



## Enhancement in Iron Removal from Raffinate in Sarcheshmeh Copper Complex Leaching Process: A Case Study

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Iron concentration increasing in raffinate of Sarcheshmeh Copper Complex leaching unit is a significant problem that it must be controlled. The sedimentary technique is a general method for controlling concentration of iron. This technique is based on the pH changing with addition of calcium carbonate to acidic wastewater for increasing the pH of solution; so, the iron ion precipitated and removed as iron hydroxide. In this study, it is found that the addition of water to acidic wastewater before adding calcium carbonate not only decreases the iron concentration but also gave reproducible results for the removing of iron ion from raffinate.

**Keywords:** Removal of iron, Metallurgy of copper, Iron precipitation.

### INTRODUCTION

The removal of iron from mining effluents with pH adjustment is well known and various methods have been proposed for it [1]. The precipitations varied by change of sedimentary condition and iron(III) is precipitated at lower pH than iron(II). The precipitation of iron in iron(III) form in the acidic wastewater is being more economic [2].

Different chemical and biological procedures have been proposed for the oxidation of Fe(II) to Fe(III) for increasing iron precipitation efficiency [3-7]. The impact of different factors on the precipitation condition including pH, temperature and rate of reaction have also been properly investigated [2].

To the best of our knowledge, no study has been reported on addition of water to wastewater as an affecting factor for iron precipitation. In this study, dilution of the wastewater solution with pure water has been considered as a key factor in the sedimentary process. Conventional removal processes of iron decreased the concentration of iron in different yields that it depends on the acidity of wastewater composition in different mines.

### EXPERIMENTAL

The acidic mine drainage from raffinate outlet of the solvent extraction unit of Sarcheshmeh copper complex leaching was sampled. The pH, oxidation reduction potential (ORP) and density of the solution were 1.25, 394 mv and 1.13 Kg/L, respectively. Analysis of the raffinate sample composition was obtained by ICP technique in the laboratory of Labwest Australia (Fig. 1).

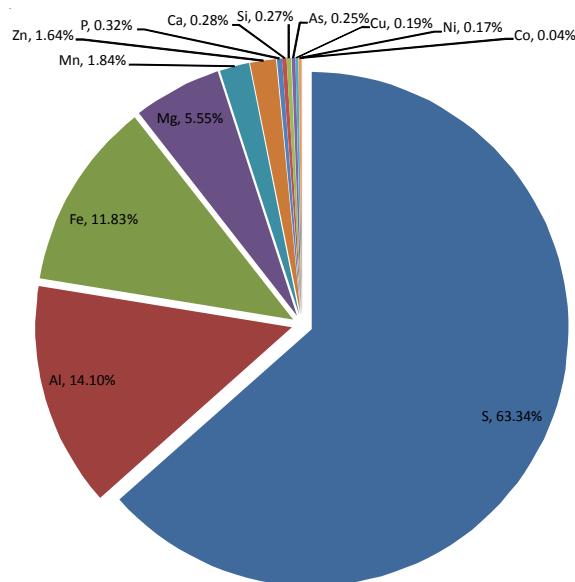


Fig. 1. Raffinate composition obtained by ICP technique

The sulfuric acid 97 % was used from Merck for adjustment of the pH of the treated solution.

The limestone ( $\text{CaCO}_3$ ) prepared from Qom limestone mine was used to adjust the pH of the raffinate. The XRF result for used limestone reported in Table-1. Distilled water was prepared from resin available in Sarcheshmeh Cathodic Copper refinery. The values of iron(II) and iron(III) were determined by Sarcheshmeh Copper Complex central laboratory. The samples were filtered using the Whatman paper filter No. 42.

TABLE-1  
XRF ANALYSIS OF Qom LIMESTONE MINE

|                                |         |                  |         |
|--------------------------------|---------|------------------|---------|
| Al <sub>2</sub> O <sub>3</sub> | 0.46 %  | K <sub>2</sub> O | 0.08 %  |
| CaCO <sub>3</sub>              | 94.06 % | SiO <sub>2</sub> | 1.26 %  |
| MgO                            | 1.81 %  | Total            | 97.81 % |
| Fe <sub>2</sub> O <sub>3</sub> | 0.14 %  | Uncertain digits | 0.1     |

The elemental analysis was performed on a Philips model PW1480 XRF spectrometer. The concentration of total iron and copper were obtained with flame atomic absorption technique using Varian AAS Spectra 220 in the central laboratory of Sarcheshmeh Copper Complex.

The pH and ORP were measured using a pH Meter Metrohm model 827 with 6.0228.010 electrode and WTW pH 325 with Sentix ORP electrode, respectively. Sartorius GP-4102 scale was used to measure the weight. The stirrer of Heidolph MR Hei-end and laboratory oven of Thelco were used for mixing and drying all samples, respectively.

**Methods:** Fresh raffinate samples were sent to the laboratory for determination of iron(II) and iron(III) concentration.

**Method 1:** A 110 mL of fresh raffinate with pH and ORP 1.40 and 398 mv were used as test sample. 10 mL of this sample was used for analysis as reference (or control solution). The remained of raffinate solution mixed with 2 g of limestone powder. The mixture was stirred using a stirrer at 450 rpm for 1 h at room temperature. Colour of the solution was changed from light green to dark red. The resulting solution was filtered. The pH of this solution was 3.2 and then was decreased to pH = 1.25 by addition of 0.9 mL of 97 % sulfuric acid. The 10 mL of treated solution and control sample (reference) were sent to laboratory to measure the values of iron and copper. This test was repeated 3 times. The treated solution was filtered and the precipitations were collected. Filtrate solution volume was 70 mL that its pH was 3.32.

**Method 2:** A 140 mL of fresh raffinate was mixed with 60 mL of distilled water. The pH and ORP of 10 mL of the solution were 1.70 and 404 mv, respectively. 2 g of powder limestone (CaCO<sub>3</sub>) was added to 130 mL of the solution. This mixture was stirred by stirrer at 450 rpm for 1 h at room temperature. The solution was filtered and the solution volume was 100 mL. The pH and ORP of the resulted solution were 3.20 and 321 mv, respectively. The 0.8 mL of 97 % sulfuric acid was added and the solution pH was reduced to 1.25.

The pH and ORP of distilled water used for dilution were 5.47 and 74 mv, respectively. The precipitations were dried for the 8 h in oven at 60 °C, then the samples were collected and sent to XRF laboratory.

The weight difference of before and after addition of limestone was 0.75 g. This is equal to value of exit CO<sub>2</sub> gas. In fact, the tank containing of solution was placed on the scale and the scale was set to zero immediately after the addition of limestone. The scale was shown weight decrease of 0.75 g after the reaction was completed.

## RESULTS AND DISCUSSION

Results of treatment of raffinate without adding water (method 1) are shown in Table-2.

The average result for three tests for method 2 and XRF (after addition of water) are shown in Tables 3 and 4.

TABLE-2  
TOTAL IRON REMOVAL RESULTS FORM RAFFINATE WITHOUT DILUTION (WITHOUT ADDITION OF WATER)

|          | Raffinate control (reference) | First test | Second test | Third test |
|----------|-------------------------------|------------|-------------|------------|
| [Fe] g/L | 13.94                         | 12.95      | 13.63       | 13.94      |
| [Cu] g/L | 0.67                          | 0.02       | 0.11        | 0.49       |

TABLE-3  
TOTAL IRON REMOVAL RESULTS FOR RAFFINATE DILUTED WITH WATER (FROM METHOD 2)

|          | Raffinate control (reference) | Treated raffinate |
|----------|-------------------------------|-------------------|
| [Fe] g/L | 11.38                         | 7.81              |
| [Cu] g/L | 0.67                          | 0.49              |

TABLE-4  
XRF ANALYSIS OF PRECIPITATION PRODUCED BY DILUTED RAFFINATE REACTION (FROM METHOD 2)

|                                |         |                                |         |
|--------------------------------|---------|--------------------------------|---------|
| CaSO <sub>4</sub>              | 68.68 % | Al <sub>2</sub> O <sub>3</sub> | 5.62 %  |
| MgO                            | 1.15 %  | SiO <sub>2</sub>               | 14.78 % |
| Fe <sub>2</sub> O <sub>3</sub> | 8.13 %  | TiO <sub>2</sub>               | 0.29 %  |
| CaHPO <sub>4</sub>             | 0.50 %  | Total                          | 99.15 % |

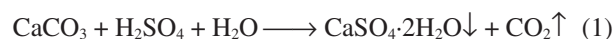
The results of fresh raffinate for iron(III) and iron(II) were shown in Table-5.

TABLE-5  
CONCENTRATION OF DIFFERENT IRON SPECIES IN THE FRESH RAFFINATE

| Concentration (g/L)  |         | Concentration (g/L)  |         |
|----------------------|---------|----------------------|---------|
| [Fe(tot)]            | 12.30   | [Fe <sup>3+</sup> ]  | 1.83    |
| [Fe <sup>2+</sup> ]  | 10.47   | Fe <sup>3+</sup> (%) | 14.87 % |
| Fe <sup>2+</sup> (%) | 85.13 % | Uncertain digits     | 0.1     |

## Conclusion

The reaction between the calcium carbonate and sulfuric acid generated gypsum precipitation and increased the pH of the solution is shown in eqn. 1 [8]:



Based on eqn. 1, the reaction has been accompanied with the consumption of water and H<sub>2</sub>SO<sub>4</sub>. Indeed, one mole of water is consumed per mole of sulfuric acid. The consumption of water leads to more concentrated solution. Thus, the pH would not increase as it is expected. On the other hand, decreasing of water value from the solution caused the concentration of hydrogen ions decreased less than one is expected. The experimental results showed that 30 % volume of the solution was reduced during the reaction. The weight reduction of content of reaction about 0.75 g confirmed progress of reaction. With ignoring the water evaporation, this weight decreasing is a good approximation that can be take into account to all CO<sub>2</sub> produced in the reaction. This involves 0.017 moles CO<sub>2</sub> which is equal to moles of water consumed. As gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) is forming 0.35 mL of water is consumed as water of crystalline lattice. However, this is only part of the water lost. The water can be lost by other ways such as water trapped in the iron hydroxide and so on. Furthermore, other factors can affect that it will need further studies.

Decreasing of water affects more in concentrated raffinate so that the results are not reproducible for removal of iron. The removal efficiency of iron will be very low at around 7 % of total types of dissolved iron. The value of iron(III) in raffinate was obtained about 14 % of total iron. So, half of it will be removed as instable. Therefore, if water is added in the same condition, 10 % of the total iron is removed by chemical reaction as repeatable. In the other hand, the dilution decreases about 23 % of total iron concentration. Totally, the combination of chemical and physical methods decreases about 33 % of total iron concentration.

Comparing value of consumed  $\text{CaCO}_3$  and produced  $\text{CaSO}_4$  showed that: (1) All  $\text{CaCO}_3$  powder was completely consumed. This indicates that  $\text{CaCO}_3$  was completely reacted with the acid and acid neutralization reaction has been completely done. (2) Molar percentage of  $\text{Fe}_2\text{O}_3$  in the precipitation was significantly more than the consumed  $\text{CaCO}_3$ . This clearly confirms the significant removal of iron. (3) The presence of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  in precipitate and the absence of them in original  $\text{CaCO}_3$  confirmed that  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  precipitations are a result of increasing pH which led to their concentration reduction in raffinate.

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