Chloride solution leaching of platinum from Indonesia gold ore artisanal mining

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Abstract. Platinum has been growing in economic importance in recent years. Limited occurrence of large scale deposits and ever-increasing demand have encouraged the utilization of deposits with low grade ore. Efficient yet small scale applicable method of extraction is needed to utilize those deposits. Chloride solution based leaching facilitates excellent condition for platinum dissolution by significantly reducing its reduction potential and through formation of stable aquochlorocomplexes. This paper reports optimization of chloride solution based platinum leaching from Indonesian artisanal ore under variation of lixiviant concentration, leaching time, pulp ratio, and leaching temperature. The Taguchi method was used to optimize the process. Hydrochloric acid was chosen as primary source of chloride ion and H2O2 were added as oxidizer. Parameters were arranged in L-9 orthogonal arrays and optimized through signal to noise ratio (S/N Ratio). Analysis of variance was utilized to identify the influence of each parameters to overall leaching process. The suggested optimized condition was: HCl concentration= 12 M, leaching time= 6 h, pulp ratio = 0.1, and temperature= 75 °C. It has been identified that time was the most influential parameter.

1. Introduction

Platinum and other platinum group metals (PGM) are precious metals with high and growing economic importance. Primary producer of platinum and other platinum group metals are South Africa, Russia, Canada, Zimbabwe, United States, and Colombia. South Africa controls over 95% of global deposit of PGM or about 63 000 ton PGM ores [1]. In 2016 global platinum supply deficit reached 861 troy ounces, which was almost 10% of the entire demand of 8677 troy ounce [2].

The extraction of Platinum and other PGM is traditionally carried out through pyrometallurgical routes of matte-smelting-refining technique from high grade ore. Environmental cost is the primary problem of this technique as it produces large volume of pollutants [3]. On the other hand, hydrometallurgical routes provide a promising alternative both in economic and environmental senses as platinum dissolves and form stable complex in several media such as chloride, cyanide, halide, and hypochlorite [4, 5].

Among several other available leaching media chloride media based leaching facilitate excellent condition for platinum dissolution by significantly reduce its reduction potential and through the formation of stable chloridometalate complexes [6]. In addition, this leaching method does not require pressures higher than the atmospheric pressure [3, 4]. Platinum dissolution in chloride media is based on reactions shown in equation (1) and (2).
\[
\text{Pt} + 6\text{Cl}^{-} \leftrightarrow \text{PtCl}_6^{2-} + 4e^- \quad E^\circ = -0.744V \quad (1)
\]
\[
\text{Pt} + 4\text{Cl}^{-} \leftrightarrow \text{PtCl}_4^{2-} + 2e^- \quad E^\circ = -0.73V \quad (2)
\]

Several other researchers have successfully leached platinum and other PGM metals by using chloride solutions. Leaching of platinum from industrial catalyst using a combination of 60% H$_2$SO$_4$ and 0.1 M NaCl has been successfully conducted, yet the leaching time was quite long [4]. Primary platinum ore from South Africa has also been successfully leached using 6M HCl and chlorine gas [7]. Study of different types of chloride media has proven that the combination of HCl and H$_2$O$_2$ is the most effective lixiviant to dissolve platinum from spent automotive catalyst, however high concentration of HCl were needed [5]. Reaction of platinum dissolution after addition of H$_2$O$_2$ is as listed in equation (3).

\[
\text{Pt} + 4\text{HCl} + 2\text{Cl}^- \leftrightarrow \text{H}_2\text{PtCl}_6 + \text{H}_2\text{O} \quad (3)
\]

\[
\text{Anodic} : \quad \text{Pt} + 6\text{Cl}^- \leftrightarrow \text{PtCl}_6^{2-} + 4e^- \quad E^\circ = -0.744V \quad (4)
\]

\[
\text{Cathodic} : \quad \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow 2\text{H}_2\text{O} \quad E^\circ = 1.76V \quad (5)
\]

Based on the discovery of platinum element in some of gold ore artisanal Mining found in Indonesia, the extraction of platinum contained in Indonesian gold ore is become increasingly attractive. However, to maximize the economic gain of the extraction of platinum contained in these ore, an environmentally friendly process with high efficiency is needed. In order to develop such process, this study carried out single-step leaching of platinum from Indonesian artisanal ore by using HCl and H$_2$O$_2$ to examine the influence of several leaching parameter to the recovery of platinum. Evaluated parameters were temperature, HCl concentration, pulp ratio, and time. Taguchi method was implemented in experiment design and was used to identify the influence of each parameter involved in the recovery of platinum.

2. Experimental method

2.1. Materials

Indonesian artisanal gold ore was used in this study. The received sample has been roasted and nitrogen pre-treated. Sample was ball milled and sieved. Sample with size of less than 74 µm was used as feed of the leaching process. Platinum content in the sample was known to be 16 ppm. All of the reagent used in this study were of analytic grade. The reagents used were HCl (37%, Merck), and H$_2$O$_2$ (30%, Merck). Demineralized water was used to diluting the solutions.

2.2. Methods

Leaching procedure was carried out in 250 mL Erlenmeyer flask. Magnetic stirrer and hot plate were used to agitate the leaching solution and adjust its temperature during leaching process. Watch glass was used as a stopper on the top of the Erlenmeyer flask during all experiment; it was put loosely, preventing the change in pressure in the Erlenmeyer flask. Fine cotton filters (GE Healthcare) with pore size of about 2.5 µm was used to filter the leaching solution at the end of each experiment. Filtration was done at ambient temperature after the solution cooled down. Filtrated solution was then diluted for analysis. Elemental analysis was carried out using AAS (Perkin Elmer). The recovery was calculated based on dissolved platinum in the filtered solution compared to the mass of platinum contained in received sample.

2.3. Taguchi method

In order to optimize the process parameters and minimize the number of experiments needed, this study utilize Taguchi Robust Parameter Design or Taguchi Method. The Taguchi method is a statistical method developed by Taguchi and Konishi to optimize processes involving various parameters with
minimal amount of experiment [8]. Through this method relative influence of a particular parameter to the overall process can be characterized. Taguchi method uses orthogonal array that governs the configurations of parameters used in each experiment therefore that the number of experiments can be minimized. On a study with four parameters and three level for each parameter involved, traditional method requires $3^4$ or 81 experiments, while through utilization of this method only 9 experiments are necessary [9]. This method utilizes Signal-to-noise ratio (S/N) to analyze the output in graphical form [10]. Signal-to-noise ratio is a logarithmic function that combines the contribution of the mean value and the variation of the sample value into a single value [11]. In this study, larger-the-better S/N ratio were used, since the objective of the study is to achieve the highest recovery of platinum. The larger-the-better S/N ratio formula is shown in equation (6).

$$S/N_{\text{larger-the-better}} = -10 \log\left(\frac{1}{n} \sum \left(\frac{1}{y_i}\right)\right)$$  \hspace{1cm} (6)

### Table 1. Taguchi’s L9 orthogonal array design.

| Exp. | Temperature (°C) | HCl Concentration (Molars) | Pulp Ratio | Time (h) |
|------|------------------|---------------------------|------------|----------|
| 1    | 25               | 3                         | 0.1        | 2        |
| 2    | 25               | 6                         | 0.25       | 4        |
| 3    | 25               | 12                        | 0.5        | 6        |
| 4    | 50               | 3                         | 0.25       | 6        |
| 5    | 50               | 6                         | 0.5        | 2        |
| 6    | 50               | 12                        | 0.1        | 4        |
| 7    | 75               | 3                         | 0.5        | 4        |
| 8    | 75               | 6                         | 0.1        | 6        |
| 9    | 75               | 12                        | 0.25       | 2        |

Through this method relative influence of each parameter involved can also be characterized through ANOVA analysis. Formulas involved in ANOVA analysis is shown in equations (7), (8), and (9). Several researchers have proven the robustness and usefulness of this method in field of extraction [7-10].

$$m_i = \left(\frac{1}{N_i}\right) \sum S / N$$ \hspace{1cm} (7)

$$\text{Sum of squares (SOS)} = N \sum_{i=1}^{i=j} \left( m_i - \langle m_i \rangle \right)^2$$ \hspace{1cm} (8)

$$\text{Parameter influence} = \frac{\text{SoS}}{\text{DoF} \times \sum \left( \frac{\text{SoS}}{\text{DoF}} \right)}$$ \hspace{1cm} (9)
Four parameters (temperature, HCl concentration, pulp ratio, and time) in three levels were considered in this study. Taguchi's L9 orthogonal array design was utilized to dictate the combination of each parameter for each experiment. The design of L-9 orthogonal array for the study is presented in contained in received sample. contained in received sample.

3. Results and discussion

3.1 Ore characteristic

The XRD spectrum of the ore is shown in Figure 1. It is shown that the most prominent peaks are belongs to quartz (SiO$_2$) and iron oxide (Fe$_2$O$_3$). XRF analysis as listed in Table 2 confirms that quartz is the main component of the ore. The presence of Fe$_2$O$_3$ indicate the occurrence of FeS on pre-roasted ore, as Fe$_2$O$_3$ is the final product of FeS roasting [12]. From these information, it is clear that the ore used was came from quartz-gold veins which is the common type of gold deposit found in Indonesia. The presence of high Fe concentration in the ore was a problem since Fe also dissolved in chloride solution, causing inefficiency of lixiviant usage. Another metallic element contained in the ore also possesses similar threat.

![XRD patterns of ore sample used in the experiments.](image)

Figure 1. XRD patterns of ore sample used in the experiments.

3.2 Process optimization

The recovery and S/N ratio of each experiment are given in Table 3. The effects of each parameter on the recovery of platinum are listed in Table 4. It is shown in Table 4 that leaching time was the most influential parameter (96.37%) while temperature was the least influential parameter (0.3794%).

### Table 2. XRF Analysis of five major elements of the ore.

| Element  | Atomic Mass (z) | Concentration (wt.%) |
|----------|-----------------|----------------------|
| Iron     | 26              | 43.05                |
| Silicon  | 14              | 14.17                |
| Aluminum | 13              | 3.751                |
| Sodium   | 11              | 0.685                |
| Titanium | 22              | 0.4188               |
It can be noted that compared to leaching time, other parameters are insignificant. Figure 2 illustrate the S/N ratio of each parameter. Taguchi’s S/N ratio predicts that the optimum leaching condition (corresponding to highest S/N) for platinum extraction is at temperature of 75 °C, pulp ratio of 0.1, HCl concentration of 12 molar, and at 6 hours long. The leaching experiments were carried on temperature range from room temperature to 75 °C. Figure 2 shows that extraction of platinum increased with increasing temperature. Platinum dissolution kinetics becomes more favorable at higher temperature. However, ANOVA analysis has shown that temperature effect on platinum recovery was insignificant (0.3794%).

![Figure 2. S/N Graph for platinum extraction.](image)

HCl was chosen based on previous study that shows combination of HCl and H₂O₂ is the best lixiviant to dissolve platinum compared to several other lixiviant [5]. S/N ratio of HCl concentration on Table 3 shows platinum recovery was directly proportional to HCl concentration used. ANOVA analysis, as shown in Table 4, revield that HCl concentration increase effect on platinum recovery was only 1.435%. Such minimal effect explains the reason that several other researchers could achieve effective leaching of platinum in relatively low HCl concentration.

**Table 3. Recovery and S/N ratio of each experiment.**

| Experiments | Recovery (%) | S/N Ratio (dB) |
|-------------|--------------|----------------|
| 1           | 36.85        | 31.04          |
| 2           | 11.58        | 21.22          |
| 3           | 46.01        | 33.11          |
| 4           | 18.74        | 25.36          |
| 5           | 18.59        | 25.35          |
| 6           | 73.36        | 37.23          |
| 7           | 18.00        | 24.26          |
| 8           | 89.05        | 38.93          |
| 9           | 54.92        | 34.79          |
Pulp ratio was defined as ratio of feed mass (g) to volume of lixiviant (ml) used. S/N graph of pulp ratio which is shown in Figure 2 shows that pulp ratio 0.1 has highest S/N ratio (35.73) while pulp ratio of 0.25 and 0.5 have relatively comparable S/N ratio (27.13 and 27.57). Low pulp ratio means more lixiviant available to every gram of feed which also means more cost on lixiviant. ANOVA analysis has shown that pulp ratio is the second most influential parameter of the study with effect of 1.8%.

Table 4. Effect of each parameter on the recovery of platinum.

| Parameters | Level | Yield | %Effect |
|------------|-------|-------|---------|
|            |       | mi    | mi      | SOS     |         |
| Temperatur | 25    | 28.46 | 30.14   | 29.60   | 0.3794  |
|            | 50    | 29.31 | 30.14   | 75.31   | 1.806   |
|            | 75    | 32.66 | 30.14   | 29.60   | 0.3794  |
|            | 3     | 26.89 | 30.14   | 29.60   | 0.3794  |
| [HCl]      | 6     | 28.50 | 30.14   | 112.0   | 1.435   |
|            | 12    | 35.04 | 30.14   | 29.60   | 0.3794  |
|            | 0.1   | 35.73 | 30.14   | 29.60   | 0.3794  |
| PR         | 0.25  | 27.13 | 30.14   | 141.0   | 1.806   |
|            | 0.5   | 27.57 | 30.14   | 29.60   | 0.3794  |
|            | 2     | 91.18 | 30.14   | 29.60   | 0.3794  |
| Time       | 4     | 27.57 | 50.41   | 7518    | 96.37   |
|            | 6     | 32.46 | 50.41   | 7518    | 96.37   |

Time was the most influential parameter of this study as reviled by ANOVA analysis (Table 4). With effect of 96.37% it renders other parameters insignificant. S/N ratio graph for time effect on leaching of platinum shown in Figure 2 did not shows a perfect directly proportional line. The drop on S/N ratio from 2 hours to 4 hours was caused by decomposition of H₂O₂. While at the early hours of the leaching H₂O₂ helped oxidation of platinum and speeds up dissolution process, decomposition of H₂O₂ reduce this effect on latter hours of leaching. Nonetheless, H₂O₂ has never decomposed completely, therefore platinum dissolution was still occurred at latter hours of the leaching although in slower pace of platinum dissolution.

4. Conclusion
Study on leaching of platinum content of Indonesia artisan ore have been carried out. Taguchi S/N ratio suggest that the optimum condition for platinum extraction is at temperature of 75 °C, pulp ratio of 0.1, HCl concentration of 12 molar, and at 6 hours long. The most influential parameter in this study was leaching time with influence of 96.37%, followed by pulp ratio with 1.806%, HCl concentration with 1.435%, and the least influential parameter was temperature with influence of only 0.3794%.

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