Additional of NaCl on Chloride Leaching of Gold Ore from Indonesian Artisanal Mining

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Abstract. An alternative method of amalgamation to extract gold in small-scale industries was investigated by means of chloride-ion-based solution leaching. In this study, the addition of NaCl and optimization of chloride-ion-based leaching of gold was analyzed by using the Taguchi Method. Indonesia gold ore processed from artisanal mining was utilized in this study. The solutions of HCl (11.6 mol/L)-H₂O₂ (1 vol%) were used as lixiviants. The effects of temperature, pulp ratio, leaching time, and NaCl addition were examined. The optimum leaching condition was predicted using a signal to noise ratio and the influence of given input parameters were studied through the analysis of variance. More than 78% extraction of gold was achieved after 3 hours using pulp ratio of 0.5, a temperature of 75 °C, and the addition of 0.05 M of NaCl.

Keywords: Taguchi method, environmental friendly, pre-treatment ore, hydrochloride acid, traditional mining

1. Introduction
In extractive metallurgical industry, gold is extracted from gold ore minerals, mostly associated with other minerals, such as quartz, carbonate, tourmaline, and pyrites [1-3]. The gold ores are classified as free-milling ores and refractory ores. The first type ores can be leached directly without pre-treatment. Refractory ores are difficult to leach by a simple leaching process. In industrial-scale, gold extraction is conducted by cyanidation process followed by carbon in pulp or ion exchange process. The solvents commonly used in the cyanidation process are NaCN, KCN, Ca (CN)₂, or a mixture of all three solvents. The simplest solvent used is NaCN because it can dissolve gold better than other solvents [4].

However, in Indonesia artisanal mining and/or extraction by home industry, amalgamation methods are selected due to its simplicity of the process, even the process is very harmful in terms of public health and environmental impact issues. Amalgamation is the process of dissolving gold particles by mercury and forming an amalgam (Au-Hg). Amalgamation is the most effective process for extracting high-grade gold ore with the size of more than 74 microns in obtaining free native gold. In the final stage, amalgam is heated to decompose into mercury and gold bullion. It can be conducted in a small retort. Here, mercury will evaporate, leaving silver and gold in the retort [5].

Actually, many studies have been conducted to leach gold ore by using other solutions than cyanide solution [6-8]. The utilization of chlorides solutions was also investigated to leach some other precious metals such as PGM from spent catalyst [9] and gold from electronic waste [10].
Table 1. The stability constants of complex ion formation in gold [11]

| Complex          | Gold (I) β₂       | Complex          | Gold (II) β₄ |
|------------------|-------------------|------------------|--------------|
| Au(CN)₂⁻        | 2×10³⁸            | Au(CN)₄⁻        | 10⁶⁶         |
| Au(SCN)₂⁻        | 1.3×10¹⁷          | Au(SCN)₄⁻       | 10⁴²         |
| AuCl₂⁻           | 10⁹              | AuCl₄⁻           | 10²⁶         |

Figure 1. The diagram of reduction potential (Eh) - pH of gold (Au) on chloride solutions. The dashed area shows the possibility of Au to dissolve in chloride solution as AuCl₄⁻ [modified from 12]

The feasibility of the gold reaction in chloride solution was evaluated thermodynamically by using reduction potential (Eh) - pH diagram (Figure 1). In general, gold leaching is conducted by forming stable complex ions within the leached solution. To be stable in the leachate solution, it requires a suitable ligand and oxidizing agent. In the formation of chemical compounds, Au had the number of oxides +1 (aurous) and +3 (auric). Table 1 shows the stability constant of some gold complex ions in cyanides and chloride solutions.

Based on the Eh-pH of the gold diagram in the chloride-based solution (Figure 1), the formation of stable complex ions occurred at a low pH and high potential [12]. It also indicates that in Figure 1 (dashed area) that leached gold is possible in chloride solutions. The gold leaching in chloride solutions might have reaction mechanism as shown in the following equations [13]

\[
\text{Au} + 2\text{Cl}^⁻ \leftrightarrow \text{Au(Cl)}_2^- + e^- \quad E^\circ = -1.113 \text{ V} \quad (1)
\]

\[
\text{Au(Cl)}_2^- + 2\text{Cl}^- \leftrightarrow \text{Au(Cl)}_4^- + 2e^- \quad E^\circ = -0.994 \text{ V} \quad (2)
\]
With this condition, it is an opportunity to use chloride-based solutions to extract the golds from their ores. Also, the utilization of chloride-based solution may provide alternative solutions which are relatively more environmentally friendly rather than amalgamation process which is used commonly in the gold extraction from artisanal mining, especially in Indonesia. Therefore, this study aimed to investigate chloride solutions to extract the gold from artisanal mining ore. In this study, the effect of NaCl addition into an HCl solution was examined. Taguchi method was used to optimize the leaching condition.

2. Methods

2.1. Materials and methods

The fine pre-treated gold ores from artisanal mining were used in the experiments. The characterization of the feed ore was conducted by using a scanning electron microscope and electron dispersive spectrometer (SEM-EDS). The samples were weighed based on their concentration in a 250 ml Erlenmeyer flask, Erlenmeyer flasks filled with ore placed on the magnetic stirrer with the temperature variation setting at 25 °C, 50 °C, and 75 °C. Then, an HCl solution was poured with the volume of 50 ml with a concentration of 11.6 Kmol/m³. Next, NaCl solution was added with the concentration variations of 0.05, 0.1, and 0.2 M. Then, 1% vol H₂O₂ was dropped carefully into the solution mixture when the desired operation temperature was achieved. The flasks were covered with a watch glass to protect the excess vaporization. The leaching process was undertaken for 2, 3, and 6 hours. The solutions, then, were filtrated to obtain the gold ion rich solutions. The concentrations of the resulted filtrates were characterized by using atomic absorption spectroscopy (AAS). The recovery of the leaching process was calculated as a ratio between the gold in the filtrate and in the ore and it was presented in %.

2.2. Taguchi Method

The Taguchi method was employed to provide the optimum process by minimizing the number of experiments performed [13]. The experimental design used by the Taguchi method was described as an orthogonal array (OA) listed as a matrix. The column section represents a controllable factor that affected the results in the experiment and the row represents the number of levels to obtain the optimum result. Table 2 shows an example table for the Taguchi method with four variables. The table shows that there were 9 experiments that should be undertaken with 4 variables variations.

A, B, C, and D were the factors that influenced the research results, where 1, 2, 3 are the level, and Y₁-Y₉ are the parameter which contained the value obtained from the experimental results. In this study, the parameter was a gold recovery. The experiments which used the Taguchi method could optimize the number of experiments performed. The important thing was that each variable should be an independent variable that did not affect each other. The selection of experiments was an experiment that included all variables but without repeating in another variable inside the experiment. Then, the experimental data were analyzed based on the signal-to-noise ratio (S-N ratio or S/N). The S-N ratio gave a comparison of the response relative to the variation or noise. From Table 2 there were three categories of the signal to noise ratio (η):

- **Nominal-the-best** function to get a configuration with a certain value, with the followed equation:
  \[
  S/N \text{ nominal-the-best} = -10 \log(\sigma^2)
  \]  
  (3)

- **Larger-the-better** functions to get the configuration that generates the greatest value with the following equation:
  \[
  S/N \text{ larger-the-better} = -10 \log \left( \frac{1}{n} \sum_i \left( \frac{1}{y_i^2} \right) \right)
  \]  
  (4)

- **Smaller-the-better** functions to get the configuration that produces the least value with the following equation:
  \[
  S/N \text{ smaller-the-better} = -10 \log \left( \frac{1}{n} \sum_i (y_i^2) \right)
  \]  
  (5)
where, \( \sigma \) is the standard deviation, \( y_i \) is measured value for the test \( i \) in a series of \( n \) tests performed in similar condition. Because the desired result was the greatest or the highest recovery, a larger-the-better category was used in this study.

Table 2. L9 array of Taguchi Method [14].

| Experimental Number | Control Factor | Parameter | S/N ratio |
|---------------------|----------------|-----------|-----------|
|                     | A   | B   | C   | D   | Y1  | \( \eta_1 \) |
| 1                   | 1   | 1   | 1   | 1   | Y1  | \( \eta_1 \) |
| 2                   | 1   | 2   | 2   | 2   | Y2  | \( \eta_2 \) |
| 3                   | 1   | 3   | 3   | 3   | Y3  | \( \eta_3 \) |
| 4                   | 2   | 1   | 2   | 3   | Y4  | \( \eta_4 \) |
| 5                   | 2   | 3   | 3   | 1   | Y5  | \( \eta_5 \) |
| 6                   | 2   | 3   | 1   | 2   | Y6  | \( \eta_6 \) |
| 7                   | 3   | 1   | 3   | 2   | Y7  | \( \eta_7 \) |
| 8                   | 3   | 2   | 1   | 3   | Y8  | \( \eta_8 \) |
| 9                   | 3   | 3   | 2   | 1   | Y9  | \( \eta_9 \) |

3. Results and Discussion

3.1. Minerals particles morphology and composition

The characterization of the pre-treated gold ores was employed by using SEM and EDS, as shown in Fig. 2. Backscattered image and spot analysis of the particles were conducted to the particles which were labeled (a), (b) and (c) (Figure 2). In addition, an elemental identification was found in the ore particles surface from EDS characterization that is also listed in Table 3. There are some minerals detected from EDS on the particles surface. Particles (a) in Fig. 2 indicated some elements such as Fe (39.5 wt%), Si (2.2 wt%), O (55.7 wt%). Other elements, such as arsenic and aluminum were also detected. In the case of the particle (b), the composition analysis indicated the presence of silicon oxide minerals. However, the elemental analysis of the particle (c) showed the occurrence of the gold element (17 wt%) and silver (7.5 wt%) with iron, oxide, and other elements such as carbon, aluminum, and iodine. Some of the peaks are not shown in Figure 2.

There were also other minor elements which acted as impurities of the minerals. In addition, the existence of impurities such as pyrite was detected. It can be observed that this gold ore was a type of sulfide ores. Pre-treatment process by roasting of the ores decomposed the sulfide to oxide minerals. The observation of the minerals texture on the particle surface in Figure 2 (c) showed that gold seemed to be readily liberated. This is the characteristic of free milling ore as a precious metal not wrapped with impurities and founded on the surface of the ore.

Table 3. Elemental composition characterized by EDS on the ore particles surface shown in Fig. 2.

| Point | O (wt%) | Fe (wt%) | Si (wt%) | Au (wt%) | Ag (wt%) | Other elements (wt%) |
|-------|---------|----------|----------|----------|----------|---------------------|
| (a)   | 55.7    | 39.5     | 2.2      | n.d.*    | n.d      | 2.6                 |
| (b)   | 60.5    | n.d      | 39.5     | n.d      | n.d      | n.d                 |
| (c)   | 22.1    | 45.4     | 0.5      | 17.0     | 7.5      | 7.5                 |

*n.d.: not detected
3.2. Gold leaching and recovery
The gold concentration of leaching filtrate solution was characterized by using AAS according to an array of the Taguchi method listed in Table 3. The gold recovery of each experiment is also listed in Table 4. The results shown in Table 3, then, were calculated and converted to the S-N ratio (signal to noise ratio). The S-N ratio of the results is described in Figure 3 showing the effect of the determined variables.

**Figure 2.** Backscattered image and EDS results at points (a), (b), and (c) on ore particles surfaces
Figure 3. Signal to Noise ratio plot of temperature (a), Pulp ratio (b), NaCl concentration (c), and Leaching time (d), the effect on gold recovery

Figure 3 (a) shows the temperature effect on the S-N ratio of gold recovery. It could be observed that leaching temperature up to 50 °C gave less significant to the S-N ratio. According to this results, the higher leaching temperature than 50 °C increased the S-N ratio which also meant that it improved the gold recovery. In the case of Figure 3(b), the pulp ratio of the samples gave a significant effect on the S-N ratio. Up to 2 g/ml pulp ratio increased the S-N ratio significantly. It showed that gold recovery could be increased by controlling the pulp ratio in a higher value. NaCl addition to leaching solution reduced the S-N ratio. It could be observed that the gold recovery did not significantly increase with the addition up to 0.1 M, however, more than 0.1 M of NaCl addition may improve the gold recovery in the leaching process. Fig. 3 (d) shows that holding leaching time longer gave a slight improvement to the gold recovery, as indicated by the response of S-N ratio.

Considering the results of S-N ratio, the parameter effect to the gold recovery during HCl leaching with NaCl addition could be calculated. Table 4 shows the parameter effect on the gold recovery. Based on the parameter effect, the contribution of each parameter to achieve the best gold recovery is listed in Table 4.

Table 4 Gold recovery from the selected experiments based on the Taguchi method

| No | Temp. (°C) | [NaCl] (M) | Pulp Ratio (g/ml) | Leaching Time (Hours) | Gold Recovery (%) |
|----|------------|------------|-------------------|-----------------------|-------------------|
| 1  | 25         | 0.05       | 0.1               | 2                     | 35.77             |
| 2  | 25         | 0.1        | 0.15              | 3                     | 64.86             |
| 3  | 25         | 0.2        | 0.5               | 6                     | 68.49             |
| 4  | 50         | 0.05       | 0.15              | 6                     | 62.50             |
| 5  | 50         | 0.1        | 0.5               | 2                     | 31.11             |
| 6  | 50         | 0.2        | 0.1               | 3                     | 8.40              |
| 7  | 75         | 0.05       | 0.5               | 3                     | 78.41             |
| 8  | 75         | 0.1        | 0.1               | 6                     | 12.15             |
| 9  | 75         | 0.2        | 0.15              | 2                     | 42.19             |
Table 5. It shows that the significance of parameters to provide the best result in the gold recovery was in the order (from greater to the lower) pulp ratio, temperature, [NaCl], and leaching time, respectively. Then, it can also be summarized that the condition listed in Table 6 was an optimum condition for the gold recovery in HCl leaching with NaCl addition. Here, the optimum condition of gold recovery in HCl leaching was set at 25 °C. The additional NaCl concentration into the leaching solution was 0.05 M. During the leaching process, the solid and solution (pulp) ratios were controlled at 0.15 g/ml and the leaching time was conducted for 6 hours.

Table 5. Parameter effect on the gold recovery

| Parameter       | Level | S/N | Parameter effect (%) |
|-----------------|-------|-----|----------------------|
| Temperature (°C)| 25    | 34.5| 27.2                 |
|                 | 50    | 21.7|                      |
|                 | 75    | 27.5|                      |
| NaCl (M)        | 0.05  | 34.6| 24.2                 |
|                 | 0.1   | 22.8|                      |
|                 | 0.2   | 26.3|                      |
| Pulp ratio (g/ml)| 0.1  | 18.2|                      |
|                 | 0.15  | 34.4| 48.3                 |
|                 | 2     | 31.1|                      |
| Time (h)        | 2     | 27.0|                      |
|                 | 3     | 28.1| 0.36                 |
|                 | 6     | 28.5|                      |

Table 6. The optimum conditions of the gold recovery from HCl leaching

| Parameter        | Level |
|------------------|-------|
| Temperature [°C] | 25    |
| NaCl Concentration [M] | 0.05 |
| Pulp Ratio [g/ml]  | 0.15  |
| Time [hours]      | 6     |

3.3. Optimization of the gold recovery

The statistical calculation based on ANOVA results is listed in Table 7. It describes the value of the degree of freedom (DF), Sum of Squares (SS), Mean of squares (MS), F-value, and p-Value. By applying further calculation of these values, a multilinear equation could be obtained as follows:

\[
\% \text{ Gold Recovery Equation} = 45.2 - 0.242 T - 104 [\text{NaCl}] + 67.0 \text{ PR} + 1.97 t
\]  

(6)

where T is the temperature (°C), NaCl is additional NaCl concentration (M), PR is pulp ratio or the ratio of solid feed and the leaching solution volume (g/ml), and t is time (h). From this equation (6), it can be used to create contour plots with temperature and pulp ratio as independent variables, with a time of 6 hours and a concentration of NaCl addition of 0.05 M as a fixed variable. In this case, the gold recovery was used as independent variables. The contour result is shown in Figure 4. From Figure 4, it could be observed that the prediction of the optimum value of Taguchi was in the entire upper left corner region where the gold recovery in the region was predicted by more than 75%. It means that the region was the highest gold recovery.

Actually, the results are very prospective to be applied, even though the gold recovery in the optimum condition was still relatively low, about 78%. However, if they are compared with the previous study, the results have several advantages. For instance, the study of Pangum and Browner (1996) for refractory
gold ores extraction, they still used the solution mixtures of HCl and H2SO4 in a pressurized atmosphere and in a higher temperature [15]. Here, the proposed process could be undertaken in a room temperature and pressure. The other studies utilized chloride-hypochlorite solutions without HCl solution to extract gold from oxide and sulfide ores [16, 17].

Table 7. Statistical results based on ANOVA

| Parameters     | The degree of freedom (DF) | The sum of squares (SS) | The mean of squares (MS) | F-values | p-values |
|----------------|-----------------------------|-------------------------|--------------------------|----------|----------|
| Temperatures   | 1                           | 220.5                   | 220.5                    | 0.29     | 0.622    |
| Pulp ratio     | 1                           | 1280.0                  | 1280.0                   | 1.66     | 0.267    |
| [NaCl]         | 1                           | 382.2                   | 382.2                    | 0.49     | 0.521    |
| Leaching time  | 1                           | 100.4                   | 100.4                    | 0.13     | 0.737    |
| error          | 4                           | 3090.2                  | 772.6                    | -        | -        |
| Total          | 8                           | 5073.2                  | -                        | -        | -        |

Figure 4. The contour plot of the optimum leaching conditions based on the Taguchi method on gold recovery

4. Conclusion
Taguchi method was applied as a statistical tool to evaluate an additional NaCl in the leaching of gold from artisanal ore mining by HCl solutions. The optimization conditions as predicted by the Taguchi method gave the gold recovery as much as 78.4%. It also showed that NaCl addition to the leaching process affected a less significant to higher gold recovery. The effect of parameter which was more to less significant to the gold recovery was in order of pulp ratio, NaCl concentration addition, temperature, and leaching time, respectively. The Taguchi Method suggested that the optimum leaching parameters for gold recovery was the leaching temperature of 25 °C, with the concentration of NaCl addition of 0.05 M, the pulp ratio which was set at 0.15 g/mL, and the leaching time for 6 hours, respectively.
References

[1] Zhou J, Jago B 2004, Establishing the Process Mineralogy of gold ores, (SGS Lakefield Research limited, Canada, 2004), p.2
[2] Nunes D 2016, Mineral Commodity Summaries (U.S. Geological Survey)
[3] Pge A and Pge T 2009, “Definition, mineralogy and deposits,” September, USA, 165-169.
[4] Marsden, J O and House C I 2006, Chemistry of Gold Extraction (SME, England, 2006). p.233-263
[5] Habashi F 1998, Principle of Extractive Metallurgy: Amalgam and Electrometallurgy, (Quebec: Metalurgie Extractive Quebec), p. 295-306
[6] Nam K S, Jung B H, An J W, Ha T J, Tran T, Kim, M J 2008 Int. J. of Minerals Processing 86 131-140.
[7] Mohammadi E, Pourabdoli M, Ghobeiti-Hasab M, Heidarpour A 2017 Int. J. of Minerals Processing 164 6-10
[8] Munive G T, Romero M A E, Vazquez V M, Garcia J L V, Soto A V, Lopez, J H C 2017 J. of Metals, v. 69 n. 10, p. 1901-1908.
[9] Harjanto S, Cao Y, Shibayama A, Naitoh I, Nanami T, Kasahara K, Okumura Y, Liu K, Fujita T 2006, Materials Transaction, v. 47, n. 1, p. 129-135.
[10] Yazici E.Y., Deveci H. 2015 Int. J. of Minerals Processing 134, p. 131-140
[11] Marsden, J O and House C I 2006, Chemistry of Gold Extraction (SME, England) p 236-238
[12] Marsden, J O and House C I 2006, Chemistry of Gold Extraction (SME, England) p 273
[13] Marsden, J O and House C I 2006, Chemistry of Gold Extraction (SME, England) p 12
[14] Kong. T 1995, “Taguchi Methods in Experimental Design”, The Advantage Group, Inc.
[15] Pangum L S and Browner R E 1996, Minerals Engineering 9 (5) pp. 547-556.
[16] Baghalha M 2007, Int. J. Miner. Process, 82 pp. 176-186.
[17] Hasab M G, Rashchi F, Raygan S 2013, Minerals Engineering, 50-51, pp. 140-142

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