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Preparation of TiO_2 pigment from ilmenite ore concentrate by molten alkaline process

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Abstract:

TiO_2 pigment production from an ilmenite concentrate via a molten alkaline process was investigated. The ilmenite concentrate (54.19% TiO_2) was first roasted in the molten NaOH system at various temperatures ranging from 600 to 800°C while the mass ratio of NaOH/ilmenite was varied within the range of 0.8-1.2 for 1 hour. The achieved roasted efficiency was up to 93.93% at a temperature of 700°C and NaOH/ilmenite ratio of 1:1. The roasted product was first leached in water and then in a solution of HCl 20% at 50°C for 2 hours. The $TiOCl_2$ solution was hydrolysed at 95°C for 2 hours. Precipitation of the hydrolysis process was then calcinated at 800°C. The final obtained product contained up to 96.37% of TiO_2. Ilmenite can be used as a raw material in a molten alkaline process. It is obvious that not only high purities of TiO_2 could be achieved, but also the reduction of waste materials, raw materials, energy, and time.

Keywords: **ilmenite, NaOH, roasting, rutile, TiO_2.**

Classification numbers: **2.2, 2.3**

1. Introduction

Titanium dioxide pigment (TiO_2) has high chemical and thermal stability, is non-toxic, has corrosion resistance, and a high optical refractive index. Therefore, this pigment has been widely used in a variety of areas including paint, paper, plastic, and cosmetics, among others, due to its remarkable qualities [1].

There are more than 100 different minerals containing more than 1% TiO_2. Among them, ilmenite and rutile are the minerals of choice in industry. Ilmenite accounts for more than 90% of the Ti metallurgy industry uses [2]. The ilmenite $FeTiO_3$ is one of the primary raw materials for titanium-containing material and iron production. Vietnam has large titanium ore deposits with approximately 650 million tons of heavy minerals located mostly along the middle coast of Vietnam spreading from Thanh Hoa province to Ba Ria - Vung Tau province [3]. Recently, the Vietnamese titanium industry processed high grade ore and titanium slag with around 80% TiO_2 content. Despite this, TiO_2 pigment has not yet been processed in Vietnam [4, 5].

There are two commercial processes for recovering TiO_2 including the sulfate process and chloride process [1, 2]. In the past decade, a new process called the "molten alkaline process" was investigated for the synthesis of TiO_2 pigment [6-15]. Titanium slags were used as raw materials containing ~80% TiO_2. Recently, some metallurgists used ilmenite ore ($FeTiO_3$) to replace titanium slag in molten alkaline processes [14, 15].

The exploratory research of TiO_2 pigment production using ilmenite as raw materials through the molten alkaline process has been proposed as a new method for obtaining high quality TiO_2 and also to reducing the amount of waste, save raw materials, energy, and time.

In this study, TiO_2 pigment was prepared from Ha Tinh ilmenite ore concentrate (IOC) via the molten alkaline process.

2. Experimental procedure

Ha Tinh IOC was used as a raw material; its chemical composition was analysed by X-ray Fluorescence (XRF-Viet Space 5008P) as shown in Table 1 which contains 54.19% TiO_2. The X-ray diffraction (XRD- Bruker D8-Advance) analysis of the ilmenite concentrate (Fig. 1) indicates that the main titanium components are $FeTiO_3$, TiO_2, $Fe_2Ti_3O_9$, and Fe_2O_3.

Table 1. Chemical compositions of Ha Tinh IOC.

Component	Content (wt. %)
TiO_2	54.19
FeO	34.16
SiO_2	4.01
Al_2O_3	4.28
MnO	2.82
Nb_2O_3	0.17
ZrO_2	0.32
Other	0.05

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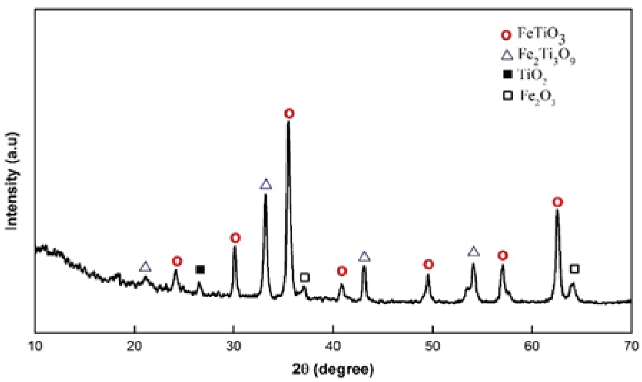

Fig. 1. X-Ray diffraction pattern of Ha Tinh IOC.

TiO_2 was produced from IOC by the alkaline molten salt process. IOC mixed with NaOH were roasted in nickel crucibles inside a muffle furnace. The alkaline roast was then leached in water to remove both the excess NaOH as well as soluble impurities such as silicate and aluminate. After the first leaching, the water-leached sample was subsequently subjected to hydrochloric acid leaching. The solution was then subjected to hydrolysis, and precipitation was calcinated as shown in Fig. 2.

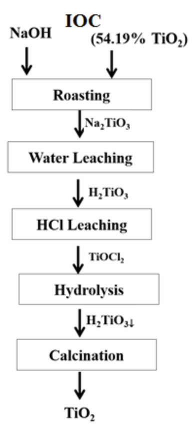

Fig. 2. The experimental procedure.

The selection of roasting temperature depends on raw materials, thus, the roasting temperature was studied at 600-800°C, which is higher than that for titanium slag or upgrading ilmenite at about 500°C based on previous research [9, 10]. The IOC (54.19% TiO_2) was first roasted in the molten NaOH system at various temperatures ranging from 600 to 800°C with the NaOH/IOC mass ratio varied within 0.8-1.2 for 1 hour. The roasted product was then leached in water and later in HCl 20% at 50ºC for 2 hours. The $TiOCl_2$ solution was hydrolysed at 95°C for 2 hours. The precipitation resulting from the hydrolysis process was then calcinated at 800°C.

3. Results and discussion

The IOC was roasted in the NaOH molten system to prepare Na_2TiO_3. The main goal of the alkaline roasting process is to destroy the very strong and compact crystal structures of pure Ti minerals (rutile, anatase, or synthetic rutile) as these minerals are extremely resistant to direct acid leaching in comparison with ilmenite, which contains much higher amounts of iron oxides that facilitate its acid digestion [16]. TiO_2 is converted to Na_2TiO_3 through the alkaline roasting process for separation of Ti from Fe and other impurities that formed like $NaFeO_2$, Na_2AlO_2, Na_2SiO_3, etc [2]. The roasting reactions occurred by the following chemical reactions:

$$4FeTiO_3 + 12NaOH + O_2 = 4Na_2TiO_3 + 4NaFeO_2 + 6H_2O \quad (1)$$

$$TiO_2 + 2NaOH = Na_2TiO_3 + H_2O \quad (2)$$

$$Fe_2O_3 + 2NaOH = NaFeO_2 + H_2O \quad (3)$$

$$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O \quad (4)$$

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O \quad (5)$$

$$MnO + 2NaOH + O_2 = Na_3MnO_4 + H_2O \quad (6)$$

$$ZrO_2 + 2NaOH = Na_2ZrO_3 + H_2O \quad (7)$$

$$Nb_2O_3 + 2NaOH + O_2 = 2NaNbO_3 + H_2O \quad (8)$$

This study focuses on determining the effect of roasting temperature and mass ratio of NaOH/IOC on the efficiency of the roasting process. The roasting temperature was varied from 600 to 800°C with a 50°C increment along with using a NaOH/IOC mass ratio of 1/1 for 60 min. The results are shown in Table 2 and Fig. 3. The efficiency of decomposed TiO_2 increases from 81.59 to 93.93% when increasing of temperature from 600 to 700°C because of the molten NaOH system. After that, the efficiency slightly decreased at a higher temperature of 800°C (93.58%).

Table 2. Effect of temperature on efficiency of TiO_2 roasting.

Temperature (°C)	Roasting efficiency of TiO_2 (%)
600	81.59
650	84.81
700	93.93
750	93.93
800	93.58

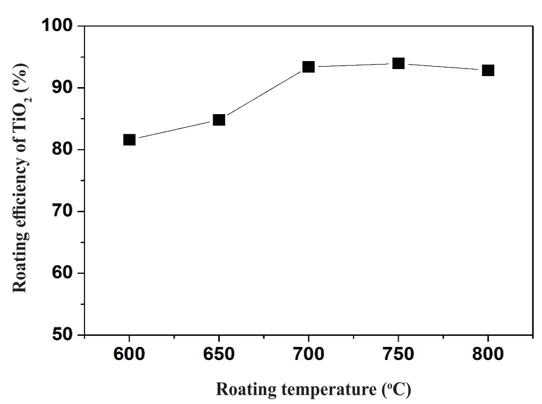

Fig. 3. Effect of roasting temperature on roasting efficiency of TiO_2 (%).

In previous research, the effect of roasting temperature at 500-550°C for 1-1.5 hours and TiO_2/NaOH ratio of ~ 1-1.2 for titanium slag raw materials were observed [5-11]. For IOC, the reactions between NaOH and ore were negligible at a temperature of 600°C, but these reactions strongly occurred when the temperature reached 700-800°C. The optimum roasting temperature was found to be 700°C, and it agrees well with the results of other works [12, 14].

To study the effect of NaOH/IOC mass ratios, the NaOH/IOC ratios were varied within the range of 0.8, 0.9, 1, 1.1; and 1.2. The results are summarized in Table 3 and collectively plotted in Fig. 4. The obtained results show that when the ratios changed from 0.8 to 1.0, the roasting efficiency of TiO_2 increased from 83.73 to 93.93% while the efficiency remained constant at higher ratios of 1.1 and 1.2. The results can be explained by the fact that the molten NaOH system acts as a high temperature ionized solvent above 350°C, in which titanium dioxide and other titanium compounds have high solubility.

On other hand, NaOH melting provides O^{2-}, and it combines with the oxygen in the air to oxidize titanium oxide (Ti_2O_3) to form Na_2TiO_3. Therefore, increasing NaOH content significantly increased the O^{2-} content in solution, thus increasing roasting speed [8].

Table 3. Effect of NaOH/IOC mass ratio on roasting efficiency of TiO_2.

NaOH/IOC mass ratio	Roasting efficiency of TiO_2 (%)
0.8	83.73
0.9	88.02
1.0	93.93
1.1	93.93
1.2	93.93

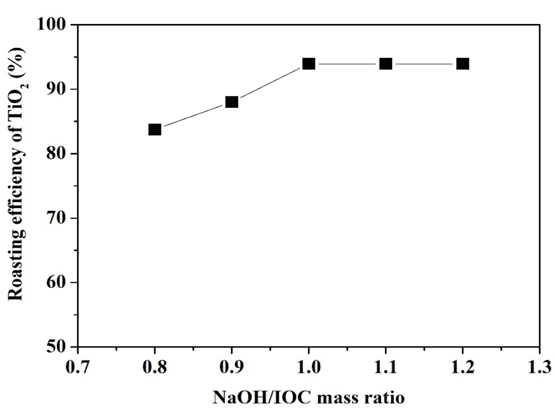

Fig. 4. Effect of NaOH/IOC mass ratio to roasting efficiency of TiO_2.

The product of roasting was analysed by XRD as shown in Fig. 5. This figure shows that the titanium exists in the form of sodium titanium oxide (Na_2TiO_3).

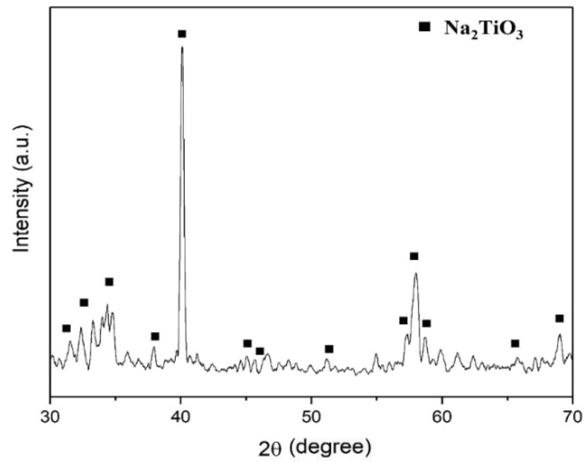

Fig. 5. X-ray diffraction pattern of IOC roasting production.

The Na_2TiO_3 was leached in water to form a solid of H_2TiO_3 at 60°C for 10 min as shown in reaction 9:

$$Na_2TiO_3 + 2H_2O = H_2TiO_3 + 2NaOH \quad (9)$$

In this process, Mn, Al, and Si form a water solute that can be removed in a water solution [12]. The obtained solid was continuously leached in a hydrochloric acid solution to form a solution as shown in the following reaction:

$$H_2TiO_3 + 2HCl = TiOCl_2 + 2H_2O \quad (10)$$

This process transfers titanium from a solid into a solution. However, iron and other impurities were also dissolved. The leaching parameter was studied as a function of HCl concentration (15-20%), a temperature range of 20-80°C, and leaching times from 30 to 150 min. The effect of HCl acid concentration on the efficiency of H_2TiO_3 is shown in Table 4 and Fig. 6.

The efficiency of the leaching process increased from 80.51 to 93.93% along with increasing HCl concentration from 15 to 20%. During the leaching process, the 15% HCl concentration can be hydrolysed into H_2TiO_3 to reduce the titanium content of the solution. At higher HCl concentrations, impurities can be dissolved in the solution that were probably caused by hydrolysis processes [15]. Based on the results, an HCl concentration of 20% was used for the hydrolysis process.

Table 4. Effect of HCl concentration on leaching efficiency of TiO_2.

HCl concentration (%)	Leaching efficiency of TiO_2 (%)
15.0	80.51
17.5	91.25
20.0	93.93
22.5	89.10
25.0	83.20

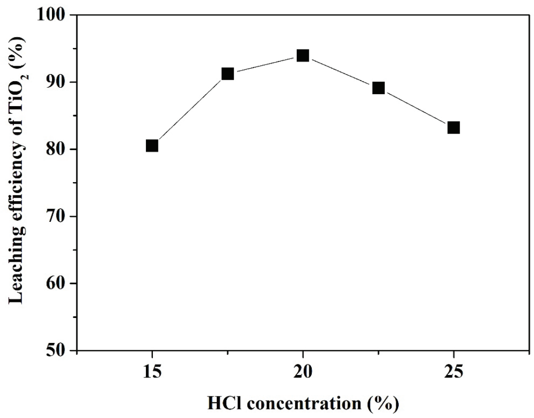

Fig. 6. Effect of HCl concentration on leaching efficiency of TiO_2.

Leaching temperature was studied as a function of 20, 40, 60 and 80^{o}C with 20% HCl for 60 min, and the results are presented in Table 5 and Fig. 7.

Table 5. Effect of leaching temperature on leaching efficiency of TiO_2.

Leaching temperature (^{o}C)	Leaching efficiency of TiO_2 (%)
20	84.81
40	88.03
60	93.93
80	89.10

Figure 7 shows that the highest TiO_2 content in solution reaches 93.93% at a temperature to 60^{o}C. At the temperature above 60^{o}C, the leaching efficiency of TiO_3 decreased because of H_2TiO_3 hydrolysis. Thus, a leaching temperature of 60^{o}C was selected for the next study.

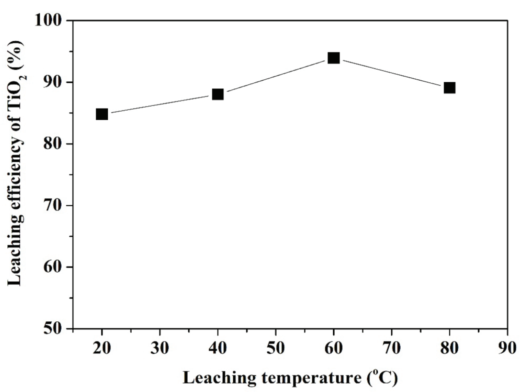

Fig. 7. Effect of leaching temperature on leaching efficiency of TiO_2.

The effect of leaching time on TiO_2 leaching efficiency was investigated as a function of 30, 60, 120, 150 and 180 min while the parameters of 20% HCl and 60^{o}C were kept constant. The results obtained are shown in Table 6 and Fig. 8. The leaching efficiency of TiO_2 increased as the leaching time increased from 30 to 60 min, and this value remained constant at higher leaching times.

Table 6. Effect of leaching time on leaching efficiency of TiO_2.

Leaching time (min)	Leaching efficiency of TiO_2 (%)
30	88.56
60	93.93
90	93.39
120	93.93

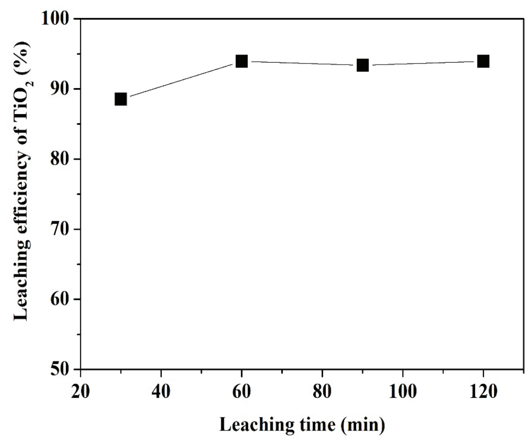

Fig. 8. Effect of leaching time on leaching efficiency of TiO_2.

The dissolved Ti can react with water molecules to form insoluble hydrate solutions through hydrolysis and precipitation of a hydrous titanium oxide compound. The product of low temperature hydrolysis (20-80^{o}C) is $Ti(OH)_4$ or $TiO_2.2H_2O$, however, that of higher temperatures (80-110^{o}C) is $TiO(OH)_2$ or $TiO_2.H_2O$ [12].

The $TiOCl_2$ solution was hydrolysed at 95^{o}C for 2 hours according to reaction (11):

$$TiOCl_2 + 2H_2O \rightarrow TiO(OH)_2 + 2HCl \quad (11)$$

The exact mechanism of the thermal hydrolysis of Ti solution is unclear, however, some have thought it to be the transfer of H^+ ions from the hydration shell of Ti ions into the solution with subsequent coordination with OH^- and colloidal aggregation [8, 12]. This hydrated compound is then calcinated to form a crystalline product. The type of TiO_2 crystal depends on the acid used during the leaching process. The hydrolysis of chloride solutions yielded rutile upon calcination [12].

To obtain TiO_2, the precipitation product of $TiO(OH)_2$ was calcinated at 800^{o}C for 2 hours. The reactions can be represented by the following reaction (12):

$$TiO(OH)_2 \xrightarrow{t^o} TiO_2 + H_2O \quad (12)$$

The chemical compound and phase content of the final product of TiO_2 was analysed by XRF and XRD, respectively, as shown in Fig. 6 and Table 4. The final TiO_2 product was a rutile crystal structure with a TiO_2 content of 96.37 wt. % (Table 7, Fig. 9).

Table 7. Chemical composition of TiO_2 product.

Component	Content (wt. %)
TiO_2	96.37
FeO	1.02
SiO_2	1.33
Al_2O_3	0.22
ZrO_2	0.70
Nb_2O_3	0.35
Other	0.01

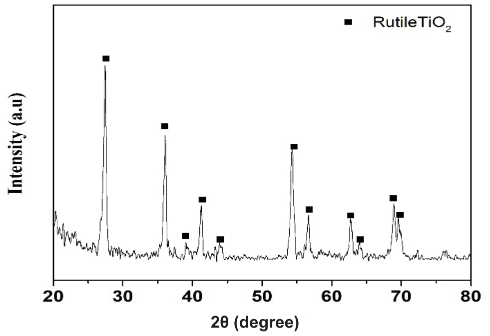

Fig. 9. X-ray diffraction pattern of the TiO_2 product.

The molten alkaline process has been introduced to produce pure TiO_2 from various titanium sources [12, 13]. A comparison of our results with the results of other research is shown in Table 8. In the table, the 98.39% TiO_2 was synthesized by the same process using raw materials of upgrading ilmenite (82% TiO_2) [13]. S. Sanchez-Segado, et. al (2015) [15] observed a similar quality to our product (95% TiO_2) from Bomar IOC.

Table 8. Comparative study of TiO_2 production.

Raw materials	Production of TiO_2 (%)	Ref.
Ha Tinh IOC (54.19% TiO_2)	96.37	This study
Upgrading ilmenite 82% TiO_2	98.39	[13]
Bomar IOC 61% TiO_2	95	[15]

4. Conclusions

This study was conducted to obtain a final TiO_2 concentration of 96.37 wt. % from a Ha Tinh IOC (54.19% TiO_2) by a molten alkaline process with roasting conditions of 700°C and a NaOH/ilmenite ratio of 1:1. The roasted product was first leached in water at 60°C for 10 min and then in a solution of HCl 20% at 50°C for 2 hours. The $TiOCl_2$ solution was hydrolysed at 95°C for 2 hours and then calcinated at 800°C to obtain a product containing up to 96.37% of TiO_2. This result demonstrates that the molten alkaline process can be applied to the synthesis TiO_2 from the IOC of Vietnam. The molten alkaline process was used in the fabrication of TiO_2 pigment by various raw materials from low grade TiO_2 (ilmenites) to high grade TiO_2 (slag, upgrading ilmenite). This process not only yielded high grade TiO_2, but also used ilmenite ores in a direction in which the impurities, materials, time, and energy were reduced.

CRediT author statement

Thi Thao Nguyen: Conceptilization, Methodology, Formal analysis, Writing; Ky Nam Pham: Data analyst; Thi Hinh Dinh: Data analyst; Vu Diem Ngoc Tran: Formal analysis, Review, Editing; Aman Ullah: Review, Data analyst.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

[1] W. Zhang, Z. Zhu, C.Y. Cheng (2011), "A literature review of titanium metallurgical processes", *Hydrometallurgy*, **108(3-4)**, pp.177-188.

[2] S. Sin, S.H. Joo, D. Lee, J.S. Kang, et al. (2020), "Leaching behavior of titanium from Na_2TiO_3" *Mater. Trans.*, **61**, pp.150-155.

[3] B. Nam, H. Giao (2016), "Status of development orientations for mining titanium placer in Vietnam", *Горные Науки и Технологии*, **1**, pp.40-50.

[4] Prime Minister (2013), "Approving the zoning plan for exploration, extraction, processing and exploitation of titan ores by 2020 with vision to 2030", *Decision No. 1546/QD-TTg dated September 3, 2013*.

[5] T.N. Than, N.B. Duong, T.T. Nguyen, V.D.N. Tran (2016), *Manufacturing Processes for The Production of Titanium Dioxide Pigment*, Metallurgical Engineering & Advanced Materials Technology, pp.172-177.

[6] M. Gázquez, J. Pedro, R. Vaca, et al. (2014), "A review of the production cycle of titanium Dioxide pigment", *Materials Sciences and Applications*, **5**, pp.441-45.

[7] Y. Zhang, T. Qi, Y. Zhang (2009), "A novel preparation of titanium dioxide from titanium slag", *Hydrometallurgy*, **96(1-2)**, pp.52-56.

[8] S. Middlemas, Z.Z. Fang, P. Fan (2013), "A new method for production of titanium dioxide pigment", *Hydrometallurgy*, **131**, pp.107-113.

[9] Y. Han, T. Sun, J. Li, L. Wang, et al. (2012), "Preparation of titanium dioxide from titania-rich slag by molten NaOH method", *Int. J. Miner. Metall. Mater.*, **19**, pp.205-211.

[10] S. Zaki (2017), "Alkali Roasting of Titania Slag for Preparation of High Grade-TiO_2", *Inorg. Chem. Ind. J.*, **12(1)**, pp.1-9.

[11] S.C. Middlemas (2014), *Energy-Conscious Production of Titania and Titanium Powders from Slag*, University of Utah, 212pp.

[12] A. Manhique, W. Focke, C. Madivate (2011), "Titania Recovery from Low-grade Titaniferrous", *Hydrometallurgy*, **109(3)**, pp.230-236.

[13] T. Ngoc, N. Thao (2019), "New process to improve of TiO_2 content from upgrading ilmenite using molten NaOH", *Journal of Metal Science and Technology*, **84**, pp.38-42.

[14] S. Parirenyatwa, L. Castejon, S.S. Segado, Y. Hare, et al. (2016), "Comparative study of alkali roasting and leaching of chromite ores and titaniferous minerals", *Hydrometallurgy*, **165**, pp.213-226.

[15] S. Sanchez-Segado, A. Lahiri, A. Jha (2015), "Alkali roasting of bomar ilmenite: Rare earths recovery and physico-chemical changes", *Open Chem.*, **13**, pp.270-278.

[16] M. Ismael, O.M. Husaini, M.F. Shakat (2020), "New method to prepare high purity anatase TiO_2 through alkaline roasting and acid leaching from non-conventional minerals resource", *Hydrometallurgy*, **195**, DOI: 10.1016/j.,hydromet.2020.105399.