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Xuan-Nam Bui
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Becher Method Application for Ilmenite Concentrates of Vietnam

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Abstract. Several methods used to extract iron from ilmenite concentrate to increase TiO₂ content of ilmenite concentrates such as Benelite, Ishihara, Murso, Auspaci, and Becher methods. Benelite method uses HCl for leaching of reduced iron from ilmenite. Auspaci method uses hot HCl while Ishihara uses hot acid H₂SO₄ in the leaching stage. Murso method uses 20% HCl acid under atmospheric pressure for the leaching of roasted ilmenite. The significant advantage of Benelite, Auspaci, Ishihara, and Murso methods is high-quality product with TiO₂ content of up to 95–97%. However, the use of acid, especially hot HCl, is the principal disadvantage of these methods. They may severely impact the surrounding environment and may cause many safety and health problems. These methods have not been applied in Vietnam yet. Unlike the above methods, the Becher method relies on the iron corrosion capability of the less-toxic NH₄Cl solution for separating iron from roasted ilmenite. Therefore, it is considered to be more environmentally friendly. This paper presents the preliminary study results on Becher method applied to ilmenite concentrates of Binh Thuan province of Vietnam. From the ilmenite concentrates of Binh Thuan province with TiO₂ content of about 52%, the study has produced artificial rutile with TiO₂ content of over 85% and a byproduct superfine iron oxide powder that may be suitable for the use in pigment production. The study results show that Becher's method is suitable for the treatment of the ilmenite concentrates of Vietnam.

Keywords: Ilmenite processing · Becher method · Increase TiO₂ content · Vietnamese ilmenite concentrate

1 Introduction

Titanium is a metal with silver color. It has desirable properties of high-performance metal, including high resistance to corrosion, low density, high specific strength, and superior ballistic properties [5]. Titanium is very highly resistant to corrosion even in extreme conditions such as in seawater, aqua regia, and chlorine. This metal is widely used in most areas [10], and its application is being expanded to diverse fields of engineering. The newer generation of titanium alloys is recognized as being much stronger and lighter than the most widely chosen and used steels.

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Vietnam titanium ores are mainly of beach placer ore type, in which the leading titanium bearing mineral is ilmenite. Currently, most titanium processing technological lines are mainly concentrated on the cleaning stage, at which the obtained ilmenite concentrates are low grades that make them unusable in many applications [4].

The processing of titanium minerals not only brings economic value but also creates more jobs for local workers and creates momentum for the research and development of specific products from titanium such as pigments, titanium metals, high-strength alloys, etc. Recently, some titanium mineral processing factories have been built, such as titanium slag refining. However, the actual economic efficiency is not high since high-temperature processes consume large amounts of high power [4].

In the world, there are some methods for the production of artificial rutile such as Becher method, Benelite method, and Austpac method, etc. Which method should be used, and which is effective and suitable for Vietnam's current conditions in the context of strictly environmental pollution control?

This report presents preliminary experimental results of a study on leaching of ilmenite concentrates of Vietnam using Becher method. It proposes some suggestions on the methods for processing titanium ores that are currently applied worldwide, thereby saving time and cost in choosing the orientation for the research deployed in Vietnam.

2 Evaluation of Processing Methods

Ilmenite processing is divided into two broad groups, which are pyrometallurgical and hydrometallurgical methods. Titanium slag smelting is a pyrometallurgical method. Hydrometallurgical methods include Benelite, Austpac, Ishihara, Murso, Becher methods, etc. Here are some outstanding features of the methods.

2.1 Titanium Slag Smelting

This method, developed by Russian, is widely applied globally, particularly in Canada, South Africa, Norway, Ukraine, Japan, and China.

According to this method, ilmenite concentrate is mixed with carbon and additives. The mixture is then pressed into briquettes. The briquettes are then smelted in an electric arc furnace. At high temperatures (about 1600 °C), iron is reduced to metal form Fe, melted to form pig iron, while TiO_2 is left almost unchanged and thus transferred into slag. As a result, two products are obtained, which include pig iron and rich in titanium slag.

The method's significant advantage is that it does not require high TiO_2 content of the feed; besides, the method also obtains valuable pig iron. However, the drawback of the method is high power consumption. According to the original technology, electricity consumption is about 2,700 kWh/tonne. Even today, the two-stage smelting technology has improved electricity consumption, but it still requires about 1,000 kWh/tonne of titanium slag. This method also causes severe pollution to the surrounding environment due to a large number of emissions during the production process (Fig. 1).

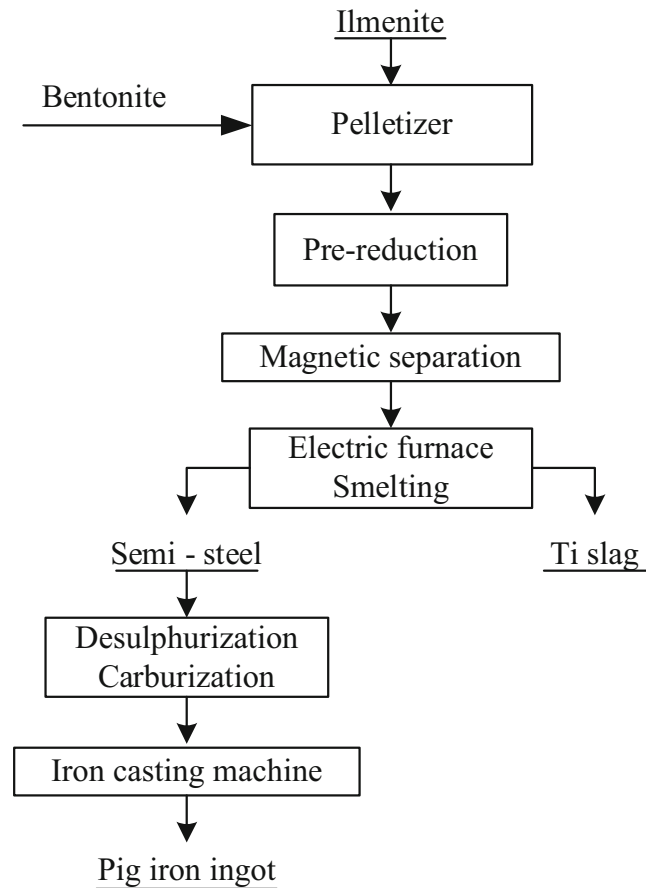


Fig. 1. Titanium slag method flowsheet [3]

2.2 Hydrometallurgical Methods for Processing of Titanium Concentrates

The Benelite Method

The Benelite method has overcome operational disadvantages associated with the direct acid leaching of ilmenite [6]. This method is used in several operations, including Malaysian Titanium Corporation's plant in Ipoh and Kerr McGee's plant in Alabama. Partial reduction roasting of ilmenite is necessary before leaching because the resultant ferrous oxides are easier soluble in a leaching solution such as chloride acid. Moreover, the partial reduction of ilmenite significantly reduces acid concentration (20% HCl) [6].

This process includes the following stages:

- + Reduction roasting of ilmenite to convert Fe(III) to Fe(II).
- + Dissolution of the roasted product in HCl solution under low-pressure conditions.
- + Filtration of leached ilmenite to receive a solid cake richer in TiO_2 content. This cake is then calcinated in order to obtain a calcined solid containing up to 94% TiO_2 . The iron-containing filtrate follows the regeneration stage to recover HCl and Fe_2O_3 simultaneously.

Austpac method

Austpac is a method for the production of high-quality artificial rutile. The method was developed by Austpac Company, and the method was applied in production since 2001. The method consists of two main processes, which are ERMS (Enhanced Roasting and Magnetic Separation) and EARS (Enhanced Acid Regeneration System) [7]. The principle of the two processes can be summarized as follows:

The sequence of the ERMS process for producing artificial rutile is as follows: reduction roasting → magnetic separation → dissolution in hot HCl solvent. After filtration and calcination, the final solid product is the artificial rutile with TiO₂ content of up to 97% that is most suitable for commercial purposes.

Unlike the ERMS process, EARS adds FeCl₂ solution to recover HCl and Fe₂O₃ as materials suitable for steel making. Artificial rutile produced by Austpac method have higher rutile quality (97–98% TiO₂) in comparison to other methods. However, hot and dense acids create several issues related to equipment erosion and the environment.

Ishihara Method

Like Benelite method, ilmenite concentrates are roasted in rotary tube furnaces to convert Fe(III) into Fe(II). Magnetic separation is used for the removal of any residual coke from partially reduced ilmenite. The product is then dissolved in an H₂SO₄ solvent at a temperature of 130 °C for several hours. Artificial rutile contains up to 95% TiO₂ [8]. The leaching step's reject acid solution can be used as a raw material in an ammonium sulphate plant or it may be re-used by adding make-up acid.

Murso Method

Before reducing ilmenite at 800–850 °C, the ore concentrate is oxidized at 900–950 °C to convert Fe(II) to Fe(III). The roasted product is dissolved in 20% HCl acid under atmospheric pressure. Impurities such as Mn, Mg, Al and V are also dissolved during dissolution. The obtained rutile contains 95% TiO₂ [9]. The method has been proved to be efficient in a pilot-scale [6].

Becher Method

Becher method, named in honor of Robert Gordon Becher (Australia), results from the extensive studies on the enrichment of ilmenite concentrates by selective roasting of ilmenite and subsequent corrosion of iron in NH₄Cl solution under air bubbling [10]. This technology's final products include artificial rutile with TiO₂ content of around 90% and iron oxide powder. In 1961 Becher was granted a U.S patent. This method's main disadvantages are the requirement of high-quality ilmenite feed (TiO₂ ≥ 55%) [2], and the processing time is relatively long.

2.3 Evaluation and Selection of Processing Methods

As mentioned, titanium slag smelting has the main disadvantage of consuming immense power. Therefore it is only suitable for countries where power sources are abundant and cheap, but not the case for Vietnam. The hydrometallurgical methods such as Benelite, Austpac, Becher, Ishihara, Murso, etc. allow processing of ilmenite concentrates with varying quality in a wide range, relatively complete iron removal, and relatively low

power consumption in comparison to slag smelting method, the obtained artificial rutile with high TiO_2 content. Except for the Becher method, most hydrometallurgical methods use leaching to solve relatively high concentrations of acidity. Therefore, the need to use high corrosion-resistant and high-pressure equipment became the major disadvantage of these methods. In practice, the applications of these hydrometallurgical methods are mainly limited in laboratories and some pilot-scale use, for example, Austpac method.

Currently, Becher method is widely used in industrial-scale in Western Australia, India, and China to produce artificial rutile. This method has many advantages as it is a fast and straightforward process with the environment [2]. The method also requires less energy.

Becher method is summarised, according to Fig. 2. This method is based on the possibility of electrochemical corrosion of Fe metal in NH_4Cl solution [1]. The difference in

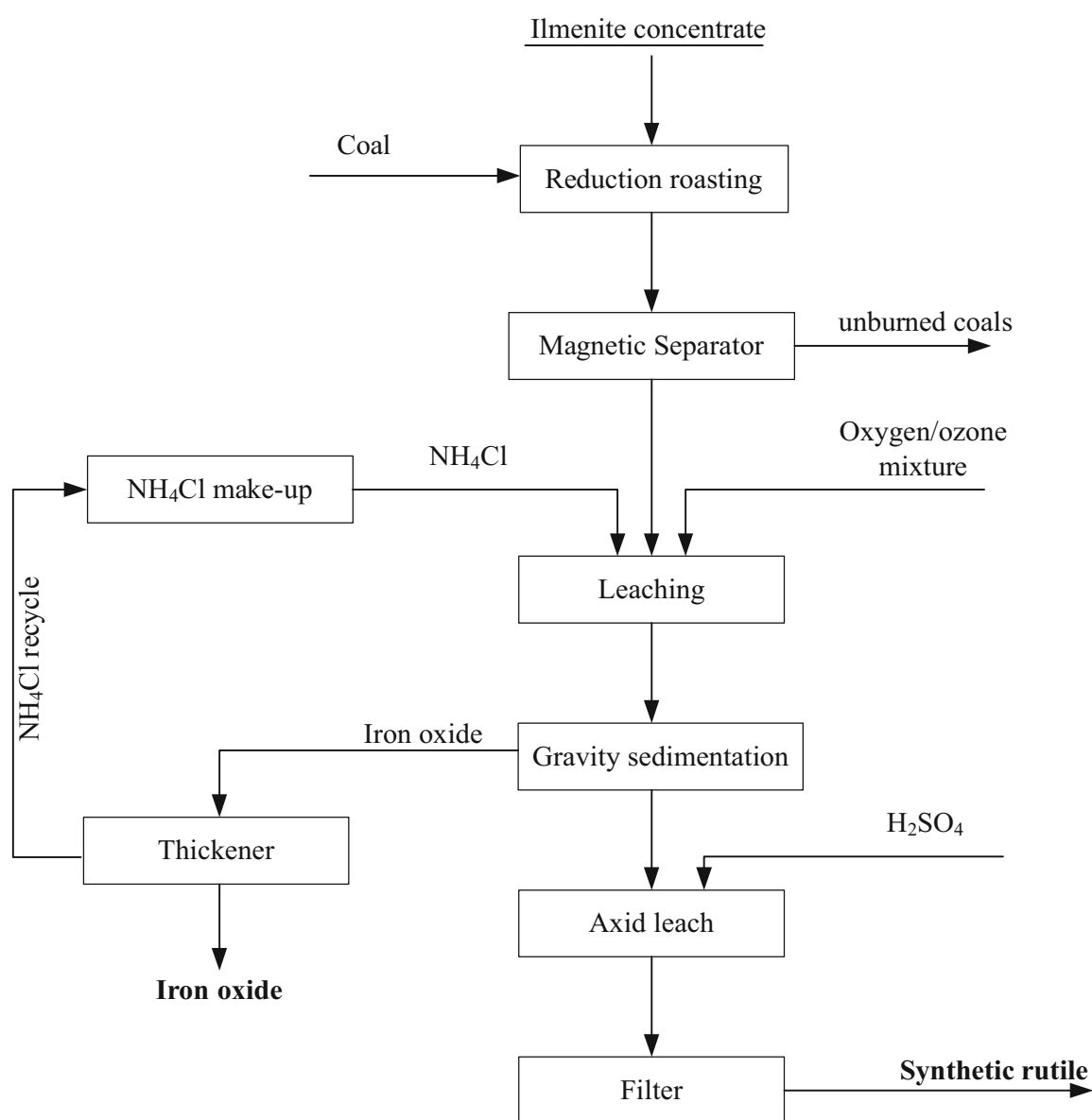
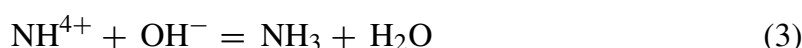


Fig. 2. Becher method flowsheet

the electric potential of oxygen and iron causes the following electrochemical reactions:



In normal conditions, ion Fe^{2+} are easy to combine with OH^- to form $\text{Fe}(\text{OH})_2$ that may be deposited on ilmenite particles' surface and retard further dissolution of Fe from ilmenite. Thanks to the actions of NH_4^+ and Cl^- ions, the formation and deposition of iron hydroxide on the surface of ilmenite particles are minimized [1, 2]. NH_4^+ ions dissociated from NH_4Cl reacting with hydroxyl ions according to the reaction:



Then, NH_3 from the above reaction acts with iron ions to form iron-containing complexions. Complex $\text{Fe}(\text{NH}_3)_x^{2+}$ ions transport Fe^{2+} from the ilmenite surface to the solution and then decompose to form superfine iron oxide or hydroxide particles [1].

As a result, the process is not only separating iron from ilmenite particles to form artificial rutile but also creating a byproduct of superfine iron oxide that can be used as a raw material to produce pigments.

According to the above analysis, based on actual electricity, ore reserves, and quality of ilmenite in some mining areas in Vietnam and cared for environmental issues, the Becher method is considered highly feasible in both technical and economic sense also to be an environment-friendly method.

3 Results and Discussions

Several experiments were conducted on the ilmenite concentrates of placers of Binh Thuan province to verify the Becher method's ability.

Diffraction analysis of the ilmenite concentrate samples (Fig. 3) show that the main components of concentrates include: ilmenite (FeTiO_3), pseudorutile ($\text{Fe}_2\text{Ti}_3\text{O}_9$), small amounts of rutile (TiO_2), and hematite (Fe_2O_3).

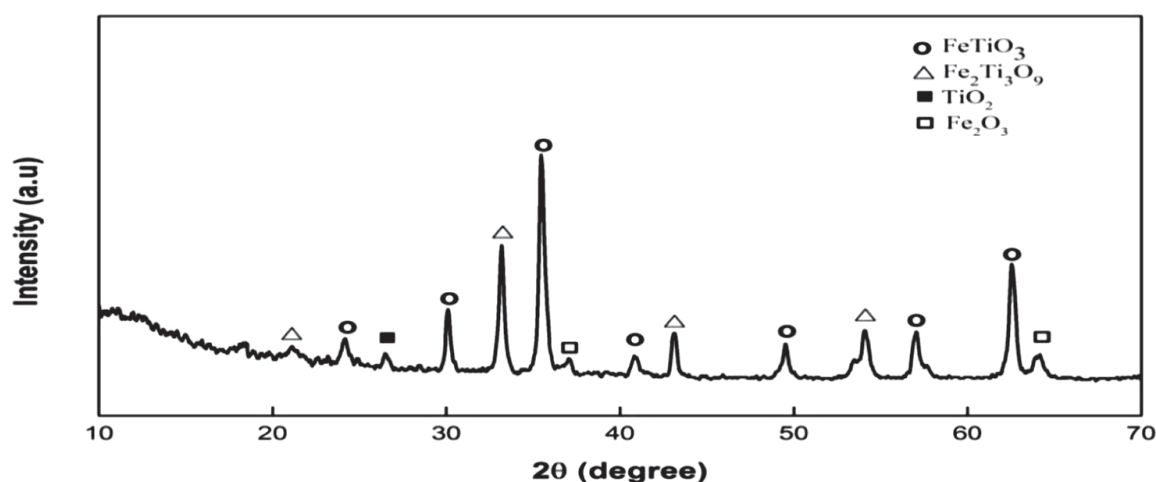


Fig. 3. XRD analysis image of ilmenite concentrate sample

Table 1. Composition of ilmenite concentrate sample (by weight)

Oxide	% by weight	Oxide	% by weight
TiO ₂	52.18	CaO	0.20
Al ₂ O ₃	0.95	MgO	0.36
Fe ₂ O ₃	30.40	MnO	2.77
FeO	11.52	Cr ₂ O ₃	0.11
SiO ₂	1.50	ZrO ₂	0.33
P ₂ O ₅	0.04	SO ₃	0.36

The analytical results also showed that, in the composition of Binh Thuan ilmenite concentrate, iron existed in ilmenite in both forms of oxide FeO and Fe₂O₃ (Table 1). Fe₂O₃ accounts for 72.52% of total iron oxide, bringing a benefit because it becomes easier to reconstitute than FeO [1]. The ilmenite is also quite fine, and the size fraction 0.1–0.2 mm was predominant (Table 2). Therefore, there is no need to use the grinding process for this concentrated sample.

Table 2. The size distribution of the ilmenite concentrate sample

Size (mm)	>0.5	0.5–0.2	0.2–0.1	<0.1	Total
% by weight	0.19	7.91	60.76	31.14	100.00

A reduction roasting pretreated the samples at 1100 °C for about 3 h. Fine coals were used as fuel for reduction roasting. A magnetic separator removed any unburned coals in the roasted product. The roasted ilmenite concentrate samples were leached in NH₄Cl solution to form iron oxide and artificial rutile. The formed fine iron oxide was removed by gravity sedimentation. The resulted solid product rich in TiO₂ was then further leached by enhancing sulfuric acid to remove residual iron.

The X-ray analysis (Fig. 4) showed that there was still some unreduced iron amount, which existed as FeTi₃O₁₀, FeTiO₃. The chemical analysis results used to evaluate the reduction level showed that over 85% of Fe in ilmenite concentrates had been converted to metal iron (Fig. 4). According to the Becher method, unreduced iron would not be removed from ilmenite by leaching solution. Further studies on the reduction process for ilmenite concentrates of Vietnam should be conducted in the future to obtain the highest reduction efficiency (Fig. 5).

The studied leaching parameters included the concentration of NH₄Cl solution, the solution's temperature, and leaching time. The artificial rutile product was analyzed by TiO₂ to evaluate leaching efficiency. The results are shown in Table 3 and Figs. 6, 7, and 8. Experiment results showed that most of the iron were removed from ilmenite and precipitated as oxide with a superfine particle size (<42 µm) in red color. This byproduct may be used in the production of pigments.

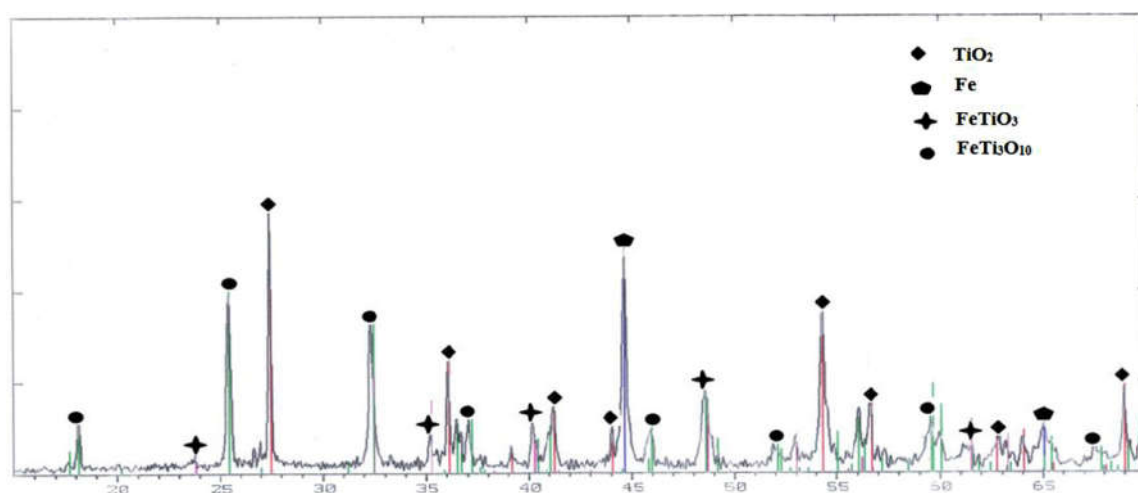


Fig. 4. XRD analysis image of ilmenite concentrate after reduction

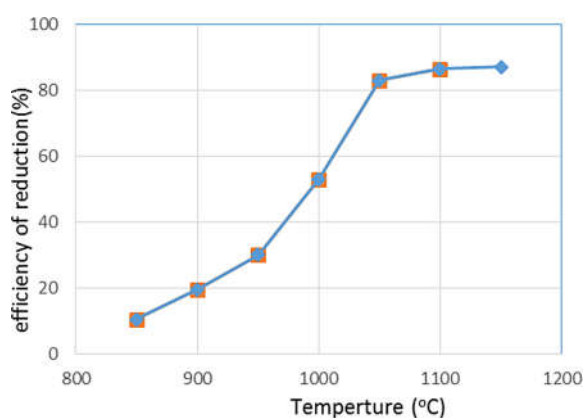


Fig. 5. Effect of temperature on reduction efficiency

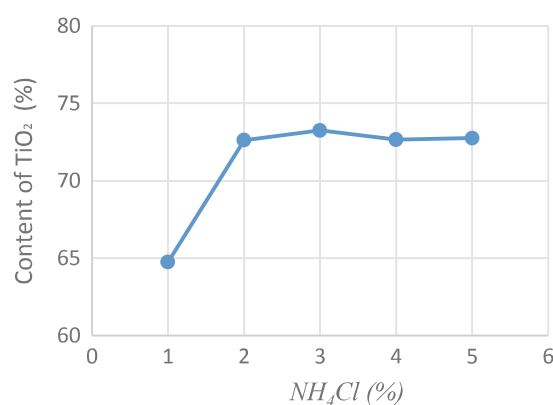


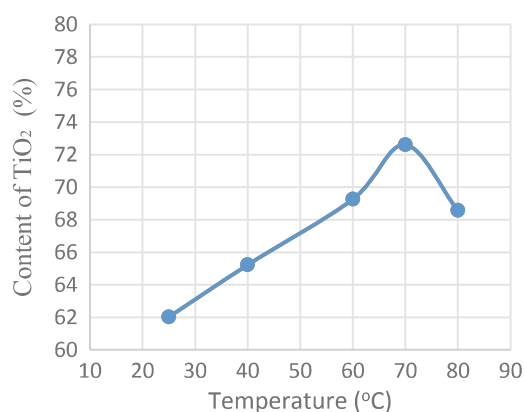
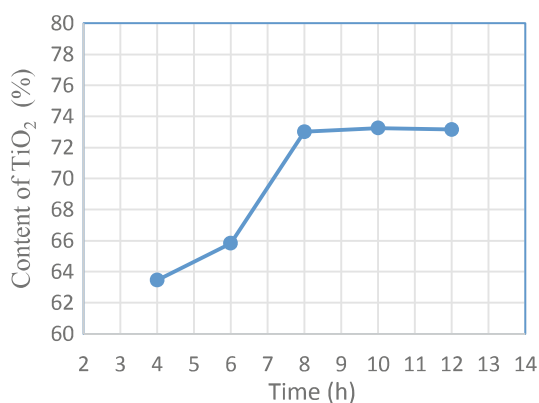
Fig. 6. Effect of NH₄Cl concentration

Table 3. Results of tests at different technological leaching modes

Solution NH ₄ Cl (%)	% TiO ₂	T (°C)	% TiO ₂	Time (h)	% TiO ₂
1	64.74	25	62.02	4	63.45
2	72.61	40	65.23	6	65.83
3	73.25	60	69.26	8	73.01
4	71.85	70	72.61	10	73.25
5	72.15	80	68.58	12	73.15

Figure 7 shows that the content of TiO₂ increased gradually and reached the peak at 70 °C, then reduced with a further increase of the temperature due to the opposing effects of oxygen solubility and its diffusivity with the temperature increase [10].

A small amount of iron was not separated from ilmenite because the reduction roasting process was not perfect. Hence, the existing iron in the form of oxide was not

**Fig. 7.** Effect of leaching temperature**Fig. 8.** Effect of leaching time

(a)



(b)

Fig. 9. Synthetic rutile (a); By-product iron oxide powder (b)

removed from ilmenite or because a part of iron was oxidized and deposited back on the surface of ilmenite particles during the process of separation. This iron can be treated with acid. After the acid leaching process for removing residual iron, the TiO₂ content is increased above 85%. The Fe content is dropped to 3.15% (Table 4).

Table 4. Results after 2 h leaching with acids

TiO ₂ (%)	
Before leaching	After leaching
73.25	85.38

4 Conclusions

According to studies, Becher method has shown to be a promising method in the future for Vietnamese titanium ore processing. With this method, not only artificial rutile with

high TiO_2 content can be produced, but also byproduct is produced in the form of superfine red iron oxide powder. The leaching process is carried out in a non-toxic, less corrosion NH_4Cl solution (Fig. 9). Although acids are used in the method, this is only in an auxiliary stage to remove the residual iron. If the extraction process is optimized, the excess iron is reduced, so the acid is no longer a big problem. Therefore, this is an environmentally friendly method that aligns with current and future technology trends.

Preliminary experimental results on actual ilmenite concentrate also produced artificial rutile products with TiO_2 content of over 85% and superfine iron oxide powder with a bright red color used for pigment production. Although the actual experimental results were not such high as the published works about the Becher method, these were just results of the initial experiments for the ilmenite concentrates of Vietnam. To apply this method, it is necessary to have more in-depth studies on the iron reduction roasting process of ilmenite concentrates, on separation and use of by product in form of superfine iron oxide powder and different technological modes.

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