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Preparation of nano gold powder from acid leaching tail solution

M. Kargar Razi [1,*], M. Khosravi [1], R. Sarraf Mamoory [2], M. Mohammadi [3]

[1]Islamic Azad University, North Tehran Branch, Iran
[2]Tarbiat Modares University, Tehran, Iran
[3]Mouteh Gold Complex, Iran

Abstract

According to the unique properties and many applications of nano gold powder, it was prepared from an acid leaching tail solution. The low value residual gold ions existed in acid leaching tail solution in Mouteh gold mine in Iran with fellow heavy metals as pollutants (Fe^{2+}, Cu^{2+}, and Zn^{2+}). Preparation of nano gold particles is achieved by two steps: First, by addition of ammonia as separation step and second by using the suitable reagents for precipitation and extraction step. Control conditions include pH, residence time, temperature, agitation, molar ratio of reducing agents to reagents. The optimum results show that nano gold powder was prepared by temperature of 250 $^{\circ}C$, urea to gold molar ratio of 3:1, and reduction time of 20 min. Also, heat treatment improves dispersion of nano sized gold particles. The properties of gold nano powders were evaluated by SEM, A.A and UV-Vis spectroscopy methods and the size of particles were about 80 to 90 nm.

Key words: *Nano gold powder, leaching tail , urea , precipitation*

1. Introduction

The unique properties of nano-sized metal particles have been attracting a great deal of interest in various fields in all over the world [1,2]. Accompanying the increase in studies of their physical properties, various preparation methods for nano sized metal particles have been developed. Nowadays application of gold nano particles (AuNPs) or gold colloid has been greatly expanded in a new generation of optical and electronic devices. One of the reasons for the considerable current interest in nano particle is because such materials display unusual physical and chemical properties (i.e. structural, electronic, optical, magnetic and catalytic) [3,4]. GNPS (gold nano particles) have been studied in electrochemistry for its special physical and chemical characteristics. Accompanying the increase in studies of their physical properties, various preparation methods for nano-sized metal particles have been developed [5]. Producing nano-sized particles is basically

*Corresponding author: Maryam Kargar Razi
Islamic Azad University, North Tehran Branch,
Tehran,Iran.
Tel +98 912 644 4815
Email mkargarrazi@yahoo.com

upon powder metallurgy technology . Respect to high economical value of nano-sized gold powder compared to metal's bar shape value and considering existence of potential capacity in Mouteh mine, this project was very essential.

Three common hydrometallurgical processes for industrial waste treatment are solvent-extraction, ion-exchange, electro-oxidation; precipitation [6]. This work was base on precipitation reaction followed by combustion reactions. So gold was extracted from waste solution after that it was transformed to nano shape.

2. Materials ans methods

A process of gold reclamation from waste was consisted of the following steps:

1.   The industrial waste solution containing substantial quantities of valuable component that was gained from cathode acid leaching process in gold room at Mouteh mine was filtered.
2.   HCl (conc.) was added to waste solution to form $HAuCl_4$.
3.   Ammonia (8molar) added to solution, then adding was stopped at pH=10.5.
4.   After 60 minutes, residue was mixed with water and sodium bisulphate in it.
5.   First step of leaching was with sulphuric acid 8 M in order to remove silver and other metals.
6.   Second step of leaching was with nitro-hydrochloric acid.
7.   In leaching process optimum conditions were established when temperature was 40 ^{oC} with 7 hr stirring.

Final step was taken to prepare nano gold from $HAuCl_4$ solution. Here the best efficiency was resulted when we used urea with mol ratio of 3:1 to gold at 800 ^{oC} for 10 minutes. Nanosized gold was investigated with UV-visible and SEM (scanning electron microscope).

3. Results and discussion

As we know there can be lots of gold in the waste solution of an industrial pilot in mine. Now our purpose is gaining this amount of metal .The gold recovery process from industrial wastes is very important from two points of view: first is the economical problem, as we know gold is one of the most valuable metals and the second is that because gold belongs to heavy metals group. We have to protect environment from the dispersed toxic compounds, especially compounds of heavy metals.

Quantity of silver, gold, copper, zinc and iron in industrial solution were estimated with atomic absorption as follow: 25 ppm, 86 ppm, 2536 ppm,169 ppm, 16731ppm.
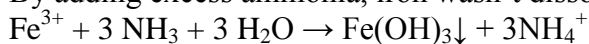
3.1. Effect of pH on gold separation via ammonia

Figure 1 shows variation of pH at silver nitrate solution.By adding 0.18 cc ammonia (1.33 M) to silver nitrate solution (0.00023M) pH was suddenly increased. because at pH=9.32 Ag_2O was prepared and free OH was consumed, following this reaction at pH=10.33 total Ag_2O was converted to $[Ag(NH_3)_2]^+$ and OH^- was released. This pH was used for our industrial solution to have total Ag as form of $[Ag(NH_3)_2]^+$ in solution. Gold was remained as solid form and was filtered for purification process. Atomic absorption and UV−vis spectra results indicated that at pH (10.5) total Ag was converted to $[Ag(NH_3)_2]^+$ and there were no gold and iron in mother liquor. Respect to ligand field theory (LFT), complex formation of metals with ammonia is stable. Gold

ions in industrial solution was converted to gold complex as $HAuCl_4$ by adding HCl (conc.). Using ammonia until the pH was increased to 10.5 could transform gold ions to brown residues as $Au_2O_3.3NH_3+NH(ClNH_2Au)_2$ and $Au(OH)_3$ and other reactions occurred as shown below:

By adding excess ammonia, copper was transferred to solution
$$Cu^{2+} + 2\ NH_3 + H_2O \rightarrow CuO + 2\ NH_4^+$$
$$H_2O + CuO + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2OH^-$$
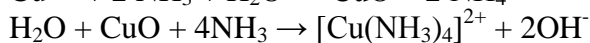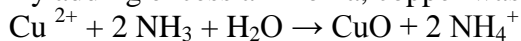
By adding excess ammonia, iron wasn't dissolved
$$Fe^{3+} + 3\ NH_3 + 3\ H_2O \rightarrow Fe(OH)_3\downarrow + 3NH_4^+$$

By adding excess ammonia, zinc was transferred to solution
$$Zn^{2+} + 2\ NH_3 + 2\ H_2O \rightarrow Zn(OH)_2\downarrow + 2\ NH_4^+$$
$$Zn(OH)_2\downarrow + 4\ NH_3 \rightarrow [Zn(NH_3)_4]^{2+} + 2OH^-$$
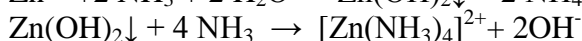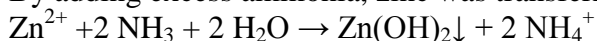
By adding excess ammonia, silver was transferred to solution
$$2Ag^+ + 2\ NH_3 + 2\ H_2O \rightarrow Ag_2O\downarrow + 2\ NH_4^+$$
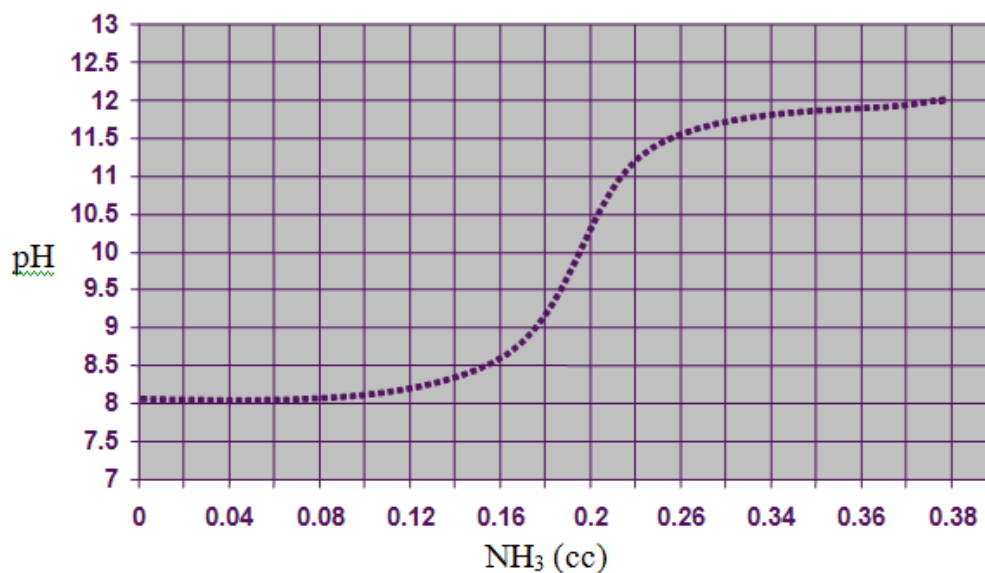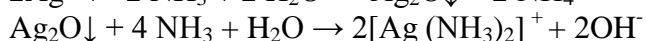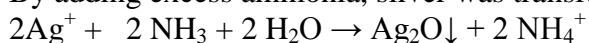$$Ag_2O\downarrow + 4\ NH_3 + H_2O \rightarrow 2[Ag(NH_3)_2]^+ + 2OH^-$$

Fig.1. variation of pH at silver nitrate solution

3.2. Effect of acid leaching on purification of gold particles

Figure 2 has shown the effect of using sulphuric acid and nitric acid on gold purification. Respect to Figure 2. The gold obtained is of 100% purity.

Atomic absorption results demonstrated that after precipitate was leached with H_2SO_4 then HNO_3 there was no gold but iron in mother liquor. By adding sodium bisulphate (stiochiometrey ratio with gold) to brown residue (concluded of fulminating gold and $Au(OH)_3$ and $Fe(OH)_3$) these components were reduced after washing the residue with H_2SO_4 then HNO_3. All components except gold were dissolved . Gold was remained as gold metal with 100% purity.
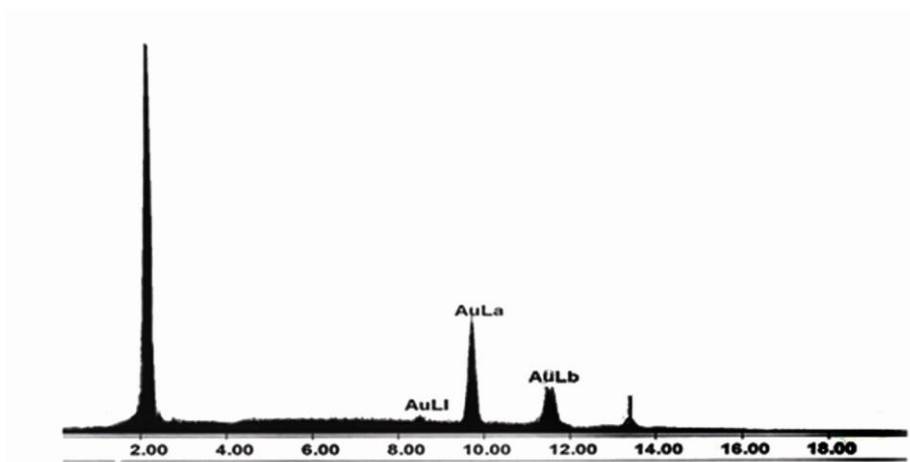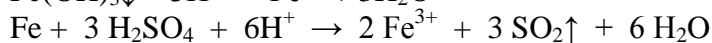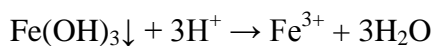
$$Fe(OH)_3\downarrow + 3H^+ \rightarrow Fe^{3+} + 3H_2O$$
$$Fe + 3H_2SO_4 + 6H^+ \rightarrow 2Fe^{3+} + 3SO_2\uparrow + 6H_2O$$

Fig.2. EDAX Analysis of extracted gold from industrial solution by acid leaching with H_2SO_4 and HNO_3

3.3. Effect of different parameters on size of nanogold
Based on Beer's law UV-Vis absorption is directly proportional to concentration and size of particles. Due to optical properties of nano sized gold, UV-visible absorption behaviors for nano gold have been recorded. Intensity of absorption spectra is related to nanoparticle's agglomeration and dispersion in solution [8-12].

3.4. Effect of different kind of fuel on nanoparticle's size
The UV-Visible curves of nano gold particles produced under different kind of fuel (glycin, acid citric, urea) at 800^{oC} for 10 minutes with constant mole ratio of 3:1(fuel to gold) is shown in Figure 3.
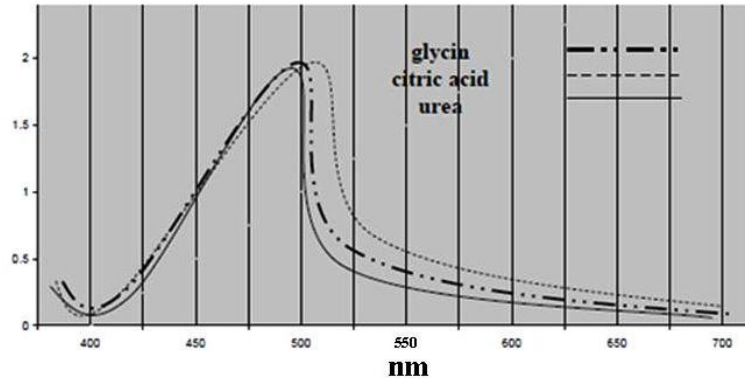
Fig.3. The UV-Visible curves of nano gold particles produced under different kinds of fuel at 800^{oC} for 10 minutes with mole ratio of 3:1(fuel to gold)

We can see that with changing the fuel in combustion reaction there was a red shift in the absorption peak of the spectrum. It has been long known that the maximum absorbance peak will shift to longer wavelength when the particle size becomes larger. Therefore urea was selected as fuel for our experiment.

3.5. Effect of different reaction temperature on nanoparticles size

The UV-Visible curves of nano gold particles produced under different temperatures (200 ^{o}C- 400 ^{o}C - 800 ^{o}C for 10 minutes with constant mole ratio of 3:1(fuel to gold) shown in Figure 4. The high reaction temperature from 200 to 450 lead to red shift of the absorption peak, indicating that the size of gold nano particles became larger with the increase of temperature in this range ,when all other reaction conditions were the same. That consisted with Ostwald data. But after increasing temperature to 800 ^{oC} combustion reaction was started. Beside the reaction a mount of gas was produced that leads to increase of nucleation and limitation growing process (Figure 5).
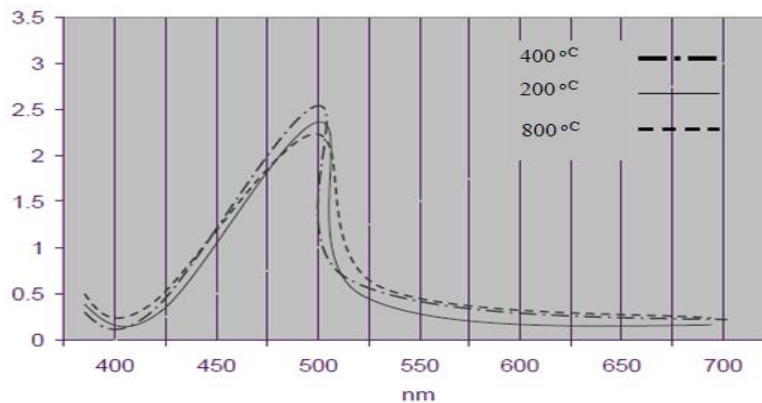

Fig.4. The UV-Visible curves of nano gold particles produced under different temperatures for 10 minutes With mole ratio of 3:1(fuel to gold)
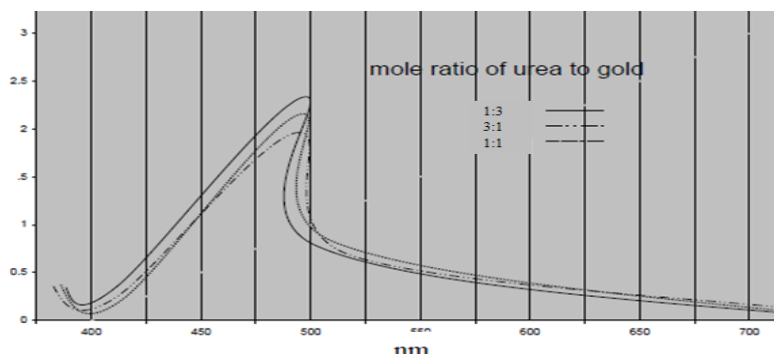
Fig.5. The UV-Visible curves of nano gold particles produced under different mole ratio of urea to gold at 800^{oC} for 10 minutes

It can be seen that the higher the urea concentration is the lower maximum absorbance wavelength becomes, and therefore, the smaller nanoparticles form. And this result indicated that increasing concentration of gold ion can promote the growth of nanogold particles and lead to increasing particle size.

3.6. SEM images of prepared nanogold particles

In comparing Figure 6 and 7 for standard solution if higher temperature and mol ratio 3:1(urea to gold) is used the size of particles will decrease. In figure 6 the size of particles is less than 90 nm. In comparing Figure 8 and 9 nanogold particles produced from industrial solution, urea with mole ratio of 3:1 to gold at 800^{oC} for 10 minutes have smaller size. In Figure 9 the size of particles is less than 90 nm and according to Figure 10 purity homogeneity of particles is 96.96%. The gold recovery method presented above has been adopted for gold recovery from various solutions and leads to economic recovery of valuable metals from waste solution.
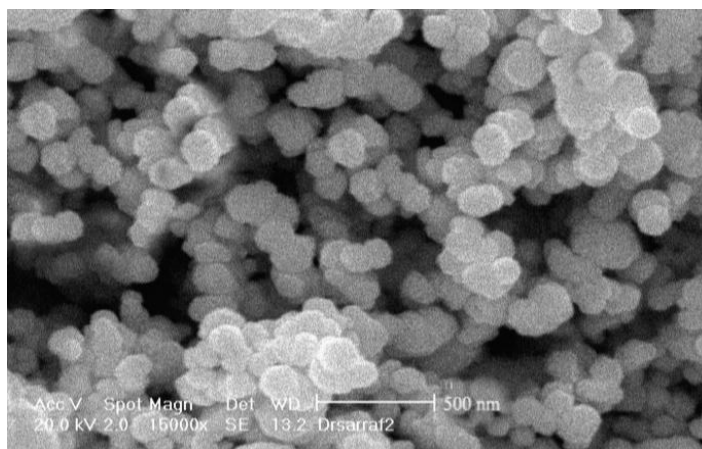

Fig.6..SEM image of nanosized gold prepared from standard solution by adding urea with mole ratio of 3:1 to gold at 800 ^{oC} for 10 minuets

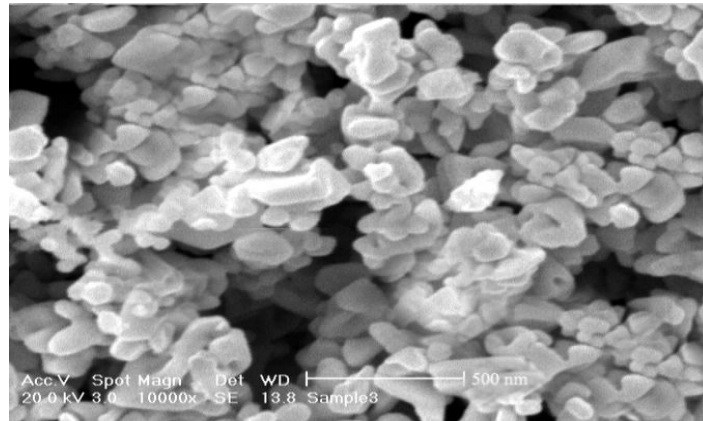**Fig.7.** SEM image of nanosized gold prepared from standard solution by adding urea with mole ratio of 1:1 to gold at 200 ᵒC for 10 minuets
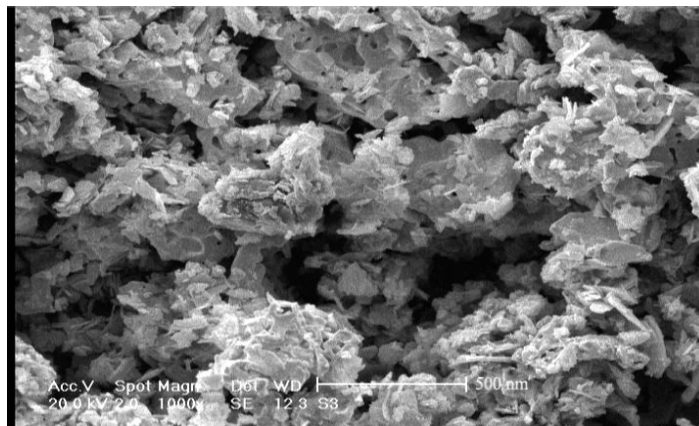

Fig.8. SEM image of nanosized gold prepared from industrial solution by adding urea with mole ratio of 1:1   to gold at 200 ᵒC for 10 minuets
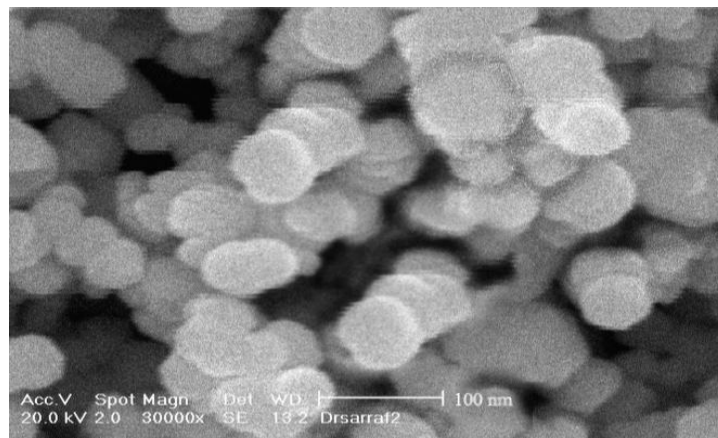

Fig.9. SEM image of nanosized gold prepared from industrial solution by adding urea with mole ratio of 3:1 to gold at 800 ᵒC for 10 minuets
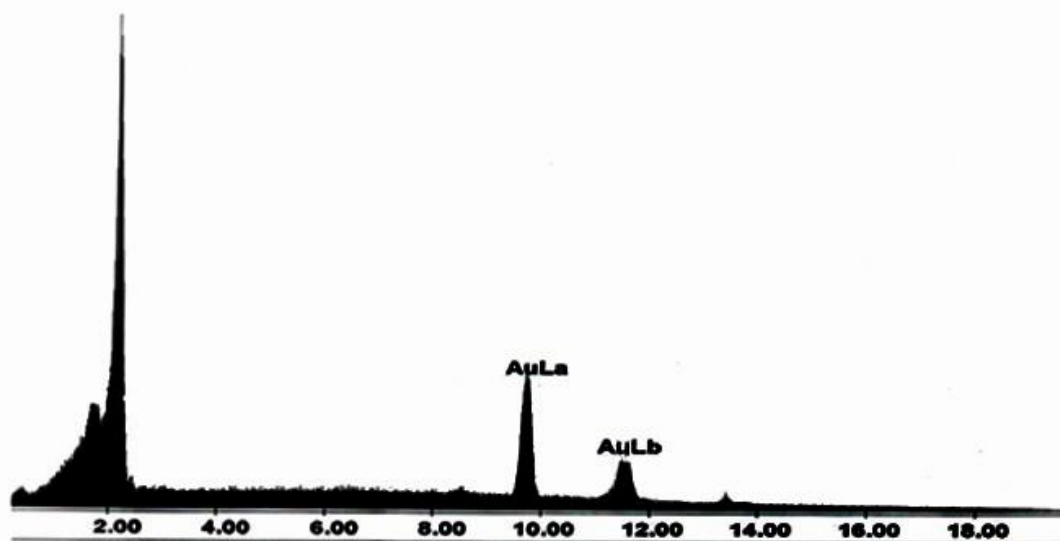
Fig.10. EDAX Analysis of nanogold prepared from industrial solution

4. Conclusion

The recovery of gold from acidic tailing waste solution has been investigated. Gold can be effectively changed to nano powder with high efficiency.

Gold separation from the other metals in industrial waste is possible in pH variations in addition of ammonia. Gold nano powder <90 nm from industrial waste solution by urea is obtained.Preparation nano gold particles with lower size and more homogeneity from the industrial waste by control of temperature and change of molar ratio urea to gold reductant proper is accomplished.The proposed method should be useful for the metal separation and especially gold of other waste water samples and also nano gold preparation of that is applied.

Acknowledgments

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