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Recovery of Ammonium Metavanadate from Spent Catalyst

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Abstract

Utilization of spent catalysts serves to meet the needs of vanadium and to overcome the environmental problem since vanadium is categorized as a hazardous and toxic material. Vanadium from the spent catalysts can be recovered in the form of V_2O_5 or NH_4VO_3. However, vanadate compounds (NH_4VO_3) are considered to be more valuable due to their higher price and easier production process, compared with V_2O_5. This study aims to find adequate operating conditions to obtain high yields and high purity of NH_4VO_3 crystals. The results show that the presence of iron compounds in the extract made the crystals contaminated by brownish colour, so it decreased its purity. Therefore, iron compounds need to be separated first with precipitation. Crystals of NH_4VO_3 with yield of 60% on spent catalysts and purity of 75% were obtained by extraction using solvent Na_2CO_3 1.887 M for 60 minutes at room temperature with weight ratio of V_2O_5 in spent catalyst toward solvent volume (R_{vp}), 0.006 gram V_2O_5/mL Na_2CO_3. It was then continued by precipitation of iron compounds at pH of 12 for 2 hours and crystallization of NH_4VO_3 using NH_4Cl 11.215 M for 4 - 5 hours at 60°C.

Keywords: vanadium, vanadate, catalyst, waste, extraction

1. Introduction

Vanadium is a transition metal with many benefits, but its amount is limited. Vanadium level in Earth's crust is very low, only 0.015% (Kleinberg, et al., 1960). 85% of vanadium is used for metal industry, e.g. in processing titanium alloy and iron. As a catalyst, vanadium serves to make catalysts of dehydrogenation, hydrogenation, alcohol oxidation, dioxide hydrogenation, hydrocarbon oxidation, haloperoxidation, sulphur oxidation, aldehyde/ketone oxidation, and ROMP (Langeslay et al., 2019). One of the most frequently used vanadium oxides in the industry is V_2O_5. In Indonesia, these compounds are commonly used as catalysts of contact process in sulphate acid production. Besides V_2O_5, vanadium compound frequently used in industry is ammonium metavanadate (NH_4VO_3) (Nordberg, 1998). These compounds are used as catalyst, dye, chemical reagent, and ceramic coating (Ayres, et al., 1998).

This need for vanadium keeps increasing, while its availability keeps decreasing. Metal ore has vanadium at small amount (less than 2% or ppm scale) (Nejad et al., 2018). Therefore, it requires innovations to get vanadium. Considering that the main use of vanadium is as catalyst, the spent catalyst is one of potential sources of vanadium. An average use of vanadium catalyst (including regeneration) is 10 years; after this period, the catalyst becomes non-active due to thermal degradation, fouling, and poisoning, so it cannot be used for commercial process (Yin & Finke, 2005). Vanadium catalyst waste belongs to dangerous, toxic waste according to Indonesia Constitution No. 32 Year 2009, so it can lead to environmental problems (Ifa, et al., 2017). Thus, the use of vanadium from spent catalyst is beneficial in terms of economy and useful for prevention of environmental problem (Zeng, et al., 2009).

Recovery process of vanadium from catalyst or metal ore can be performed with pyrometallurgy or hydrometallurgy (Navarro et al., 2007). This process is then continued with crystallization to get a purer product. This process has been developed for recovery of other metals with high values, such as molybdenum from spent catalyst (Kar, et al., 2005). Pyrometallurgy can be done by roasting or direct smelting which requires high temperature (above 300°C to get the best purity) (Kar et al., 2005). On the other hand, leaching/extraction of solvent (with hypochlorite, acid, base, ammonia, or biological agents) (Zhang, et al., 1995) (Zhang, et al., 1996), ion exchange (Li et al., 2009)(Beolchini et al., 2012), carbon adsorption (Namasivayam & Sangeetha, 2006), and precipitation (Mazurek, 2013) belong to hydrometallurgy. Although its operating cost is low, precipitation is not capable of providing good vanadium yield. Besides, productivity and flexibility of the activated carbon which is low and limitation of ion exchange scale-up encourage the diversity of research about solvent extraction for recovery of vanadium (Marafi & Stanislaus, 2008). High molecular weight amines (HMWA) solvent and organophosphorus acid are used commercially for this function, but it can form an emulsion which inhibits the next segregation process (Tavakoli & Dreisinger, 2014). Besides, alkaline phosphatase solvents, such as DEHPA and TOPO, have a low selectivity since it can form an emulsion and extract iron and aluminum at several pH ranges (Sahu et al., 2013). Current research about Cyanex 271 organophosphorus can solve problem in forming an emulsion and reach vanadium yield up to 99%, but it is still limited by vanadium purity since aluminum, iron, and titanium are also dissolved (Painuly, 2015). When using three leaching stages with 15% of sulphate acid (100°C and solid/liquid ratio of 0.2), oxidative precipitation, and extraction with 60-70% of HNO_2 (120°C) (Khorfan & Reda, 2001), a recovery efficiency in vanadium around 70% is obtained. Another research for separating nickel and vanadium from the spent catalyst for making sulphate acid shows that acidic leaching (0.3-1M H_2SO_4) provides recovery efficiency in vanadium of 59% when combined with alkali-acidic leaching (4 M NaOH, continued with 0.5 M H_2SO_4) to reach 78% (Ognyanova et al., 2009). The use of oxalate acid 0.50 M and 0.66 M H_2O_2 to process the spent catalyst Ni-Mo/Al_2O_3 is known to provide vanadium yield of 80% at a temperature of 70°C (Szymczycha-Madeja, 2011). Alkali leaching is preferred over acidic leaching since it can dissolve vanadium more selectively (Mohanty et al., 2011).

The impurities can reduce the purity of NH_4VO_3 crystal, though its yield shows high value. Therefore, a modification is required for the recovery process of vanadium from the spent catalyst. This research discusses two recovery stages of vanadium into NH_4VO_3 from the spent catalyst, with a wider scope at crystallization stage due to the limitation of previous literature to discuss that matter. This research aims to obtain an adequate operating condition to obtain NH_4VO_3 crystal with high yield and purity through alkali leaching process, by adding H_2O_2. Operating conditions in which its effect will be studied toward yield and purity of ammonium metavanadate are (1) concentration of leaching agent, reaction time, mass ratio of V_2O_5 in the spent catalyst on solvent volume (R_{vp}) for extraction stage and (2) temperature and process pH for crystallization stage.

2. Methodology

2.1. Materials

The chemicals used for extraction stage were the spent catalyst from contact process in PT Petrokimia Gresik, Na_2CO_3 1.887 M solvent, and H_2O_2 as oxidizer. For crystallization stage, the materials used were V_2O_5 in Na_2CO_3 solution (as model solution 1), iron in Na_2CO_3 solution (as model solution 2), H_2SO_4 9 M and NaOH 6 M as pH regulator in the iron precipitation, and NH_4Cl 11.215 M solution as the salting out agent in crystallization of NH_4VO_3.

2.2. Extraction Stage

The first stage of this research was the vanadium extraction from the spent catalyst based on the Rokukawa Method. The extraction was done by stirring in chemical glass of 1 L which contained the spent catalyst with a particle size of 100 mesh, Na_2CO_3 solvent, and H_2O_2 solution for 60 minutes at room temperature. The variables in this stage were R_{vp}, comparison of V_2O_5 weight in spent catalyst on the volume of Na_2CO_3 (0.002 - 0.011 gram V_2O_5/ml Na_2CO_3) solvent, and concentration of H_2O_2 (0.0 – 2.4 M) solution.

The suspension of extraction yield were filtrated using Buchner funnel. Volume of filtrate (extract) was then measured. An analysis was conducted on the extract with titrimetric method to identify vanadium level with atomic absorption spectrophotometry (AAS) method to identify the content of iron, aluminum, and silica.

2.3. Crystallization Stage

The second stage of this research was the crystallization of the model solution based on Baker Method. There were two model solutions to be fed in this stage, namely Na_2CO_3 which only contained V_2O_5 (model solution 1) and Na_2CO_3 solution which contained V_2O_5 and iron compounds (model solution 2).

2.3.1. Crystallization of model solution 1

The crystallization of model solution 1 was performed by pouring model solution 1 which had been heated up to 60°C into a chemical glass which contained the heated solution of NH_4Cl 11.215 M, with a ratio of 1:1. The crystallization was performed at room temperature and 60°C, with the time variation of 2-8 hours. For the crystallization at room temperature, the chemical glass which contained the model solution and NH_4Cl was placed in a fume hood and left for a certain crystallization time. Meanwhile, for the crystallization at a temperature of 60°C, the chemical glass was placed in a water bath with a temperature that had been set up. The formed crystal was then separated from its solution with a simple filtering method. After that, the crystal was dried and measured until its weight was constant. For the analysis, the dry crystal was dissolved in H_2SO_4 solution with heating. An analysis was conducted in titrimetry to identify vanadium in the crystal.

2.3.2. Crystallization of model solution 2

Before conducting the crystallization, iron compounds in model solution 2 must be reduced/eliminated by precipitation at certain pH for 120 minutes. In this research, the pH of iron precipitation was varied between 2-13. With the initial pH of the solution of around 10, the pH was regulated by adding H_2SO_4 9 M and NaOH 6 M solutions. After the pH was obtained, the formed solid was precipitated for 120 minutes and separated from its solution with a simple filtering method. The obtained filtrate I was analyzed using titrimetry method to identify the vanadium content and AAS to identify the iron content.

2.3.3. Choosing crystallization method for filtrate

Furthermore, the filtrate for crystallization was chosen based on its iron and vanadium content. The selected filtrate was filtrate with low iron content and high vanadium content. An analysis of the iron and vanadium content was conducted by dissolving dry crystal in H_2SO_4 solution with heating. An analysis of the iron content was conducted with AAS, while the vanadium analysis was performed with titrimetry. A crystallization was conducted to model solution 1 at temperature of 60°C with time variation between 240-480 minutes. The formed crystal was then separated from its solution with a simple filtering method, while its crystal was dried and measured until its weight was constant.

2.4. Crystallization Test on the Spent Catalyst Extract

The test was conducted on an extract of the spent catalyst with R_{vp} of 0.006 gram V_2O_5/ml Na_2CO_3 without H_2O_2 as oxidizer. In this test, iron precipitation was performed only at pH above 10.

2.5. Experimental Variable

This research was conducted with variables as shown in Table 1.

Table 1. Experimental Variable

Stage	Variable
Extraction	• Concentration of H_2O_2 in feed: 0; 0.8; 1.6; and 2.4 M • Comparison of V_2O_5 weight on solvent volume (R_{vp}): 0.002 ; 0.004 ; 0.006 ; 0.008, and 0.011 gram V_2O_5 / ml Na_2CO_3
Crystallization of model solution 1	• Crystallization time: 120; 180; 240; 300; 360; 420; and 480 minutes • Crystallization temperature: 30 and 60°C
Crystallization of model solution 2	• pH of iron compounds precipitation: 2 – 13 • crystallization time NH_4VO_3: 240; 300; 360; 420; and 480 minutes

2.6. Analysis Method

An analysis was conducted on the spent catalyst, model solution, filtrate of iron precipitation result, and NH_4VO_3 crystal. The methodology used was:

1. Gravimetric to determine the content of SiO_2 and Al_2O_3 in the spent catalyst;
2. Titrimetry to determine the content of V_2O_5 and iron (Jones Reduktor) in the spent catalyst and V_2O_5 in spent catalyst extract, model solution, filtrate yield of iron and crystal precipitation, NH_4VO_3;
3. Atomic Absorption Spectrophotometry (AAS) to determine the content of vanadium, iron, aluminum, and sodium in the spent catalyst; the content of vanadium, iron, aluminum, and silica in extract of the spent catalyst and NH_4VO_3 crystal; vanadium and iron in model solution and filtrate yield of iron precipitation.

Solids which were analyzed with titrimetry and spectrophotometry methods must be dissolved in acid solvent or melted with base (NaOH) to be dissolved in acid.

3. Result and Discussion

3.1. Spent Catalyst Analysis

The analysis result of the spent catalyst in contact process from PT Petrokimia Gresik is shown in Figure 1. Vanadium in the spent catalyst is larger than in the titanomagnetite ore (0.08–1.6%-b V_2O_5) which was made as the primary source of vanadium all this time. Therefore, the spent catalyst is highly potential to be a vanadium source. However, this catalyst contains impurities which can affect the quality of yield.

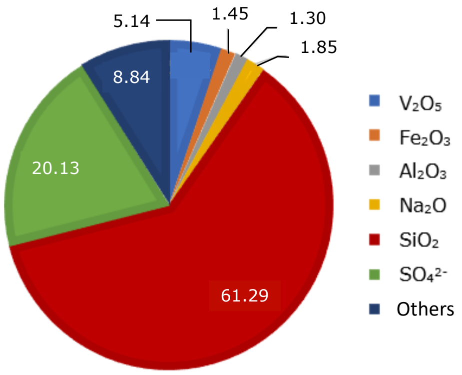

Figure 1. Composition of the spent catalyst in contact process

3.2. Extraction Stage

Rokukawa Extraction used H_2O_2 solution to oxidize the vanadium compounds with valence under 5 into V_2O_5 based on the reaction in equation 1. This oxidation increased the amount of the extracted vanadium since the compound which can be extracted with Na_2CO_3 solvent was V_2O_5 based on equation 2 (Baker, et al., 1950).

$$V_2O_4 + H_2O_2 \rightarrow V_2O_5 + H_2O \qquad (1)$$
$$V_2O_5 + Na_2CO_3 \rightarrow 2\ NaVO_3 + CO_2 \qquad (2)$$

Figure 2 shows that the use of H_2O_2 did not affect the extraction yield, though the added amount of H_2O_2 had been excessive. The use of H_2O_2 30-90 times of its stoichiometric comparison did not increase the extracted vanadium amount. It was different from a result obtained by Rokukawa (1988) in which the use of H_2O_2 that much can increase the extraction percentage to 80-85%. This shows that the spent catalyst used by Rokukawa still had vanadium compounds with valence under five (Rokukawa, 1988). Meanwhile, the spent catalyst in this research was mostly in V_2O_5, so it did not require additional H_2O_2 solution. Furthermore, this pattern was shown by another research using oxalate acid as the acidic leaching agent for the spent Hydrodesulfurization (HDS) catalyst for 4 hours. At a temperature of 50°C, an addition of H_2O_2 up to 3.0 M increased recovery of all metals (90% Mo, 94% V, 65% Ni and 33% Al) (Mulak et al., 2006).

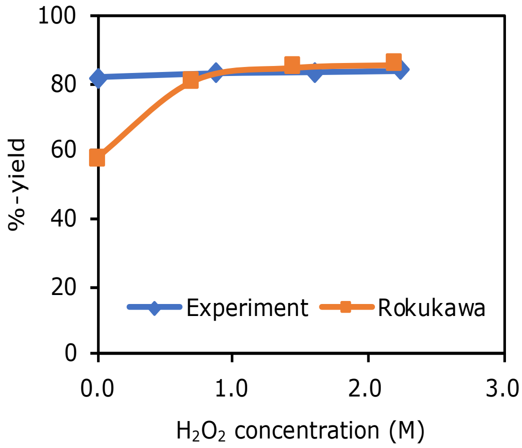

Figure 2. Effect of H_2O_2 on V_2O_5 yield

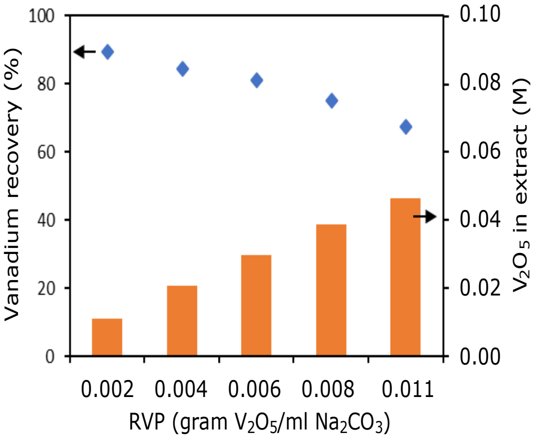

Figure 3. Effect of R_{vp} on yield and concentration of V_2O_5

At the extraction stage, V_2O_5 in the spent catalyst was diffused into a Na_2CO_3 solvent due to the concentration gradient. The smaller the weight comparison of V_2O_5 in the spent catalyst on the solvent (R_{vp}) volume, the higher the vanadium extract amount will be. The affordable price of R_{vp} shows that much solvent was used, so the feed became aqueous and made the concentration gradient larger, while the mass transfer rate was quite high. Meanwhile, a large R_{vp} (feed was not aqueous) obtained a small concentration gradient and as the result, its mass transfer rate was low. Thus, when the extraction was done at the same time (60 minutes), amount of V_2O_5 extracted in an aqueous feed was larger than in a dense feed.

The extract yielded in this stage was fed for a crystallization stage. The concentration of V_2O_5 in the extract determined whether or not NH_4VO_3 was precipitated. In Baker crystallization, the comparison between the NH_4Cl solution and the extract ($NaVO_3$ solution) was 1:1. When it was assumed that the whole $NaVO_3$ was converted into NH_4VO_3, the vanadium concentration in solution at the crystallization process became half of the vanadium concentration in the extract due to the addition of NH_4Cl. To make the NH_4VO_3 precipitated, the NH_4VO_3 concentration in the solution must be larger than the NH_4VO_3 solubility in an NH_4Cl solution, 0.0094 M V_2O_5.

Figure 3 shows that when R_{vp} 0.002 gram V_2O_5/ml Na_2CO_3 was used (based on what was used by Rokukawa), the obtained vanadium in the extract was 0.011 M V_2O_5 and its concentration crystallization process was 0.0055 M V_2O_5. NH_4VO_3 was not precipitated since this concentration was smaller than the NH_4VO_3 solubility in NH_4Cl. When using R_{vp} 0.004 gram V_2O_5/ml Na_2CO_3, the obtained vanadium in the extract was 0.021 M V_2O_5 and its concentration crystallization process was 0.0105 M V_2O_5. This concentration was larger than the NH_4VO_3 solubility in NH_4Cl. However, the vanadium compound in this solution decreased due to the impurities elimination in the extract, so the concentration in the crystallization process was expected to decrease up to lower than the NH_4VO_3 solubility in NH_4Cl.

The use of R_{vp} 0.006 gram V_2O_5/ml Na_2CO_3 resulted in the extract with a vanadium concentration of 0.030 M V_2O_5, so its concentration crystallization process was 0.015 M V_2O_5. This concentration was much larger than the NH_4VO_3 solubility in NH_4Cl, so the solution concentration in the crystallization process decreased below its solubility in the process of extract-polluting compound elimination. Although the use of R_{vp} was larger than 0.006 gram V_2O_5/ml Na_2CO_3, it resulted in an extract with a high vanadium concentration at a low extraction percentage, so it was not recommended to be used. Based on these reasons, R_{vp} in this extraction stage was 0.006 gram V_2O_5/ml Na_2CO_3. The result of the spent catalyst extraction for 60 minutes with R_{vp} 0.006 gram V_2O_5/ml Na_2CO_3 and concentration of Na_2CO_3 1.887 M is shown in Table 2.

These values tended to approach a vanadium yield from the spent catalyst of selective catalytic reduction (SCR) with the leaching agent of 2 M NaOH and 0.2 M Na_2CO_3, and ratio of solid and liquid 1:20, of 86% (Kim et al., 2015). Table 2 shows that the Na_2CO_3 solvent extracted V_2O_5 from the spent catalyst and dissolved compounds of iron, aluminum, and silica, but the extracted amount of aluminum and silica was little, so it can be assumed that these two compounds did not affect the yield quality. Meanwhile, iron compounds were extracted at a quite large amount. Although it was smaller than the vanadium concentration, iron was highly influential to the colour of the NH_4VO_3 crystal since it made the crystal brown. In order to improve the yield quality, in terms of colour and purity, the concentration of iron compounds must be lowered or before crystallization process.

Table 2. Result of the spent catalyst extraction

Component	Concentration (M)	Yield (%)
V_2O_5	0.03	81.27
Fe_2O_3	0.005	42.02
Al_2O_3	0.00007	0.42
SiO_2	0.00096	0.07

3.3. Crystallization Stage

In this stage, two feed types were used, namely Na_2CO_3 which contained V_2O_5 (model solution 1) and a Na_2CO_3 solution which contained V_2O_5 and iron compounds (model solution 2). The concentrations of vanadium and iron in feed were in accordance with the extract of the spent catalyst, namely 0.030 M and 0.005 M Fe_2O_3.

The crystallization of model solution 1 was affected by temperature and the time of crystallization as shown by Figure 4 which indicates that the amount of NH_4VO_3 crystal yield increased along with the temperature rise. Its reaction speed increased along with the increasing temperature, so the yield increased. Thus, based on the experiment, the crystallization of NH_4VO_3 should take place at a high temperature, around 60^{o}C.

Figure 4 shows that the amount of the formed NH_4VO_3 crystal kept increasing, but it tended to be constant after the crystallization more than 360 minutes. At that time, the NH_4VO_3 crystal yield was quite high, around 93%, which showed that almost all vanadium was crystallized. However, this high yield was not followed by a high purity of NH_4VO_3 crystal yield. Figure 5 shows that the crystal purity decreased along with the additional time for crystallization. It was caused by the forming of NH_4Cl crystal as the result of evaporation during the crystallization. It decreased the solution volume, while at a time the NH_4Cl concentration exceeded its solubility in water, so NH_4Cl was crystallized. The existence of NH_4Cl crystal can be identified with white acid when the crystal was heated in a H_2SO_4 solution.

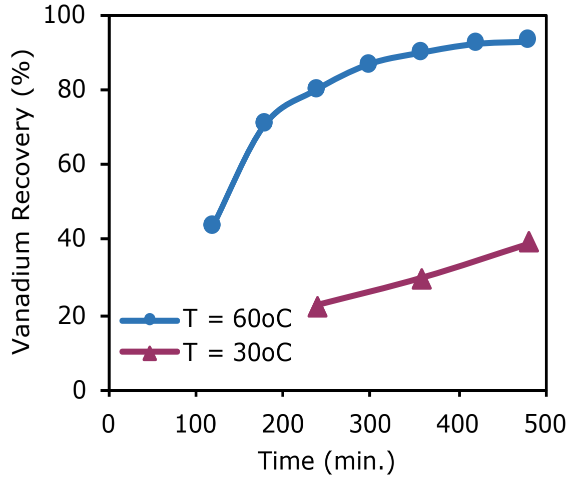

Figure 4. Crystallization result of model solution 1

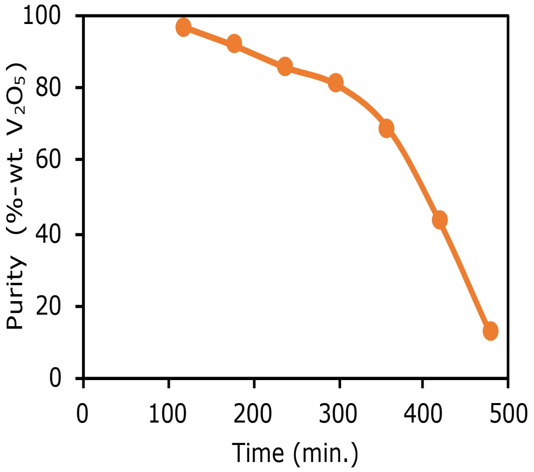

Figure 5. Purity of NH_4VO_3 crystal

Based on Figures 3 and 4, the crystallization process of model solution 1 should be performed for 240-300 minutes (4-5 hours). At that interval, the NH_4VO_3 crystal had high yield and a purity of 80.34%-w which exceeded the purity of commercial NH_4VO_3 (76.74%-w). Crystal with higher purity can be achieved when the NH_4Cl crystal is not formed during crystallization. One of the methods to achieve this is reflux.

An extraction process cannot be directly performed in model solution 2 since the solution still contained iron. Thus, a reduction/elimination of iron compounds from the solution needed to be performed with precipitation at a certain pH. The effect of pH on the precipitation result is shown in Figure 6. Iron in the filtrate decreased at a pH range of 2-7. It means that Fe^{2+} can be precipitated since its solubility decreased along with pH increase. Fe^{2+} was precipitated as $Fe(OH)_2$ based on equation 3. On the other hand, iron in the filtrate increased with pH increase from 7 to 9. It shows that the dissolved $Fe(OH)_2$ sediment became $HFeO_2$- based on equation 4.

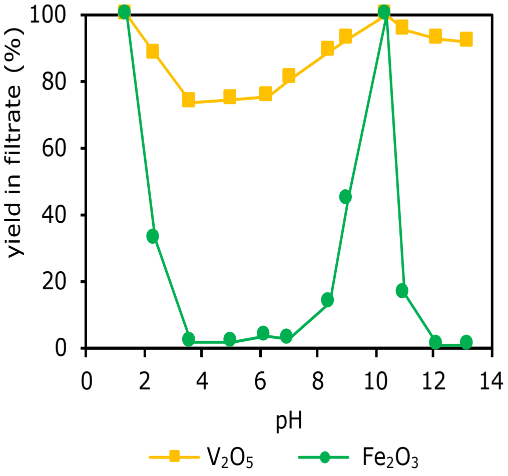

Figure 6. Effect of pH on precipitation result

The solubility of $HFeO_2$- increased along with the pH increase, while its solubility was larger than $Fe(OH)_2$ for pH above 9. However, at pH above 10, the amount of iron in filtrate decreased. It shows that the iron compounds were precipitated again as $Fe(OH)_3$ based on equation 5. Precipitation was started at pH around 10.68 (Pourbaix, 1974).

$$Fe^{2+} + H_2O \rightarrow Fe(OH)_2 + 2\,H^+ \quad (3)$$
$$Fe(OH)_2 \rightleftharpoons HFeO_2^- + H^+ \quad (4)$$
$$HFeO_2^- + H_2O \rightleftharpoons Fe(OH)_3 + e \quad (5)$$

Research shows the result (Figure 6) that iron compound precipitation can be performed in two pH ranges, namely 3.6-8.4 and 11-13.2. However, at pH range of 3.6-8.4, much vanadium compounds were precipitated (11.63-26.8%), while it was only 4.85-7.87% at pH of 11-13.2. Besides, the filtrate that was obtained by the precipitation process at pH 11 and pH range of 3.6-8.4 was brown; it shows much Fe_2O_3 compounds at the low concentration (8.85×10^{-5} – 7.63×10^{-4} M). Thus, in order to get a vanadate solution which was quite pure, iron compound precipitation should be performed at a pH range of 12 - 13.2. Therefore, the crystallization feed used in this part was model solution 2 in which its iron content has been reduced at pH 12-13.2. This range was different from the precipitation using $(NH_4)_2SO_4$ which was better at pH 7.2-7.6 (Gladyshev et al., 2015).

The crystallization of model solution 2 was performed at a temperature of 60°C and time variation between 4-8 hours. The crystallization result is shown in Figure 7. The amount of the formed NH_4VO_3 crystal increased along with the increase of crystallization time and it tended to be constant after more than 360 minutes of crystallization. At that time, the yield of NH_4VO_3 crystal of around 82% was recommended for model solution with iron precipitation at pH 12 and 13. This yield was smaller than the crystallization yield of model solution 1 which reached 93% at the same time. Vanadium compounds were also precipitated when reducing/eliminating the iron compounds. Meanwhile, the purity of NH_4VO_3 crystal yield decreased along with the crystallization time, as shown in model solution 1. As previously described, it was caused by the forming of NH_4Cl crystal.

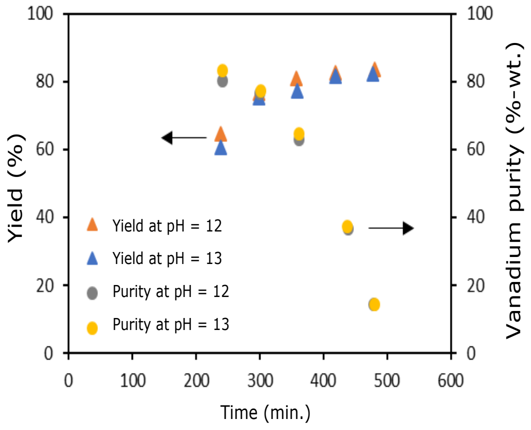

Figure 7. Yield and purity of NH_4VO_3 crystal from model solution 2

In Figure 7, iron precipitation at pH 12 and 13 did not provide a meaningful difference, in terms of the yield and purity of NH_4VO_3 crystal. Therefore, iron compound precipitation was performed at pH 12 since it can result in a colourless filtrate with a tiny iron concentration, namely 1.66×10^{-5} M Fe_2O_3. In terms of time, the crystallization of model solution 2 should be performed for 4-5 hours since the NH_4VO_3 crystal yield was quite high at that time and the purity was 77.93 %-w, exceeding the commercial NH_4VO_3 (76.73 %-w) purity. Like crystallization of model solution 1, the crystal purity can be improved using a reflux implementation.

3.4. Crystallization on Spent Catalyst Extract

The recovery result of vanadium from the spent catalyst is shown in Figure 8. It shows that the vanadium extracted from the spent catalyst was quite high, around 81.27%. However, this yield decreased into 71.98%, after reduction/elimination of iron compounds from the extract. It means that vanadium compounds were precipitated in the iron precipitation process.

The vanadium yield from the crystal was smaller than in filtrate I. It shows that not all vanadium in filtrate can be crystallized. It was caused by the consideration to stop the crystallization before much NH_4Cl was crystallized again, though there was a possibility that NH_4VO_3 kept increasing. As the result, the NH_4VO_3 crystal yield decreased. Besides, the forming of NH_4Cl decreased the purity of the NH_4VO_3 crystal, so it must be avoided (Figure 8).

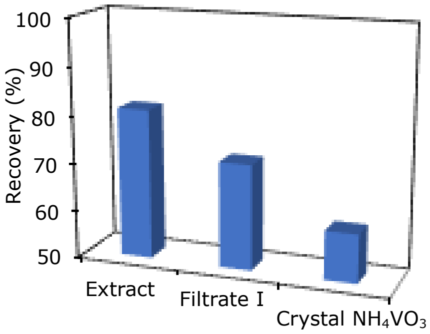

Figure 8. Recovery result of vanadium from the spent catalyst

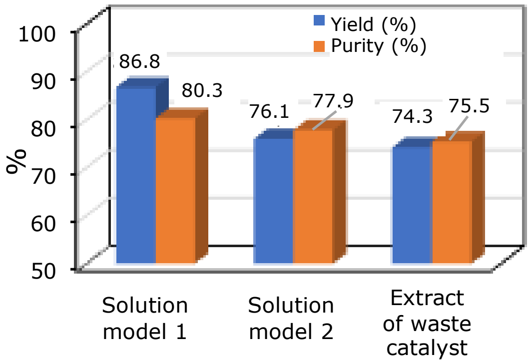

Figure 9. Comparison of crystallization result in model solution 1, model solution 2, and extract of the spent catalyst

As shown in Table 3, vanadium in NH_4VO_3 crystal in the research result was still below the standard of commercial NH_4VO_3 crystal. Meanwhile, compounds of iron, aluminum, and silica were relatively the same with commercial NH_4VO_3 crystal. In order to improve the purity in NH_4VO_3 crystal yield, excess NH_4Cl should not crystallize again.

Crystallization test on the spent catalyst extract was conducted by following the crystallization procedure of model solution 2. It was caused by the consideration that the polluting compounds in the spent catalyst extract were only iron compounds. The crystallization was performed at a temperature of 60°C for 5 hours with the extract feed in which iron precipitation was performed at pH 12.

A comparison of the crystallization result in model solution 1, model solution 2, and the extract of the spent catalyst is shown in Figure 9. The NH_4VO_3 crystal yield from model solution 2 and the spent catalyst extract was smaller than yield in model solution 1. Vanadium compounds were also precipitated when reducing/eliminating the iron compounds. Beside the yield, the crystal purity in model solution 2 and the catalyst extract was lower than in model solution 1 since it had the polluting compounds in the solution. Model solution 2 had iron compounds, while the spent catalyst extract had iron, silica, and aluminum.

Table 3. Composition of NH_4VO_3 Crystal

Component	Composition (%-b)	
	Research	Commercial
V_2O_5	75.48	76.73
Fe_2O_3	0.01	0.01
Al_2O_3	<0.01	0.01
SiO_2	<0.10	0,10

Table 3 shows a comparison of the NH_4VO_3 crystal composition in the research result and commercial crystal. The vanadium content from the research was still below the standard of commercial NH_4VO_3 crystal. Meanwhile, it can be said that the compounds of iron, aluminum, and silica almost met the standard of commercial NH_4VO_3 crystal. Therefore, to improve the purity of NH_4VO_3 crystal yield, a recrystallization of NH_4Cl excess must be prevented as discussed in previous section.

4. Conclusion

The spent catalyst in contact process of PT Petrokimia Gresik has a potential to be made as a source of vanadium. For the preparation in crystallization stage, the best condition of the extraction stage is a ratio between the V_2O_5 weight in spent catalyst and the solvent volume of around 0.006 gram V_2O_5/ml Na_2CO_3. Iron compounds are the most influential impurities on quality of NH_4VO_3 crystal yield. Other impurities such as silica and aluminum are relatively negligible. The iron concentration in feed solution at crystallization stage must be reduced with precipitation. In order to get the best result, iron precipitation is performed at a pH of 12. With a crystallization at a temperature of 60°C, the NH_4VO_3 yield for feed of the spent catalyst extract reached around 75% with a crystal purity of around 76%-b.

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