Copper Oxide Ore Leaching Ability and Cementation Behavior, Mesgaran Deposit in IRAN

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Abstract

One of the Iranian copper deposits that is located east of Iran and also known as a primeval one in that area is Mesgaran Field. Old mining works have been clearly seen in the area. Iran is located on global copper belt and as a result it has numerous potential areas as copper deposits. The purpose of this study is identifying possible potentialities of copper mining in less developed regions of Iran with basic modern technologies. In this study, laboratory investigations of this field were done on samples via leaching and the cementation method. According to the study purposes, acid concentration, temperature, time and pulp density were selected as the main factors that were tested in leaching studies. Moreover, pH, temperature, time and the amount of iron powder were factors which were tested for copper cementation. Optimum conditions of leaching studies with 99.11% recovery rate were obtained after 120 grams per liter of H2SO4, 80 degrees Celsius, 2 hours and 100 grams per liter of solid to liquid. On the other hand, optimum conditions of cementation by iron powder were resulted at more than 95% with a pH of 3, 45 degrees Celsius, 1 hour and 1.5 times more than the stoichiometric equation of required iron powder amount to precipitate copper.

Keywords

Leaching, Cementation, Copper Oxide, Malachite, VMS Copper Deposit

1. Introduction

Mineral processing studies begin from initial exploration stage. As in the exploration using the geostatistics and the detection of the anomalous elements of the
economic mineralization in the region [1], it should be confirmed by analyzing the
scale of the laboratory and generalizing it to the industrial scale of the eco-

gonomic existence of these minerals [2]. Remote sensing was used earlier in the ini-
tial investigations of the Mesgaran area for potential and detection of general
alterations and lithology [3]. And the mineral anomalies of the area were also
separated by statistical methods [4]. Copper extraction from raw materials is
obtained by two main methods, Pyrometallurgy and Hydrometallurgy [5].

About 80% copper-from-ore is obtained by flotation, smelting and refining;

nearly all sulfide type minerals such as Chalcopyrite, Covellite, Chalcocite and
Bornite processed by this method which is known as the pyrometallurgy method
[5] [6]. The remaining copper minerals proportion is called oxide types, and is


treated by acid and bases reagents in the hydrometallurgy method [7] [8].

Nowadays, sulfide minerals are not as pure as 50 years ago to smelt directly in
a flash furnace and as a result, these low grade raw materials (less than 1% Cop-


er included) should be processed by the flotation method to reach to an ac-
ceptable grade (more than 22% Copper included). After this step, matte smel-
ing, matte converting and refining are applied to the product of the flotation step
to obtain copper with more than 99% purity [5] [6].

Oxide minerals as described formerly can be treated by the hydrometallurgy
method that contains three main steps 1) Leaching, 2) Solvent Extraction (SX)
and 3) Electrowinning (EW) [7] [9] [10] There are other methods to recover
copper after leaching [5]. Cementation and Ion Exchange (IX) are the two main
methods [5] [7]. Cementation is the basic method of hydrometallurgy that was
applied by alchemists many years ago [6]. Cementation is not the most economi-
cal, fastest and selective way to recover copper; however it is the cheapest me-
thod besides being easy to operate [11].

Sulfuric Acid (H₂SO₄) is the most common chemical reagent that is used for
the leaching of oxide minerals including copper ones [5]. Among the most im-
portant factors of leaching are reagent type, temperature, time and pulp density
[12] [13].

The principle of cementation is based on electrochemical differences between
ions capacity. Lead, Iron, Zinc and Aluminum are respectively the best metals
that can recover copper from PLS [6]. Cementation is widely used for Gold re-
covery from PLS by Zinc powder [14] [15].

This technical note is to report and document initial experimental findings
that could lead to a new understanding of the role of Sulfuric Acid in the reco-
very of copper from oxide minerals.

2. Data and Analytical Procedures

2.1. Geolocation of Mesgaran Copper Deposit

Mesgaran Copper Field is located 29 km south of Sarbisheh City, east of Iran.
Accessibility to the field is possible via Nehbandan-Sarbisheh Road. There is no
rough topographic area in the field and nearly all of the field is accessible by
usual cars. The geological structure of the area contains of mafic and ultramafic rocks. This field is a part of the Gold zone of Ahangaran-Bandan metallogenic province (Figure 1) [16].

2.2. Ore Geology and Mineralization

In Mesgaran mining area Copper mineralization has occurred in pillow-lava and andesite-basalt sequences of eastern Iran (Figure 2). Two mineralization zones were identified as sulfide mineralization with silicified stockworks (primary mineralization) and supergene mineralization. The primary copper mineralization in this region is mostly in accordance to silicified or carbonate veins with epidote and chlorite in volcanic basalt [3].

These veins cross out the volcanic complex as stockworks which include Chalcopyrite, Bournite and Pyrite. In this region, we observed no evidence proving massive deposit or lens shape deposit creation. The main observed minerals

Figure 1. Major geological subdivisions map of Iran [17] and location of mesgaran copper deposit (star).
are sulfide and oxide forms of copper. Malachite, Azurite and lower amounts of Tenorite and native copper in oxide supergene zone and chalcopyrite and bornite as the primary sulfides have been detected. Oxidation and erosion caused geotite and hematite around sulfide minerals like Chalcopyrite and Pyrite (Figure 3). Alteration is observed almost everywhere on the surface but the degree of alteration varies. Generally alteration occurs when rocks react to hydrothermal and magmatic fluids and this reaction leads to chemical and mineralogic changes. Chlorite alteration has occurred in large scale which is a specific form of Propylitic alteration. Al, Fe and Mg rich fluids cased chlorite alteration in basic rocks [18].

In this region, argillic alteration (presence of Montmorillonite mineral) as a secondary alteration process is observed too. Most of the copper is in oxide form on the surface and because of high degree of oxidation and erosion, sulfide mineralization is rare in outcrops so deeper samples are needed to study the deposit. Drilling is the best choice in such situations. According to mineralization and the host rock (pillow lava and andesite-basalt), the mineralization type seems to be categorized as a massive sulfide and redbed type. Generally the mineralization manner (copper mineralization as stockworks), the host rock (pillow lava and andesite-basalt), the deposit development environment (a volcanic part of an

Figure 2. View of the ophiolite sequence of the region. (a) Mild morphology and hills of ultrabasic rocks in the north of Mesraran; (b) A view of pillow basalt whose outer surface is affected by contact with sea water and cooling and its color and texture have changed.

Figure 3. Sulphide mineralization (chalcopyrite and pyrite) in basalt that has been converted into iron hydroxides, chalcocites and covellite by the supergene processes.
Ophiolite sequence) and the alterations (quartz-carbonate, epidote and chlorite) observed in this region and comparing them to the massive sulfide types leads to classify Mesgaran deposit as a Volcanic Massive Sulfide (VMS) type. But still more studies are needed to prove this claim with higher accuracy [18] [19] (see Figure 4).

2.3. Reagents and Sample Preparation

200 kg of the sample is taken from Mesgaran Field after excavation. Then the sample is crushed by a jaw crusher and milled to obtain minus 120 microns size. After milling, XRF and XRD are applied to the sample to study phases and chemical composition. All tests and devices took place in laboratories of Amir-Kabir University of Technology. The main copper mineral phase in the sample is malachite and the main mineral phase of the sample is quartz that does not react with sulfuric acid. XRF device was X’Unique II Philips (Table 1).

2.4. Leaching Tests

For leaching tests, sulfuric acid of Merck Company is selected and distilled water is used for dilution. Moreover, a hotplate and 250 ml beaker are used for these tests. The hotplate has a digital temperature regulator and magnetic stirrer. First,
the solution is prepared for each test in a beaker together with specified pH and after reaching a defined temperature, a certain amount of copper ore with a size fraction of minus 120 micron is added to the solution for doing leaching tests in certain time periods. Four factors of acid concentrations, temperature, time and pulp density has been studied in three levels by the Taguchi method. As a consequence, L9 Taguchi orthogonal array has been selected for leaching tests. Tests are designed with the Taguchi method and Variance analysis (ANOVA) has been done in Design Expert for leaching tests and Microsoft Excel for cementation tests. The value of each parameter at every level has been presented in Table 2.

2.5. Cementation Tests

The cementation process of copper by iron powder is provided by following equation:

\[
\text{Cu}^{2+} + \text{Fe} \rightarrow \text{Cu} + \text{Fe}^{2+}
\]

As a result of the differences in electrochemical potentials, a reaction will take place. The reaction potential of Iron and Copper is presented in Table 3.

\[
(\Delta G^\circ)_{298} = -20.29 - 15.54 = -35.83 \text{ Kcal}
\]

According to the Gibbs free energy equation, the reaction will be obtained

<table>
<thead>
<tr>
<th>Table 1. XRF analysis of sample.</th>
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<tbody>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>Al₂O₃</td>
</tr>
<tr>
<td>MgO</td>
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<tr>
<td>CaO</td>
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<th>Table 2. Levels of factors in leaching tests.</th>
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<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>Acid concentration (gr/l)</td>
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<tr>
<td></td>
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<tr>
<td>Time (minute)</td>
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<tr>
<td>Temperature (Celsius)</td>
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<tr>
<td>Pulp density (gr/l)</td>
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<td></td>
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</tbody>
</table>

<table>
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<tr>
<th>Table 3. Reaction equations of copper and iron.</th>
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<tbody>
<tr>
<td>Half Reaction</td>
</tr>
<tr>
<td>Cu²⁺ + 2e⁻ =&gt; Cu</td>
</tr>
<tr>
<td>Fe³⁺ + 2e⁻ =&gt; Fe</td>
</tr>
</tbody>
</table>
spontaneously. In order to perform cementation tests, 100 ml of copper ore was dissolved in the solution and added up to a 250 ml beaker, and after regulating pH, the temperature will be adjusted by the hotplate. After these steps, iron powder will be added up to the solution in order to study the test.

In order to study the cementation of copper by iron powder, four parameters of pH, temperature, time and amount of iron powder were optimized in three levels by the Taguchi method. The value of each parameter at every level has been presented in Table 4.

2.6. Taguchi Method

The technique of defining and investigating all the possible conditions in an experiment involving multiple factors is known as the design of experiments. Basically, classical parameter design, developed by Fisher, is complicated and not easy to use. Especially, a large number of experiments must be conducted when the number of the process parameters increases. To solve this problem, Taguchi method uses a special design of orthogonal arrays to study the entire parameter space with a small number of experiments only [20] [21].

Experimental designs were first introduced by Fisher as an agricultural research tool in the 1920s [22]. His primary aim was to obtain the most information possible about a process with the least number of experiments. Experimental designs and optimization methods for chemists and other engineering branches were reviewed by Bayne and Rubin [23], Debets [24] and Duckworth [25], Taguchi [26] simplified the application of experimental design by using standardized library of basic designs called orthogonal arrays, along with some simple methods to modify these layout to fit individual situations. His methodology was also developed within an industrial environment and favoured productivity and cost effectiveness over the statistical rigor. Orthogonal arrays were used to assign factors to a series of experimental combinations which results could then be analyzed by using a common mathematical procedure. The main effect of these factors and preselected interactions between the factors were independently extracted. The identification of controlling factors and the quantitation of the magnitude of the effects was emphasized rather than just the identification of statistically significant effects. The number of trial chosen for an experimental design was based on the resolution desired. In a factorial design, one could study main effects as well as interactions between factors. This latter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Level</th>
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<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>pH</td>
<td>0</td>
</tr>
<tr>
<td>Temperature (Celsius)</td>
<td>25</td>
</tr>
<tr>
<td>Time (hour)</td>
<td>0.5</td>
</tr>
<tr>
<td>Iron powder (stoichiometric amount)</td>
<td>1</td>
</tr>
</tbody>
</table>
characteristic was a major advantage of the technique but a major disadvantage of one-at-a-time variable testing. Main effects and interactions could be confounded, with one another if the experimental design of low resolution were chosen [27] [28].

3. Results and Discussion
3.1. Leaching Ability

The L9 array leaching tests which are modeled by the Taguchi method are inserted in Table 5.

3.1.1. Effects of Acid Concentration in Leaching

After 9 tests with the Taguchi method, 1 factor diagrams of acid concentration to recovery rate was obtained as shown in Figure 5. The greater acid concentration causes more H⁺ cation in the solution which increases the recovery rate individually.

3.1.2. Effect of Time in Leaching

According to Figure 6, time factor affect has an increasing role in recovery rate, but optimum conditions should be checked via more tests. Time is always a critical factor in leaching tests which can result in diverse outcomes related to nature of the element. In this study, effect of time is complex due to behavior of sample and related to interaction with other factors.

3.1.3. Effect of Temperature in Leaching

According to chemistry principles, an increase in temperature will result in a progress of elements motion which means it will lead to more reactivity of complex. Based on our test results which can be seen in Figure 7. There is a gradual progress in recovery rate with an increase in amount of the temperature.

3.1.4. Effect of Pulp Density in Leaching

Similar to most leaching tests, increasing the pulp density will cause a decrease

<table>
<thead>
<tr>
<th>No.</th>
<th>Acid concentration (gr/l)</th>
<th>Time (minute)</th>
<th>Temperature (Celsius)</th>
<th>Pulp density (gr/l)</th>
<th>Cu recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>60</td>
<td>40</td>
<td>100</td>
<td>82.74</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>90</td>
<td>60</td>
<td>150</td>
<td>62.67</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>120</td>
<td>80</td>
<td>200</td>
<td>78.75</td>
</tr>
<tr>
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<td>80</td>
<td>60</td>
<td>60</td>
<td>200</td>
<td>86.96</td>
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<td>80</td>
<td>90</td>
<td>80</td>
<td>100</td>
<td>92.44</td>
</tr>
<tr>
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<td>80</td>
<td>120</td>
<td>40</td>
<td>150</td>
<td>77.75</td>
</tr>
<tr>
<td>7</td>
<td>120</td>
<td>60</td>
<td>80</td>
<td>150</td>
<td>84.10</td>
</tr>
<tr>
<td>8</td>
<td>120</td>
<td>90</td>
<td>40</td>
<td>200</td>
<td>81.02</td>
</tr>
<tr>
<td>9</td>
<td>120</td>
<td>120</td>
<td>60</td>
<td>100</td>
<td>99.11</td>
</tr>
</tbody>
</table>
in recovery rate, where in some tests it has been seen that after a maximum level for pulp density, reactions will come to an end. In this case, the anomaly point has occurred where it is expected to further decrease the recovery rate. Incidentally, the lower level in pulp density will result in a greater recovery rate (Figure 8).
3.1.5. Effect of Factor Interactions in Leaching

According to the obtained models in the software, factor interactions have been investigated to gain better cognition of the process and increase the efficiency of operation. For this purpose, interaction of temperature and pulp density are depicted in Figure 9 where increasing the temperature and decreasing the pulp density results in a greater recovery rate of the operation. Also, interaction of time and pulp density covered in Figure 10 indicate that increasing time and
Figure 9. Interaction of temperature with pulp density on recovery rate.

Figure 10. Interaction of time with pulp density on recovery rate.

decreasing pulp density results in a greater recovery rate of the operation, while
time played a twofold role in this diagram. In addition, interaction of time and
temperature as shown in Figure 11 where the increasing level of time and tem-
perature together lead to more recovery rate, while time played a twofold role in
this diagram once more. The interaction of acid concentration and temperature
is shown in Figure 12 where an increase of acid concentration and temperature
together caused a greater recovery rate.
Interaction of acid concentration and time is shown in Figure 13 where, recovery rate stepped up with an increase of acid concentration and temperature together, to further illustrate the factors which are involved in reactions, acid concentration has the most influence besides temperature. The interaction of acid concentration and pulp density is shown in Figure 14, where an increase of acid concentration and a decrease of pulp density results in a greater recovery rate of the operation. More diagrams have been given in Figure 15 where 3D
factor diagrams have simplified the interactions cognition.

### 3.2. Cementation Behavior

#### 3.2.1. Effect of pH in Cementation

According to the obtained diagram in Figure 16, as obtained from the experiments, pH has an increasing linear boost in copper recovery rate curve in cementation operation, which it shows a decrease in amount of H⁺ cations will

**Figure 13.** Interaction of acid concentration with time on recovery rate.

**Figure 14.** Interaction of acid concentration with pulp density on recovery rate.
3.2.2. Effect of Temperature in Cementation

With a more detailed look at Figure 17, it is obvious that a raise in the temperature level will cause an increase in recovery rate and it is logical from thermodynamic aspects of the reactions.

lead to substitution of Copper ions with Iron ions in solution.

Figure 15. 3D factor interactions diagrams.

Figure 16. Effect of pH on recovery rate in cementation.
3.2.3. Effect of Time in Cementation
As it has been seen in Figure 18, after a sharp increasing result of recovery rate from 30 minutes to 60 minutes, the recovery still increases but in a gradual pattern, which shows that the optimum point is 1 hour for further economic aspects. So, according to this diagram the optimum condition of time for cementation of copper with iron powders is about 1 hour.

3.2.4. Effect of Iron Powder on Cementation
The last parameter which is examined in the tests was the total amount of iron powder that is needed for the reaction. Due to test results, increasing the amount of iron powder that is measured by stoichiometric quantities, tends to increase the copper recovery rate of the cementation process (Figure 19).

4. Conclusions
Mesgaran copper field which is also known as one of the primeval mines in east of Iran, was examined with numerous tests to be run as a modern mine with new technologies. As it has been observed, the economic mineral in this field is
malachite which is encompassed by quartz gangues that leads the experiments to
leaching tests with H\textsubscript{2}SO\textsubscript{4} instead of flotation or physical separation methods.
Hence, after taking samples from the field, the test was designed via the Taguchi
and Variance analysis method. Afterward, tests were performed in the Amirkabir
University of Technology laboratory to gain optimum conditions of leaching
and cementation operation. In the leaching operation, four factors of acid con-
centration, temperature, time and pulp density have been studied at three levels.
Moreover, in order to study copper cementation by iron powder, four factors of
pH, temperature, time and amount of iron powder, are optimized at three levels.

Finally, it is found that increasing acid concentration, temperature and time
will cause an increase in the copper recovery of ores with the leaching method.
On the other hand, increasing pulp density will have a reverse reaction. From
another stance, in the cementation process, the recovery rate of copper increased
by maximization of pH, temperature and a lower rise in time and iron powder
amount. Optimum conditions of leaching studies with 99.11% recovery rate
came after 120 gram per liter of H\textsubscript{2}SO\textsubscript{4}, 80 degrees Celsius, 2 hours and 100 gram
per liter of solid to liquid. In addition, the optimum conditions of parameters
during the cementation process with iron powder were obtained at more than
95% with a pH of 3, 45 degrees Celsius, 1 hour and 1.5 times more than the
stoichiometric amount of copper.

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**Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this pa-
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References


