Removal of cyanide from alumina smelter wastewater using precipitation and filtration technique

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Abstract. Aluminum is a metal that is used in many products because of its good conducting properties. However, in the production process, aluminum is not obtained easily but through a long process. In aluminum smelting process, wastewater that is produced indicates the existence of pollutants as determined by several indicators of water pollution, one of which is cyanide that will threaten human and environmental health if not treated properly. This study was conducted to determine the optimal dose of ferrous sulfate to remove cyanide, the precipitation and filtration process efficiency in reducing cyanide, and its effect on pH of wastewater. Data were collected from an aluminum smelting company, and experiments were conducted in the laboratory. Based on results, ferrous sulfate dose of 93 mg/l is the most optimal dose in removing cyanide with an efficiency of 58.74±0.51%, while filtration process provides an efficiency of 81.65±0.42%. Precipitation with ferrous sulfate makes pH value of wastewater decrease, but filtration process increases the value again. Throughout the whole process, cyanide can be reduced by a combination of precipitation and filtration process with the efficiency of 92.43±0.26% and an average final effluent concentration of 0.78 mg/L from an initial concentration of 10.3 mg/L.

1. Introduction

The development of the industrial sector can have a positive impact on national economic growth, as well as a negative impact due to the presence of waste that has the potential to pollute the environment if it is not treated. Wastewater in the industrial sector is a by-product of activities or processes that occur within the industrial sector. Wastewater produced by each industry has different characteristics according to the processes and materials used in the industry. This has resulted in various processing units and wastewater treatment being used in every industrial sector. Cyanide is one of the pollution parameters in wastewater. Cyanide is a substance that endangers human health and will have a very lethal effect when exposed to high concentrations for a long time. The use of cyanide in the industry has been known for a long time, especially in the mining industry. Since its first use in the mining industry in New Zealand in 1887, cyanide, especially sodium cyanide, has played an important role worldwide in extracting gold and other metals such as silver, copper, zinc, and aluminum from ores [1].

In the aluminum smelting process, cyanide in wastewater is usually produced by cooling water used in the gas cleaning system (wet scrubber) in anode baking plants, where the baking plant receives residual carbon anodes (butt) that have been processed in the reduction plant so that air penetration
makes the carbon react with nitrogen in the air and produce cyanide. If it is not appropriately treated, cyanide in wastewater will surely be able to pollute the waters. Cyanide can be removed in various ways, one of which is the precipitation process. Ferrous sulfate is known as a precipitant that can be used to remove the cyanide. The precipitate formed has a bright blue color known as Prussian blue. In the process, initially, cyanide will react with ferrous ions to form ferrocyanide ions with the following reaction.

\[ \text{FeSO}_4 \cdot \text{H}_2\text{O} \ (s) \rightarrow \text{Fe}^{2+} \ (aq) + \text{SO}_4^{2-} \ (aq) + 2\text{H}_2\text{O} \ (l) \]  
\[ \text{Fe}^{2+} \ (aq) + 2\text{CN}^- \ (aq) \rightarrow \text{Fe(CN)}_6^{4-} \ (aq) \]

Ferrocyanide ions will form precipitates with iron, copper, magnesium, cadmium, and zinc with a reasonably extensive pH range, from 2 to 11 [2]. The addition of excess ferrous sulfate will cause an excess of ferrous ions, which results in the formation of ferrous ferrocyanide compounds where these compounds will then be reduced back to bright blue ferric ferrocyanide compounds or often called Prussian blue compounds [3]. The reaction is as follows.

\[ 2\text{Fe}^{2+} \ (aq) + \text{Fe(CN)}_6^{4-} \ (aq) \rightarrow \text{Fe}_2\text{Fe(CN)}_6 \ (s) \]
\[ 3\text{Fe}_2\text{Fe(CN)}_6 \ (s) \rightarrow \text{Fe}_4\text{Fe(CN)}_6 \cdot 3 \ (s) + 2\text{Fe}^{2+} \ (aq) + 4e^- \]

The precipitate formed by the addition of ferrous sulfate will settle to the bottom of the precipitation tank and cause precipitate sludge. When the wastewater flows, the existing precipitate sludge may still be carried away by the flow, resulting in high levels of cyanide remaining in the wastewater being released into the environment. The filtration process is used to fix this problem; when the wastewater passes through the filtration unit, the media used will filter solid precipitates to be retained in the unit to obtain wastewater of better quality. Based on the described background, this research aims to determine the optimal dose of ferrous sulfate used as a precipitant to remove cyanide, the precipitation efficiency, and the dual media filtration process in reducing cyanide levels and its effect on the pH of the wastewater. This study will achieve these goals by comparing the cyanide removal efficiency from different doses of ferrous sulfate and analyzing its tendency to affect the pH of the wastewater.

2. Methodology
This research used an artificial cyanide solution whose cyanide levels were determined from secondary data obtained from an aluminum smelting company. It is related to the ability of cyanide to volatilize, making it difficult to use the original wastewater sample for this research. The sample taken for the target of reducing cyanide levels is a sample with an initial cyanide level of about 10 mg/L because from the data obtained, the highest cyanide level in the aluminum smelting company is 7.67 mg/L. With a cyanide level of 10 mg/L, it is considered to anticipate an additional aluminum smelting capacity in the future.

2.1. Material
Artificial cyanide containing wastewater was used in this study, using sodium cyanide (NaCN) and ferrous sulfate (FeSO₄·7H₂O) as precipitants. Both NaCN and FeSO₄·7H₂O were purchased from Merck with PA-grade reagent. In the filtration process, activated carbon and quartz sand were used as filter media. Activated carbon used in this research is 8 x 30 mesh size (varies between 2.38 mm and 0.595 mm), and quartz sand used is 20 x 30 mesh size (varies between 0.841 mm and 0.595 mm). The filtration unit used was purchased from Alinco Filter. The precipitation process used a magnetic stirrer (ThermoScientific RT2 Advanced Hotplate Stirrer) to mix cyanide solution and the precipitant. For pH
measurement, Hach HQ40d multimeter was used after the solution was precipitated and filtrated. Furthermore, to measure cyanide level, a Spectroquant NOVA 60A Photometer was used.

**2.2. Method**

2.2.1. **Precipitation.** In the precipitation experiment, 500 mL cyanide solution with a concentration of about 10 mg/L was put into a beaker glass and placed on the magnetic stirrer plate. Then ferrous sulfate was added to the solution with five different doses. Based on calculations using chemical stoichiometry, it was found that the dose of ferrous sulfate required to precipitate 10 mg/L sodium cyanide was about 53 mg/L. Therefore, in this research, the ferrous sulfate dose of 53 mg/L was used as the precipitant middle dose, while the other four dosage variations had a dosing interval of 5 mg/L. There are three stages of the precipitation process, namely rapid mixing, slow mixing, and sedimentation. Rapid mixing is carried out to disperse the added precipitant to bind to the cyanide ion present in the solution, while slow mixing is used to produce slow water movement that allows contact between the precipitate particles to form larger particles.

| Table 1. Chemical precipitation design criteria [4,5]. |
|-----------------------------------------------|
| Type of mixing        | Rapid mixing | Slow mixing |
| Velocity gradient     | 700-1000 /s  | 20-75 /s    |
| Hydraulic retention time | 0.5-6 minutes | 15-30 minutes |
| G.Td                 | 30,000-90,000* | 10,000-100,000 |

*For general rapid mixing

To meet these criteria, the measurement of mixing speed is crucial. Based on the calculations that have been done, the speed required for the rapid mixing process is 1250 rpm, while for the slow mixing process is 285 rpm. After the mixing process is done, a sedimentation process is carried out. Wherein this process, the beaker glass is allowed to stand to give time for the precipitate formed to be deposited on the bottom of the beaker glass. The time used in this sedimentation process is 2 hours [6].

2.2.2. **Filtration.** Filtration experiments were carried out after obtaining the most optimal precipitant dosage in removing cyanide levels in the sample. In the filtration unit, there are two filter media, where at the base of the unit is quartz sand medium with a thickness of 40 mm, and on top is activated carbon medium with a thickness of 80 mm. Meanwhile, the diameter of the filtration unit is 60 mm.

2.2.3. **Cyanide level** measurement. The cyanide level measurement in this research used a reagent test kit named Spectroquant Cyanide Test with Cat. No. 1.09701.0001 from Merck KGaA. An auto selector and two reagents were used to measure the cyanide concentration in this research. This method causes cyanide ions to react with a chlorinating agent (reagent CN-3) to form cyanogen chloride, which in turn reacts with 1,3-dimethylbarbituric acid (reagent CN-4) to form a violet dye. This dye will be detected photometrically in the Spectroquant NOVA 60A Photometer to determine the cyanide level of the sample. This method corresponds to DIN 38405-13 and is analogous to ISO 6703, EPA 353.2, APHA 4500-CN E, and ASTM D2036-09 D. To determine the cyanide level, 10 ml of the sample is put to the test tube, then two levels of the green micro spoon (in the cap of the CN-3 bottle) is put then shook briefly. Then, two levels of the blue micro spoon (in the cap of the CN-4 bottle) are put and shook vigorously until the reagent is completely dissolved. Then the sample is left for 10 minutes’ reaction time, then the sample is filled into the 50 mm rectangular cell and then measured in the photometer.
3. Result and discussion

3.1. Precipitation process
As previously described, the precipitation process using ferrous sulfate uses a dose of 53 mg/L as the middle dose with an interval of 5 mg/L for the other doses. Therefore, the variation of the dose used in this experiment was 43 mg/L, 48 mg/L, 53 mg/L, 58 mg/L and 63 mg/L. Detailed results in this experiment are shown in Table 2.

Table 2. Precipitation experiment results using ferrous sulfate.

| Repetition | Ferrous Sulfate Dose (mg/L) | Initial Cyanide Level (mg/L) | Initial pH | Final Cyanide Level (mg/L) | Efficiency | Final pH |
|------------|-----------------------------|-----------------------------|------------|-----------------------------|------------|---------|
| 1  | 43  | 10.2 | 9.03 | 5.9 | 42.16% | 7.20 |
|   | 48  |      |      | 4.7 | 53.92% | 7.14 |
|   | 53  |      |      | 5.0 | 50.98% | 5.38 |
|   | 58  |      |      | 5.3 | 48.04% | 6.80 |
|   | 63  |      |      | 4.8 | 52.94% | 6.07 |
| 2  | 43  | 10.2 | 9.03 | 5.7 | 44.12% | 6.29 |
|   | 48  |      |      | 5.7 | 44.12% | 6.03 |
|   | 53  |      |      | 5.6 | 45.10% | 4.50 |
|   | 58  |      |      | 5.7 | 44.12% | 5.49 |
|   | 63  |      |      | 5.7 | 44.12% | 5.38 |
| 3  | 43  | 10.2 | 9.03 | 5.6 | 45.10% | 5.75 |
|   | 48  |      |      | 6.1 | 40.20% | 5.55 |
|   | 53  |      |      | 5.8 | 43.14% | 5.54 |
|   | 58  |      |      | 6.0 | 41.18% | 5.54 |
|   | 63  |      |      | 4.9 | 51.96% | 5.18 |
| Average | 53  | 10.2 | 9.03 | 5.47 | 46.41 ± 4.08% | 5.14 |
|         | 58  |      |      | 5.67 | 44.44 ± 3.44% | 5.94 |
|         | 63  |      |      | 5.13 | 49.67 ± 4.84% | 5.54 |

The results above found that the dose with the highest efficiency in removing cyanide levels was 63 mg/L. Theoretically, a complete precipitate will be formed with a ferrous sulfate dose of 53 mg/L. At a ferrous sulfate dose of 43 mg/L and 48 mg/L, theoretically, there are insufficient ferrous ions to complex with all the cyanide ions [3], which will lead to a lower cyanide level removal efficiency. However, the results show that the theoretically optimal dose of ferrous sulfate does not provide the highest efficiency in removing cyanide levels. However, it should be noted that the dose of 63 mg/L is the highest dose used in this experiment, so there may still be doses above 63 mg/L that have higher efficiency in removing cyanide levels. Therefore, the second stage of the precipitation process was carried out using the stoichiometric dose of 53 mg/L as the lowest dose with an interval of 20 mg/L for the other doses.
Table 3. Second stage precipitation experiment results using ferrous sulfate.

| Repetition | Ferrous Sulfate Dose (mg/L) | Initial Cyanide Level (mg/L) | Initial pH | Final Cyanide Level (mg/L) | Efficiency | Final pH |
|------------|-----------------------------|-----------------------------|-----------|---------------------------|------------|---------|
| 1          | 53                          | 10.7                        | 8.96      | 4.8                       | 55.14%     | 5.68    |
|            | 73                          |                             |           | 4.5                       | 57.94%     | 5.05    |
|            | 93                          |                             |           | 4.2                       | 60.75%     | 4.87    |
|            | 113                         |                             |           | 4.5                       | 57.94%     | 4.77    |
|            | 133                         |                             |           | 4.7                       | 56.07%     | 4.59    |
| 2          | 53                          |                             |           | 4.5                       | 57.94%     | 5.84    |
|            | 73                          |                             |           | 4.5                       | 57.94%     | 5.13    |
|            | 93                          |                             |           | 4.1                       | 61.68%     | 4.99    |
|            | 113                         |                             |           | 4.3                       | 59.81%     | 4.90    |
|            | 133                         |                             |           | 4.8                       | 55.14%     | 4.80    |
| 3          | 53                          |                             |           | 5.2                       | 51.40%     | 5.56    |
|            | 73                          |                             |           | 5.2                       | 51.40%     | 5.20    |
|            | 93                          |                             |           | 4.8                       | 55.14%     | 4.90    |
|            | 113                         |                             |           | 4.8                       | 55.14%     | 4.84    |
|            | 133                         |                             |           | 5.1                       | 52.34%     | 4.76    |
| Average    | 93                          | 10.7                        | 8.96      | 4.37                      | 59.19 ± 3.54% | 4.92 |
|            | 113                         |                             |           | 4.53                      | 57.63 ± 2.35% | 4.84 |
|            | 133                         |                             |           | 4.87                      | 54.52 ± 1.95% | 4.72 |

In this second stage experiment, the ferrous sulfate dose of 93 mg/L had the highest efficiency in removing cyanide levels, with an average efficiency of 59.19 ± 3.54%. Below and above the dose of 93 mg/L, cyanide level removal efficiency shows a decrease. Beckenn [7] suggested that a Fe: CN ratio of 16 should be used for the effective removal of cyanide. If the initial concentration of cyanide is 10 mg/L, it will need 1.69 g ferrous sulfate to remove cyanide based on that statement. It is unnecessary because it will result in high consumption of precipitant used. This experiment produces a graph with a bell-shaped line pattern where the peak of cyanide removal efficiency is obtained at a ferous sulfate dose of 93 mg/L. It indicates that ferrous sulfate added with a dose of less or more than 93 mg/L will provide lower removal efficiency, so then it can be concluded that a ferrous sulfate dose of 93 mg/L is the most optimal dose in removing cyanide levels in the experimental sample. A detailed illustration is shown in Figure 1.
3.2. Filtration process

The next step is the filtration process after finding the optimal dose of ferrous sulfate in removing cyanide. This process involves passing effluent through a filter bed or media that can strain out the colloidal particles. There are four mechanisms of solids removal by filtration: straining, sedimentation, impaction, and interception [4]. The particles more extensive than the pore spaces in the media are trapped and removed by a straining mechanism. The flow velocity through the filter bed is usually laminar, so in the low-velocity zones, some particles are removed by sedimentation. There are sharp turns in the flow streamlines; the force of inertia moves many particles out of the flow stream, causing them to strike the media and be held there; thus, the removal is by impaction. At times, the particles following these streamlines touch a media grain, and chemical bonding or electrostatic forces hold them there due to interception. This experiment used the ferrous sulfate dose of 93 mg/L to carry out the precipitation process. After that, the solution will be left for 2 hours and taken to the filtration unit. Detailed results are shown in Table 4.

**Table 4. Result of combination process.**

| Repetition | Initial Cyanide Level (mg/L) | Initial pH | pH after Precipitation | Cyanide Level after Precipitation (mg/L) | Precipitation Efficiency | Average Precipitation Efficiency |
|------------|------------------------------|------------|------------------------|------------------------------------------|--------------------------|---------------------------------|
| 1          | 10.3                         | 9.09       | 5.31                   | 4.21                                     | 59.13%                   | 58.74 ± 0.51%                  |
| 2          | 4.87                         | 4.31       | 58.16%                 |                                          |                          |                                 |
| 3          | 7.45                         | 0.77       | 81.71%                 |                                          |                          |                                 |

| Repetition | pH after Filtration | Cyanide Level after Filtration (mg/L) | Filtration Efficiency | Average Filtration Efficiency | Total Efficiency | Average Total Efficiency |
|------------|---------------------|----------------------------------------|-----------------------|-------------------------------|-----------------|--------------------------|
| 1          | 7.06                | 0.76                                   | 82.03%                | 81.65 ± 0.42%                | 92.62%          | 92.43 ± 0.26%            |
| 2          | 6.88                | 0.81                                   | 81.21%                |                               | 92.14%          |                          |
The results in Table 4 show that the filtration process also plays a significant role in removing cyanide levels in the sample after the precipitation and sedimentation process after 2 hours, with an average efficiency of 81.65 ± 0.42%. As for the precipitation process, an average efficiency of 58.74 ± 0.51% was obtained. So, the sample's total efficiency of cyanide removal with a combination of precipitation and filtration techniques is 92.43 ± 0.26%.

3.3. Effect on pH
The optimum equilibrium pH range for the precipitation of Prussian blue is between 5.5 and 6.5. Under these conditions, it is possible to achieve deficient levels of cyanide species in solution after 5 minutes—lower pH results in the decomposition of the Prussian blue product. In alkaline solutions, ferrocyanide also becomes unstable, owing to the decomposition of the compound, and will precipitate as Fe₃O₄·nH₂O [3]. In the precipitation process of this experiment, the effect of adding ferrous sulfate to the cyanide-containing solution is shown in Figure 2.

![Figure 2. Effect on pH by adding ferrous sulfate.](image)

The dose used in Figure 2 is the dose used in the second stage of the precipitation process. It was found that the higher the dose of ferrous sulfate given, the lower the pH of the sample, or it was said to be more acidic. It follows the nature of ferrous sulfate as an acidic salt. The sharpest decrease in pH value occurred between doses of 53 mg/L and 73 mg/L.
Figure 3. Effect of precipitation and filtration processes on pH value.

Figure 3 shows that the precipitation process causes the sample to become more acidic with a decrease in the pH value, while the filtration process increases the pH value; in other words, it makes the sample more alkaline. It can be caused by the filter media used in the filtration process, where the filter media used in this experiment are quartz sand and activated carbon. Activated carbon is made through the carbonization process followed by the activation process. Two methods can be used to make activated carbon from organic base materials: physical and chemical activation methods. Activation method selection will affect the quality of the activated carbon. Each type of activator will give different effects or influences on the surface area and volume activated carbon pores. In the chemical activation method, chemicals used as an activator are acids, bases, and salts, like H$_3$PO$_4$, KOH, and ZnCl$_2$ [8].

From the results obtained, it can be concluded that activated carbon used is probably activated by the chemical activation method using alkaline chemicals. In addition, in the filtration process using activated carbon, there is an adsorption process, so when the sample passes through the activated carbon, cyanide which at the previous pH of 5.16 is mostly in the form of HCN gas, will be adsorbed so that the acidic HCN gas in the sample decreases, leaving cyanide in the form of aqueous CN$^-$, which is alkaline.

4. Conclusion

In alumina smelter wastewater, cyanide is one of the dangerous indicators found. Improper management and treatment of cyanide will harm humans and the environment. One of the methods to remove cyanide is through the precipitation process so that cyanide can be immobilized as a precipitate, while filtration is a process to hold and retain the precipitate from being carried away by the wastewater flow. One of the precipitants that can immobilize cyanide in solution is ferrous sulfate because it contains ferrous ions. Based on the experiment results, ferrous sulfate dose of 93 mg/L is the optimal dose as precipitant in removing cyanide with the efficiency of 58.74 ± 0.51%, while the filtration process provides the efficiency of 81.65 ± 0.42%. Precipitation with ferrous sulfate makes the pH value of the wastewater decrease. However, the filtration process increases the value again, which can be concluded that activated carbon used as the medium filter is probably activated by chemical activation method using alkaline chemical and cyanide which at the previous pH of 5.16 is mostly in the form of HCN gas, was adsorbed to activated carbon so that the acidic HCN gas in the sample decreases, leaving cyanide in the form of aqueous CN$^-$, which is alkaline. In the whole process, cyanide can be reduced by a combination of precipitation and filtration process with the efficiency of 92.43 ± 0.26% and an average final effluent concentration of 0.78 mg/L from an initial concentration of 10.3 mg/L.
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