gel of the generated silica is larger than the pore size of the filter unit (0.2 μm).

As shown in Fig. 6, the initial concentration of silica in the TiOCl_2 solution prepared using 7 M HCl solution is much lower than that of silica in the TiOCl_2 solution prepared using 5–6 M HCl solution. These results show that the size of majority of silica in the TiOCl_2 solution produced just after the HCl leaching was larger than the pore size of the filter

Table 3 Concentration of Si (mg/L) in the titanyl chloride solutions when 5 days had elapsed after the HCl leaching.

Molarity of HCl solution used for HCl leaching (mol/L)	Concentration of Si in HCl solution of each molarity (mol/L) at preserved temperature (T) after 5 days (mg/L) ^a		
	$T = 274$ K	$T = 297$ K	$T = 313$ K
5	1098	1078	N.D
6	1004	N.D	N.D ^b
7	N.D	N.D	N.D ^b

a: Concentration of Si was analyzed using ICP-OES, N.D: Not Detected (< 1 ppm)

b: Gelation of silica was observed after centrifugation.

Fig. 7 Residues obtained after centrifugation when the titanyl chloride solutions prepared using (a) 5 M, (b) 6 M, and (c) 7 M HCl solution were preserved at 313 K for 5 days.

unit (0.2 μm) when the HCl leaching of sodium titanate was conducted using 7 M of HCl solution. From these results, it is also apparent that the growth rate of silica in the TiOCl_2 solution prepared using 7 M HCl solution is higher than that of silica in the TiOCl_2 solution prepared using 5–6 M HCl solution.

Table 3 lists the concentration of silica in the TiOCl_2 solutions when 5 days had elapsed after the HCl leaching. In addition, Fig. 7 shows the residues obtained after centrifugation when the TiOCl_2 solution prepared using 5–7 M HCl solution was preserved at 313 K for 5 days. As shown in

Fig. 8 The results of XRD analysis of the residues obtained when the 7 M HCl solution was used and titanyl chloride solution after the leaching was preserved at (a) 313 K and (b) 297 K for 5 days.

Table 3, the concentration of silica is below 1 mg/L in the TiOCl_2 solution under six conditions depending on the preservation temperature and molarity of the HCl solution used for the leaching. However, the 3 dimensional gelation of silica, lump of gelation of silica, is observed only under two conditions. As shown in Fig. 7(a), when 5 M HCl solution is used, 3 dimensional gelation of silica in the TiOCl_2 solution is not observed although the concentration of silica in the TiOCl_2 solution is below 1 mg/L. However, as shown in Figs. 7(b) and (c), when 6 or 7 M HCl solution is used, 3 dimensional gelation of silica in the TiOCl_2 solution is observed.

When the filtration of the TiOCl_2 solution is considered, in addition to the purity of titania pigment, the form of silica grown after the desilication would also be important. When the form of silica after desilication is a particle or a micron-sized precipitate, i.e., when the silica has not grown enough to form 3 dimensional silica gel, it would be difficult to filter the TiOCl_2 solution because particles or precipitates clog the pores of the filter unit. Therefore, the conditions for the 3-dimensional gelation of silica in the TiOCl_2 solution are preferred when the filtration and purity of the pigment are taken into consideration.

Figure 8 shows the results of XRD analysis of the part of silica gel obtained when the 7 M HCl solution was used and the TiOCl_2 solution after the leaching was preserved at 297 K and 313 K for 5 days. The silica gel part in the residues was carefully collected, dried at 378 K, and then analyzed. As shown in Fig. 8, only sodium chloride (NaCl) is identified as

Fig. 9 The results of EDS mapping of the part of silica gel obtained when the 7 M HCl solution was used and titanyl chloride solution was preserved at 297 K for 5 days.

a crystalline phase by XRD analysis. Figure 9 shows the results of EDS mapping of the part of silica gel obtained when the 7 M HCl solution was used and the TiOCl_2 solution was preserved at 297 K for 5 days. These results indicate that silica in the TiOCl_2 solution is removed in a form of silicon oxide after the desilication.

3.3 Hydrolysis of the purified titanyl chloride solution

Figure 10 shows the recovery efficiency of Ti and W from the TiOCl_2 solution feed purified via the gelation of silica at 313 K for 5 days. In addition, Table 4 lists the results of the titania pigment obtained after hydrolysis and calcination.

The recovery efficiency of Ti increased from 14.6% to 63.5% when the molarity of HCl solution used for leaching was decreased from 7 M to 6 M. However, it is necessary to increase the recovery efficiency of Ti further. It is expected that the recovery efficiency of Ti can be increased by decreasing the acidity of the purified TiOCl_2 solution or by increasing the temperature for hydrolysis. It is worth noting that almost all W in the purified TiOCl_2 solution was co-precipitated with Ti by hydrolysis. W exists as tungstic acid (H_2WO_4) in the form of a solid in the concentrated acid. However, it was identified that a small amount of W was dissolved in the concentrated acid, as shown in

Fig. 10 Recovery efficiency of Ti and W from the titanyl chloride solution feed purified via the gelation of Si at 313 K for 5 days.

Table 2, owing to the solubility of H_2WO_4 in the HCl solution.¹⁹⁾ Therefore, it is expected that W dissolved in the purified TiOCl_2 solution was precipitated during hydrolysis at 363 K.

After the hydrolysis of the purified TiOCl_2 solution, a purity of 99.6–99.9% of TiO_2 was obtained, as shown in

Table 4 Analytical results of TiO_2 obtained after hydrolysis and calcination.

Molarity of HCl solution used for HCl leaching (mol/L)	Concentration of element i , C_i (mass %) ^a							
	Al_2O_3	Na_2O	Fe_2O_3	CaO	WO_3	V_2O_5	SiO_2	TiO_2^b
6	N.D	N.D	N.D	N.D	0.06	N.D	N.D	99.94
7	N.D	N.D	N.D	N.D	0.43	N.D	N.D	99.57

a: Concentration was determined using ICP-OES analysis, N.D: Not Detected (< 0.010 mass%)

b: Concentration of TiO_2 was calculated as follows: TiO_2 purity = $100 - (\text{conc. of oxides of Al, Na, Fe, Ca, W, V, and Si})$

Table 4. The only impurity detected was W. The purity of titania pigment obtained in this study satisfied the international standard for titanium dioxide pigments for paints (ISO 591-1:2000(E)), which requires 97–98% of TiO_2 . However, development of a method for the further removal of W from the purified TiOCl_2 solution is necessary.

Figure 11 shows the results of the XRD analysis of the titania pigment calcined at 973 K for 1 h. As shown in Fig. 11, a rutile type of titania pigment is obtained. Figure 12 shows the particles of the titania pigment produced after calcination; micron-sized titania pigment is obtained.

4. Conclusions

The removal of silica in the highly acidic TiOCl_2 solution obtained by HCl leaching of the sodium titanate produced using spent SCR catalyst was investigated for increasing the purity of the titania pigment product and the productivity of the process by resolving the filtration problem. The influence of acidity, preservation temperature, and time elapsed after preservation on the removal efficiency of silica in the TiOCl_2

Fig. 11 The results of XRD analysis of the titania pigment calcined at 973 K for 1 h using particles obtained by the hydrolysis of purified titanyl chloride solution prepared by (a) 7 M and (b) 6 M HCl solution.

solution produced by dissolving sodium titanate using 5–7 M HCl solutions under 10% S/L ratio (w/v) was evaluated. In addition, the titania pigment obtained by the hydrolysis of the

Fig. 12 Images of titania pigment produced after calcination using particles obtained by hydrolysis of the purified titanyl chloride solution prepared by (a) (b) 6 M and (c) (d) 7 M HCl solution.

purified TiOCl_2 solution was also evaluated. Based on the results, the following conclusions can be drawn:

- (1) When the TiOCl_2 solution prepared using 5 M HCl solution was preserved at 313 K, the concentration of silica was below 1 mg/L after 5 days had elapsed.
- (2) When the TiOCl_2 solution prepared using 6 M HCl solution was preserved at 297 K and 313 K, the concentration of silica was below 1 mg/L after 3 and 2 days had elapsed, respectively.
- (3) When the TiOCl_2 solution prepared using 7 M HCl solution was preserved at 274–313 K, the concentration of silica was below 1 mg/L after 1 day had elapsed.
- (4) Si was removed as silicon oxide, and when the TiOCl_2 solution prepared using 6–7 M HCl solution was preserved at 313 K, 3 dimensional gelation of silica occurred.
- (5) When the TiOCl_2 solution prepared using 6–7 M HCl solution was hydrolyzed at 363 K after the desilication, micron-sized TiO_2 with a purity of 99.6–99.9% was obtained.

Acknowledgments

The authors are grateful to Dr. In-Hyeok Choi, Dr. Tae-Hyuk Lee, Mr. Hee-Nam Kang and Ms. Jieun A. Ahn for their technical support and discussion throughout this study. The authors are also grateful to all the members of the Geoanalysis Department of KIGAM for their technical assistance. This research was supported by the R&D center for valuable recycling (Global-Top Environmental Technology Development Program) funded by the Korean Ministry of the Environment in Korea (Project No.: GT-11-C-01-230-0) and the Korea Evaluation Institute of Industrial

Technology funded by the Korean Ministry of Industry in Korea (Project No.: 20000970, 18-9805).

REFERENCES

- 1) J.H. Braun, A. Baidins and R.E. Marganski: *Prog. Org. Coat.* **20** (1992) 105–138.
- 2) F. Habashi: *Handbook of Extractive Metallurgy*, (VCH Verlagsgesellschaft mbH, Germany, 1997).
- 3) E.G. Roche, A.D. Stuart and E.P. Grazier: US 7485269 B2 (2009a).
- 4) E.G. Roche, A.D. Stuart, E.P. Grazier and H. Liu: US 7485268 B2 (2009b).
- 5) W. Zhang, Z. Zhu and C.Y. Cheng: *Hydrometallurgy* **108** (2011) 177–188.
- 6) K.K. Sahu, T.C. Alex, D. Mishra and A. Agrawal: *Waste Manag. Res.* **24** (2006) 74–79.
- 7) M. Matsunaga: *J. Japan Soc. Colour Mater.* **54** (1981) 680–689.
- 8) J. Kang and T.H. Okabe: *Mater. Trans.* **55** (2014) 591–598.
- 9) N. Nakamura: *Molten Salts* **56** (2013) 121–124.
- 10) R.A. Gonzalez: US 5562764 (1996).
- 11) J. Kang and T.H. Okabe: *Metall. Mater. Trans. B* **44** (2013) 516–527.
- 12) V. I. Lakshmanan, R. Sridhar, Harris, G. Bryn and G. Puvvada: US 7803336 B2 (2010).
- 13) S. Middlemas, Z.Z. Fang and P. Fan: *Hydrometallurgy* **131–132** (2013) 107–113.
- 14) H. Lefler, Y. Zhang, Z.Z. Fang, M. Free and Z. Huang: *Hydrometallurgy* **173** (2017) 218–223.
- 15) R.K. Iler: *The Chemistry of Silica*, (A Wiley-Interscience Publication, United States of America, 1979).
- 16) N.A. Milne, T. O'Reilly, P. Sancio, E. Ostarcevic, M. Beighton, K. Taylor, M. Mullett, A.J. Tarquin and S.R. Gray: *Water Res.* **65** (2014) 107–133.
- 17) E.A. Gorrepati, P. Wongthahan, S. Raha and H.S. Fogler: *Langmuir* **26** (2010) 10467–10474.
- 18) R.W. Potter and M.A. Clyne: *J. Chem. Eng. Data* **25** (1980) 50–51.
- 19) L. Honggui, Y. Jiangao and L. Kun: *Tungsten Metallurgy*, (Central South University Press, China, 2010).