# Fabrication of Arsenic Sulfide using Thermal Treatment

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#### Abstract

To remove the arsenic from gold concentrate using a thermal decomposition method, a test was conducted while changing the reaction time at 700°C. Additionally, the volatile arsenic from the gold concentrate was recovered using a bag-filter. The arsenic content in the concentrate was rapidly reduced from 12.62wt.% to 1.40wt.% after 1-hour burning and to below 1wt.% after 2 hours, indicating approximate 95% removal rate.

Keywords: Arsenic, Concentrate, Decomposition, Recovery

# 1. Introduction

The gold (Au), a typical precious metal, is widely used in various industries because of its excellent physicochemical properties. In particular, the gold is widely used as the surface coating material and the bonding wire for electrical / electronic parts<sup>1,2</sup>.

Various studies have been conducted to extract the gold from gold concentrate and tailings, but there are difficulties in the leaching process due to the environmental constraints on the use of cyanide and the various impurities contained in the gold concentrate<sup>3–6</sup>. In particular, impurities such as iron, copper, zinc, lead and arsenic, etc. are contained in the gold concentrate. In particular, if a large amount of arsenic is contained in the gold concentrate, the resultant low dissolution rate causes difficulties in separating and recovering the gold during the refining process and the high arsenic content causes difficulties in the arsenic treatment.

Korean research teams have conducted studies for the removal of arsenic and heavy metals from the tailings through soil washing. The results demonstrated that the most effective cleaning agents include oxalic acid (72% removal efficiency) and phosphoric acid (65%). The oxalic acid was very effective in removing heavy metals including Cu<sup>7</sup>. However, its arsenic removal rate was relatively low and contained an environmental risk of the secondary pollution from the waste water after soil washing, which limits its commercialization.

The studies on the arsenic removal characterization for the arsenic contained in the deposit soil of heavy metal mines using an electrokinetic separation method were conducted. In this study, the arsenic removal rate was measured using 4 different electrolytes. The results of this study showed that the arsenic removal rate was in the order of citric acid + Sodium Dodecyl Sulfate (SDS) (18.6%)> 0.1 NHNO (8.1%)> HAc (7.4%)> distilled water (6.6%). The maximum arsenic removal rate was below 20%, indicating the technical possibility, yet its low removal rate was still a large obstacle to the practical use<sup>8</sup>.

Therefore, this study was intended to improve the arsenic removal rate for gold concentrate using an environmentally friendly dry-heat treatment method, unlike the conventional processes based on a wet method only and also to maximize the gold recovery rate during the refining process. To remove and collect the arsenic

efficiently using a bag-filter, this study was conducted to remove and recover the arsenic by changing the reaction time for the gold concentrate in the form of power in an inert atmosphere furnace.

## 2. Materials and Methods

The material used in this study is the concentrate in the form of power recovered from domestic mine A and its chemical composition is shown in Table using inductively coupled plasma optical emission spectrometry (ICP-OES). It mainly contains Fe and S and about 15% As, as well as a small amount of Ca, Zn, Si, Mn and Al. The results of an analysis of the gold concentrate using X-ray Diffraction are shown in Figure 1. As shown in the results of analysis, the gold concentrate is composed of ZnS, FeS, FeAsS, and As exists only in FeAsS (arsenopyrite). Arsenopyrite containing approximately 46% arsenic is known as a typical ore containing arsenic<sup>9</sup>.



Figure 1. XRD patterns of gold concentrate.

Figure 2 is a schematic diagram of a test equipment. It was manufactured in a shape enabling it to put the reactor body into a box type electric furnace from the top. The reactor body and cover used in this test were made of SUS310 that has excellent anti- corrosiveness and durability at high temperatures to minimize the potential thermal fatigue and facture defects during test. To ensure complete sealing, the O-ring was installed between the reactor body and cover to block up the access of internal gases, and the cooling line installed beneath the cover prevented the O-ring from melting at high temperatures.

The arsenic in the form of power put in an aluminum boat was then put into the center of the reactor to facilitate the discharge of the arsenic in a gaseous state through the off-gas line. To collect the arsenic in a gaseous state at room temperature, the off-gas line was connected to the erlenmeyer flask and the bag-filter was installed at the end of the line. The arsenic in the form of power collected in the bag-filter was analyzed for its components and phase using Energy-Dispersive Spectroscopy (EDX), Scanning Electron Microscopy and X-ray Diffraction (XRD). For the test method, the gold concentrate in the spectral form was evenly distributed in the aluminum boat so that its particle height was below 5mm, and the boat was placed at the center of the reactor and then the reactor body was coupled with the body. U.H.P. argon gas was then injected at 0.2 liter / min and the temperature was raised to 700° C to immobilize the arsenic and off-gas in the bag-filter while maintaining the reaction time at regular intervals and the arsenic in a gaseous state was collected in the form of power.



**Figure 2.** Experimental apparatus for removal of arsenic from gold concentrate.

### 3. Results and Discussion

To remove and recover the arsenic from gold concentrate, this study was conducted through 2-stage continuous chemical reaction, and respective chemical reaction formulas are expressed in (1) and (2). The first chemical reaction formula (1) represents the thermal decomposition at high temperatures. As shown in Figure 3, As exists in FeAsS only in the gold concentrate and FeAsS can be decomposed into FeS and As thermodynamically at 600°C, 700°C, 800°C, and 900°C indicating that the arsenic can be removed by transforming the arsenic in a solid state to the arsenic in a gaseous state by raising the temperature in an inert gas atmosphere (UHP Ar). In the case of arsenic, the boiling point is lower than the melting point at standard atmospheric temperature, so the arsenic in a solid state is sublimated into the arsenic in a gaseous state immediately at 614°C (887K), indicating that 700°C is a sufficient condition for temperature for the removal of arsenic. Reaction Formula (2) represents the phase change from the gaseous arsenic removed to the solid arsenic at room temperature. To collect the arsenic in a solid state, the bag-filter was installed at the end of gas discharge pipe to collect the arsenic powers in the filter.



**Figure 3.** Weigh loss with time at each temperature analyzed by TGA. (a) 600°C (b) 700°C (c) 800°C (d) 900°C.

| $FeAsS \rightarrow FeS + As(g)$ | $\Delta G_{_{600}}$ | =-10.55 kcal         |    |
|---------------------------------|---------------------|----------------------|----|
| $FeAsS \rightarrow FeS + As(g)$ | $\Delta G_{_{700}}$ | =-10.24 kcal         |    |
| $FeAsS \rightarrow FeS + As(g)$ | $\Delta G_{_{800}}$ | = - 9.99 <i>kcal</i> | 1) |
| $FeAsS \rightarrow FeS + As(g)$ | $\Delta G_{_{900}}$ | = - 9.95 <i>kcal</i> |    |
|                                 |                     |                      |    |

$$As(g) \rightarrow As(s)$$

Table 2 summarizes chemical composition of gold concentrate on the effect of temperature from 600°C to 900°C and removal rate of arsenic is shown in Figure 4. The concentrate originally contained 11.07 wt.% of arsenic and 36.36 wt.% of sulfur as well. Other impurities such as iron, zinc, silicon, calcium, and aluminum were also observed by X-ray fluorescence (XRF). As temperature raised to 600°C, arsenic content was dramatically decreased from 11.07 wt.% to 0.39 wt.%. In addition, the content of arsenic remained was almost same according to increase of temperature, which is around 0.3 wt.% in gold concentrate. The content of sulfur was also removed as temperature increased and its content was reduced from 36.35 wt.% to 20.95 wt.%. It might be expected that arsenic and sulfur were evaporated and reacted together to form arsenic sulfide at the range of temperature of 600°C to 900°C.

The removal rate of arsenic was evaluated based on the test data shown in Figure 4. The results showed that the arsenic removal rate after 1-hour reaction at 600°C was about 92 wt.%, indicating that the gaseous arsenic in the concentrate was almost removed after about 1-hour reaction. The arsenic was removed up to 95% at 700°C and the removal rate remained consistently on an average basis after then, showing no difference in the removal rate when it comes to change of temperature. The arsenic contained in the gold concentrate is in the form of FeAsS. The As is separated and removed in a gaseous state through a thermal decomposition method at high temperatures. The arsenic outside the compose was decomposed thermally and then removed in a gaseous state during the initial reaction time whereas the small amount of As inside the composite was removed completely through a thermal decomposition method. This implies that the

Table 1. Chemical composition of gold concentrate analyzed by ICP

2)

| Chemical composition |       |       |        |       |       |        |       |        |  |
|----------------------|-------|-------|--------|-------|-------|--------|-------|--------|--|
| Concentrate          | Al    | Si    | S      | Ca    | Mn    | Fe     | Zn    | As     |  |
|                      | 0.140 | 2.486 | 36.355 | 1.899 | 0.302 | 32.371 | 7.777 | 11.071 |  |

 Table 2.
 Chemical composition of gold concentrate at each temperature

| Chemical composition |       |       |        |       |       |        |        |        |  |
|----------------------|-------|-------|--------|-------|-------|--------|--------|--------|--|
|                      | Al    | Si    | S      | Ca    | Mn    | Fe     | Zn     | As     |  |
| Concentrate          | 0.140 | 2.486 | 36.355 | 1.899 | 0.302 | 32.371 | 7.777  | 11.071 |  |
| 600°C                | 0.182 | 2.054 | 23.901 | 1.743 | 0.402 | 43.548 | 9.254  | 0.397  |  |
| 700°C                | 0.166 | 1.817 | 26.918 | 1.685 | 0.323 | 44.039 | 8.398  | 0.298  |  |
| 800°C                | 0.183 | 1.755 | 21.227 | 1.604 | 0.386 | 47.296 | 9.112  | 0.311  |  |
| 900°C                | 0.192 | 1.974 | 20.952 | 1.888 | 0.382 | 44.586 | 10.200 | 0.307  |  |

reaction time above the test condition is required, and this is the limitation of a dry method for the removal of arsenic.



**Figure 4.** Change of contents of Fe, S, Zn, and As in gold concentrate and removal rate of As with temperatures.

The powders collected in the bag-filter were analyzed. Only As and S were detected and the extension of the reaction time up to 7 hours after 20 minutes lapsed did not affect the quantitative change of As and S. Figure 5 shows the phases of the powder collected in the bag-filter analyzed using Energy Dispersive X-ray Spectroscopy and the powder forms observed using Scanning Electron Microscopy. The results were consistent with the those of an analysis using Energy Dispersive X-ray Spectroscopy as shown in Fig 5, and no other impurities than the pure AsS were not detected. The reason that the element collected in the bag-filter is AsS in the form of As and AsS composite deemed to be caused by the sublimation of S contained in the sulfide ore which has been discharged in a gaseous state, reacted with As and then collected in the bag-filter. As shown in the As and A chemical reaction formula (3), the Gibbs free energy is -43.83kcal, which indicates the spontaneous reactions as AsS at 700°C.

As + S(g) = AsS 
$$\Delta G_{700^{\circ}C} = -43.83$$
 kcal (3)

Figure 5 also shows the values of the gaseous arsenic collected in the form of power by installing the bag-filter at the end of the off-gas line measured using Energy Dispersive-ray Spectroscopy according to the reaction time. The collected arsenic sulfide can be uses as pigments or colorants, and the collected arsenic can be used as the additives for the lead batteries for automobiles and the semiconductor material (GaAs), thereby contributing

to minimizing the environmental issues caused by the arsenic and increasing the value of the wasted resources. Additionally, the collected AsS is in the form of spherical powder, and its diameter ( $10\mu$ m on an average basis) is consistent. The collected composite powers could be separated well in the bag-filer and collected easily in the form of spherical powders when a little shock was applied. In conclusion, the thermal decomposition method enabled it to remove As from FeAsS efficiently and also recover the powers in the form of AsS from the bag-filter. The results of this study implied that there is the necessity of further studies considering the reaction temperature, the amount of input and the size of concentrate so as to improve the removal and recovery rate of As.



**Figure 5.** XRD patterns and shape of powder collected at 700°C for 120 minutes.

### 4. Conclusion

A test was conducted to separate and remove the As contained in the FeAsS(arsenopyrite), a mineral composing gold concentration, using through thermal decomposition. The highest As removal rate was achieved when it was maintained for 2 hours at 700°C above the As sublimation temperature in an inert gas atmosphere. The As discharged as a discharge gas was in the form of AsS and was efficiently collected by the bag-filter.

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## 6. References

- 1. Marsden JO, House CI. The chemistry of gold extraction, SME; 2006.
- 2. Adams MD. Advances in gold ore pressing, Elsevier; 2005.
- Nam KS, Jung BH, An JW, Ha TJ, Tran T, Kim MJ. Use of chloride-hypochlorite leachants to recover gold from tailing. International Journal of Mineral Processing. International Journal of Mineral Processing. 2005; 86; 131–40.
- 4. Tongamp W, Takasaki Y, Shibayama A. Selective leaching of arsenic from enargite in NaHS-NaOH media. Hydrometallurgy. 2010; 101:64-8.
- 5. Curreli L, Garbarino C, Ghiani M, Orru G. Arsenic leaching from a gold bearing enargite flotation concentrate. Hydrometallurgy. 2009; 96:2581–63.

- 6. Yang JS, Lee JY, Baek K, Kwon TS, Choi J. Extraction behavior of As, Pb, and Zn from mine tailings with acid and base solutions. Journal of Hazardous Materials. Journal of Hazardous Materials. 2009; 171:443–51.
- 7. Kim TS, Kim MJ. Remediation of mine tailings contaminated with arsenic and heavy metals: removal of arsenic by soil washing. Journal of Korean Society of Environmental Engineers. 2005; 30:808–18.
- Shin HM, Yoon SS. Removal characteristics of arsenic from abandoned metal mining tailings by electrokinetic technique. Journal of the Environmental Science. 2006; 15:279–86.
- Hurlburt CS, Klein C. Manual of Mineralogy, 20<sup>th</sup> edn., John Wiley & Sons, Inc; 1985.