



Research Article

Removal of mercury from cyanide solution

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ABSTRACT

Keywords:

Gold ores,
cyanidation,
mercury,
removal

The gold/silver ores contain certain amount of mercury, which is a heavy metal and has high toxicity. During the treatment of gold with cyanide, mercury is also leached with gold and silver. Since mercury cyanide complexes are very stable, they cause contamination in leaching solution and are dangerous for the environment and health. For this reason, removal of mercury by fast, energy efficient, low cost, selective, stable and non-hazardous separation methods is very important in economic and environmental terms. In this study; removal of mercury from cyanide leach solutions were investigated using sodium sulfide (Na₂S), sodium diethyl dithio-carbamate (Na-DDC) and ammonium pyrrolidine dithio-carbamate (APDC) as precipitant by precipitation. In addition, the effect of coagulant (FeCl₃) and flocculant (Superfloc A130) addition on mercury removal efficiency was investigated. With the use of APDC, Hg concentration was decreased from 8.0 mg L⁻¹ to 0.087 mg L⁻¹ in a yield of 98.9%.

TR

Siyanürlü çözümlerden cıvanın uzaklaştırılması

ÖZ

Anahtar kelimeler:

Altın cevherleri,
siyanürleme,
cıva,
uzaklaştırma

Altın/Gümüş minerallerini içeren cevher yataklarında çoğunlukla belirli bir miktarda ağır metal ve toksisitesi yüksek olan cıva bulunmaktadır. Altının siyanür ile muamelesi esnasında altın ve gümüşle birlikte cıva da liç edilmektedir. Cıva-siyanür kompleksleri çok kararlı olduklarından liç çözeltisinde ve liç işlemini takip eden proseslerde kirliliğe sebep olmakla birlikte çevre ve sağlık açısından tehlike arz etmektedir. Bu nedenle cıvanın; hızlı, verimli, düşük maliyetli, seçimli, kararlı ve tehlikeli olmayan ayırma yöntemleri ile uzaklaştırılması ekonomik ve çevresel açıdan oldukça önemlidir. Bu çalışmada; altın, gümüş ve cıva içeren siyanürlü liç çözeltilerinden sodyum sülfür (Na₂S), sodyum dietilditiyokarbamat (Na-DDC) ve amonyum pirolidin ditiyokarbamat (APDC) kullanımıyla çöktürme ile cıva uzaklaştırma araştırılmıştır. Ayrıca koagulant (FeCl₃) ve flokulant (Superfloc A130) ilavesinin cıva uzaklaştırma verimine etkisi incelenmiştir. Çöktürme ile uzaklaştırmada APDC kullanımıyla %98,9 verimle Hg konsantrasyonu 8.0 mg L⁻¹'den 0.087 mg L⁻¹'ye düşürülmüştür.

1. Introduction

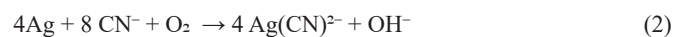
Mercury are released into the environment by human activities such as mining, combustion processes, chemical processing, and use and disposal of commercial products [1]. Mercury is ranked third in the list of the most toxic elements for human health by US Government Agency for Toxic Substances and Disease Registry [2,3]. Different mercury compounds have different effects on the nervous system, kidneys and brain, and the pathway to be followed in the body varies depending on whether the mercury taken into the body is metallic, organic or inorganic. Metallic and methylmercury have been introduced into the body, mixed with the blood to go to the brain and accumulate, while the inorganic mercury compounds have been reported to accumulate in the kidneys [4].

Approximately 83% of the world's gold production from natural sources is carried out with cyanide leaching. The most important factor in the widespread use of cyanide leaching is that the selective dissolution of precious metals in high yields can be realized economically. Some ore deposits containing gold and/or silver minerals also contain various base metals such as mercury. During

the gold cyanidation of these ore, gold and silver, as well as other precious and base metals in the ore pass into the solution, mainly as metal cyanide complexes. Mercury, in particular heavy metals, is difficult to remove from the cyanide solution and cause the most serious threat of contamination. Contamination from these reasons causes serious environmental and health hazards.

Gold, silver and mercury dissolve together in cyanide leaching [5]. Cyanide, a potent reagent for gold, is equally powerful for mercury [6]. In addition to gold and silver many deposits contain as much as 15 mg L⁻¹ of mercury. During the cyanidation process, while 85% -90% of gold dissolves, typically 10% to 30% mercury dissolves [7]. Cyanide forms complexes with all the above elements, but soluble mercury-cyanide complexes are some of the most stable ones and are particularly difficult to remove from mineral waste [8-12].

Reactions with cyanide for gold, silver and mercury extraction are as follows [7],



Cyanide process involves two conventional methods: gold / silver recovery from cyanide leach solution in the carbon adsorption process and the Merrill-Crowe zinc dust cementation process. In the first, the precious metals are adsorbed onto activated carbon, after

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loading; they are then stripped off by a hot caustic cyanide solution. This solution is in turn fed to electrowinning cells where the gold and silver are electrolytically deposited onto cathodes of steel wool. In the second case, the Merrill-Crowe product is filtered as zinc dust precipitate. The cathodes from the carbon adsorption process or the precipitates from the Merrill-Crowe process are then melted in crucible furnaces along with fluxing materials. The resultant product from smelting is precious metals typically encompassing more than 97 percent of precious metals [13]. If mercury is present in the ore, the reasons for mercury removal from cyanide solutions are;

- While gold is dissolved during the cyanidation process, co-dissolution with the mercury increases the consumption of cyanide.

- Activated carbon is used in the adsorption of Au (CN)²⁻ form gold from the loaded leach solution. Activated carbon adsorbs mercury with gold and silver. Therefore, it poses a health hazard during the regeneration of activated carbon [5, 7, 14, 15]. This leads to a decrease in the adsorption capacity of activated carbon.

- After carbon stripping, mercury accumulates in recycled leach solutions and causes pollution, because only a portion of the mercury is adsorbed onto the carbon in the loading circuit [7].

- In the CIP (carbon in pulp) process, mercury accumulates in recycled leach solutions and remains in the waste, because only a portion of the mercury is adsorbed onto carbon in the loading circuit [6,16].

- Au, Ag and Hg metals come together as an amalgam during the electro-recovery process applied following adsorption and stripping. It poses a health hazard during the melting of cathodes [7, 5].

- The low boiling point (357 °C) and the low evaporation temperature (295.6 J/g) of mercury for refining processes is used to purify unwanted mercury. This process also produces metallic mercury, which is dangerous to transport and has very limited marketability. The formation of mercury vapor is also dangerous for health [5, 15].

- Merrill-Crowe Process is used in gold purification and zinc is used in the precipitation of gold and silver together for recovery of gold and silver. It is stated that the presence of high mercury concentration (>50 g/ton) significantly reduces the effectiveness of gold cementation with zinc [6].

For these reasons and high toxicity of mercury, investigation of reagents for removal of mercury by fast, energy efficient, low cost, selective, stable and non-hazardous separation methods would be of great economic and environmental benefits.

There are some studies to remove mercury from cyanide leach solutions. These are;

- Removal by precipitation with dithiocarbamate [10, 11, 14],
- The use of organic chelating compounds [6, 8, 12, 17]
- Removal by adsorption [6, 18]
- Removal by roasting [19]
- Removal with inorganic sulfides [6, 7, 15, 16, 20, 21, 22]

In this study, the removal of mercury cyanide complexes from cyanide solutions containing gold and silver was investigated by precipitation with Na₂S, Na-DDC and APDC. In addition, the effect of aggregate formation on removal efficiency by appropriate coagulant and flocculant addition after precipitation was researched.

2. Materials and Methods

2.1. Material

The studies were carried out on laboratory scale, and synthetic cyanide solutions containing gold, silver and mercury were prepared. In the preparation of synthetic gold, silver and mercury solutions, analytical purity sodium cyanide (NaCN, Merck), mercury (II) nitrate.monohydrate (Hg(NO₃)₂.H₂O, Sigma-Aldrich), gold (Au, 1000 mg L⁻¹, Sigma-Aldrich) and silver (Ag, 1000 mg L⁻¹, Sigma-Aldrich) standard solutions; pH-adjusted dilute solutions of sodium hydroxide (NaOH, Merck) and nitric acid (HNO₃, Sigma-Aldrich); sodium diethyl dithio-carbamate (Na-DDC, Merck), ammonium pyrrolidine dithio carbamate (APDC, Sigma) and sodium sulfide

nonahydrate (Na₂S.9H₂O, Sigma) as reagents used in the precipitation experiments; iron (III) chloride.hexahydrate (FeCl₃.6H₂O, Merck) used as coagulant and Superfloc A103 (a kind of anionic flocculant with medium hydrolysis degree and medium molecular weight mainly used for mineral processing) used as flocculant for agglomerate formation were used.

2.2. Methods

Assuming 50% of the mercury will dissolve after curing in a gold ore, in the preparation of synthetic solutions with an initial concentration of 8.0 mg L⁻¹ 8000 ppb Hg, 2.0 mg L⁻¹ 2000 ppb Au and 2000 ppb 2.0 mg L⁻¹ Ag, a stock solution of 1000 mg L⁻¹ ppm Au standard, 1000 mg L⁻¹ ppm Ag standard and 1000 mg L⁻¹ ppm Hg content prepared with Hg(NO₃)₂.H₂O were used. Standards, stock solutions and calibration solutions were kept in refrigerated bottles in sealed, air-tight and light-free containers. The pH value of the test solutions was measured with Hanna HI 2211-02 desktoptable type pH meter. In the pH adjustment, pH: 11 was adjusted by using different molar concentrations of NaOH solution and 2% Nitric acid solution. Synthetic stock solution was prepared by adding 1.5 g / L NaCN to the solution whose alkaline pH was adjusted which has alkaline pH and stirring the solution with magnetic stirrer.

Precipitation experiments were carried out with 50 mL solution (pH: 11, 1.5 g / L NaCN). Sodium diethyl dithiocarbamate (Na-DDC), Ammonium pyrrolidine dithiocarbamate (APDC) and Sodium sulfide (Na₂S) were added with Hg : precipitant ratio of 1:4. In order to prevent Hg solubility with oxygen in the presence of cyanide, the flasks used in the experiments were sealed with parafilm and mixed for 30 min at 200 rpm agitation on the WiseShake orbital shaker. At the end of the mixing, 10 mL sample was taken for Hg analysis. The cyanide solution was filtered through a 0.45 µm membrane filter and acidified to pH <1 with nitric acid. In Au and Ag analyses, 10 mL sample was taken and filtered with 0.45 µm membrane filter. The samples were kept in the refrigerator until analysis. Hg analyses were performed by Perkin Elmer / FIAS-100 using cold vapor technology, Au and Ag analyses were performed using Perkin Elmer / AAS Analyst400 (Fig. 1). In addition, the effect of flocculant (0.3 mg L⁻¹ ppm Superfloc A130) and coagulant (10.3 mg L⁻¹ ppm FeCl₃) after precipitation was investigated.

Mercury is the only metal that can evaporate, even at room temperature, for atomization no external heat energy is required to the atomizer. Therefore, Mercury is analyzed only by cold vapor method. A reaction to produce mercury vapor is first carried out in a vessel outside the atomic absorption apparatus. Mercury is reduced in solution using stannous chloride or sodium borohydride in a closed system. The reaction quantitatively releases mercury (from the sample solution) and is carried by a stream of air, nitrogen or argon through a quartz absorption cell placed in the light path of an AA instrument for analysis. The detection limit for mercury by this cold vapor technique is approximately 0.02 mg/L [23, 24]

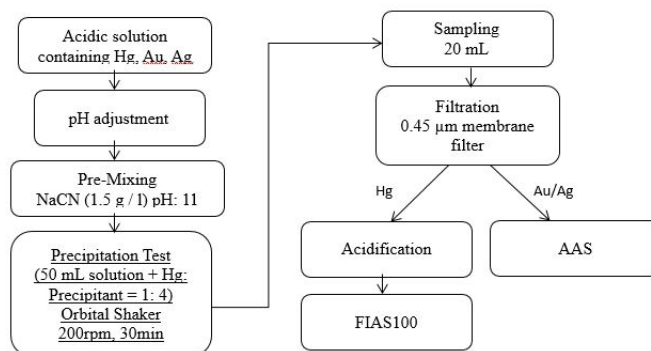


Fig. 1. Block diagram for mercury removal method by precipitation

3. Results and Discussion

Na₂S, Na-DDC and APDC in Hg: precipitant molar ratio of 1: 4 to 50 mL of solution containing initial concentration 8.0 mg L⁻¹ Hg, 2.0 mg L⁻¹ Au and 2.0 mg L⁻¹ Ag of 8000 ppb Hg, 2000 ppb Au and 2000 ppb Ag were mixed. As a result of experiments, the final Hg concentrations were reduced to 0.395 mg L⁻¹, 2.153 mg L⁻¹ and 0.087 mg L⁻¹ ppb, respectively (Fig. 2).

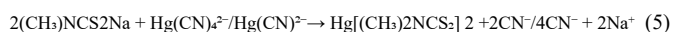
When Hg removal efficiencies are examined; Na₂S, Na-DDC and APDC are efficient removing 95.106%, 73.109% and 98.91%, respectively. It was observed that Au concentrations were not affected much by using dithio carbaomates (Na-DDC and APDC) and Ag concentrations decreased slightly. Hg removal efficiency with APDC was found to be higher than Na₂S and Na-DDC (APDC > Na₂S > Na-DDC) (Fig. 3).

In the gold / silver recovery, it is important to select the precipitant for selective removal of mercury. In this respect, Na₂S, Na-DDC and APDC are effective in removing mercury without causing gold and silver losses.

Soluble mercury can be precipitated with sulfides, as shown by the chemical equation [7];



The precipitation of mercury complexes from the solution with Na-DDC takes place according to the following reaction [10]:



Mercury-APDC complex are also given in Fig. 4 [25].

In the studies, Hg removal with Na-DDTC has shown that addition of coagulant (La(OH)₃ or Fe(OH)₃) and flocculant (Bufloc) increases the removal efficiency [9,10,13]. Fig. 5 shows the effect of coagulant and flocculant addition on grains.

After precipitation experiments with Na₂S, Na-DDC and APDC, coagulant and flocculant effects were investigated. Firstly, flocculant (0.3 mg L⁻¹ppm Superfloc A130) was added after precipitation with precipitator precipitant at 200 rpm for 30 minutes and flocculation effect was studied with 5 minutes shaking time at 100 rpm. The next study was carried out in 3 stages.

1) Precipitation with precipitator precipitant at 200 rpm for 30 min shaking time,

2) Coagulation by adding coagulant (10.3 mg L⁻¹ppm FeCl₃) with shaking at 100 rpm for 5 minutes,

3) Flocculant (0.3 mg L⁻¹ ppm Superfloc A130) was added and flocculation process was carried out one after another with a shaking time of 5 minutes at 100 rpm.

The addition of coagulant and flocculant after precipitation with Na₂S and Na-DDC increased Hg removal efficiency, but Hg removal efficiency was decreased when APDC used (Fig. 6).

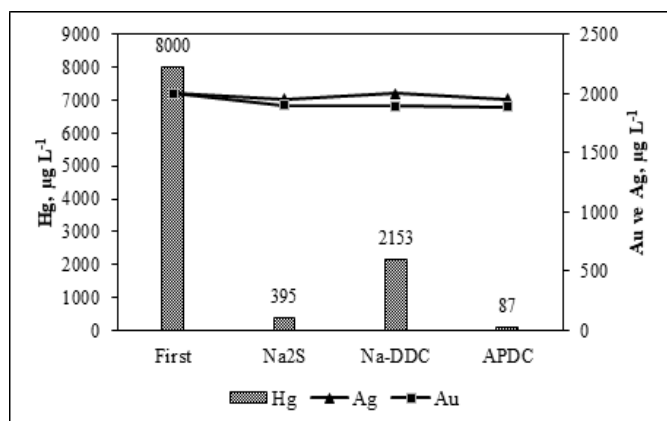


Fig. 2. Change of Hg, Au and Ag (µg L⁻¹ ppb) after precipitation experiment with Na₂S, Na-DDC and APDC (Hg: precipitant Precipitator = 1:4, pH: 11, shaking rate: 200 rpm, 30 min).

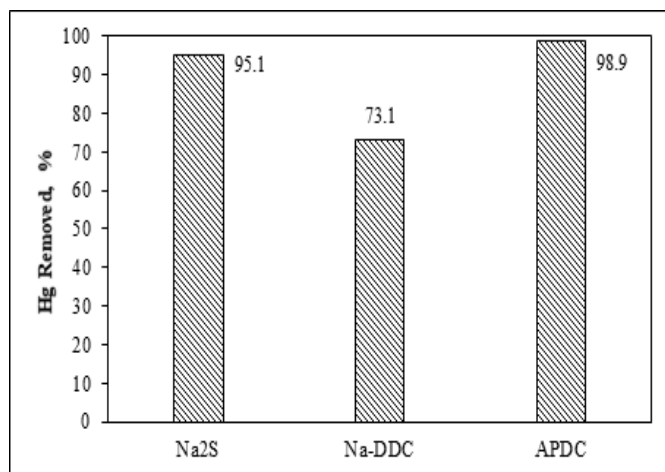


Fig. 3. Hg removal efficiency after precipitation test with Na₂S, Na-DDC and APDC

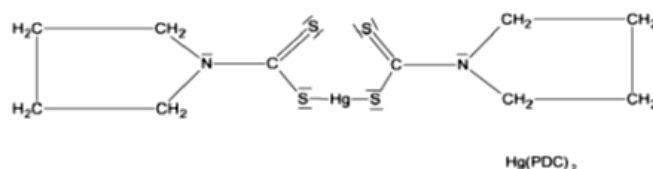


Fig. 4. Mercury-APDC complex [24]

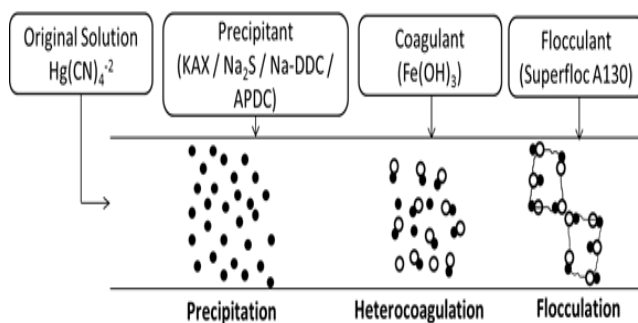


Fig. 5. Schematic representation of the effect of coagulant and flocculant addition on grains

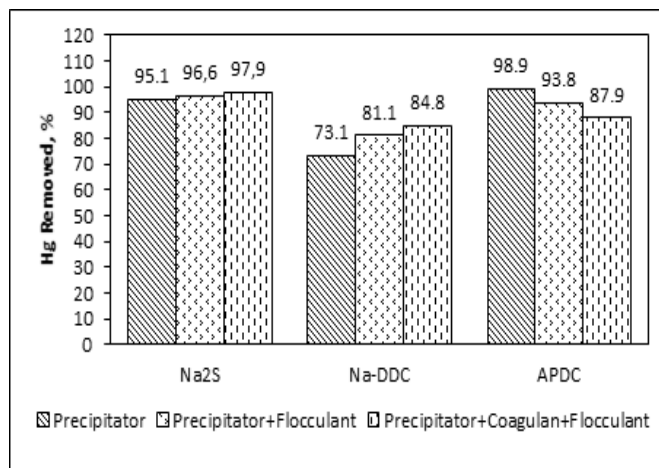


Fig. 6. The effect of coagulant and flocculant addition on Hg removal efficiency [Hg: Precipitant/precipitator = 1:4 (200 rpm, 30min), Flocculant (0.3 ppm mg L⁻¹ Superfloc A130, 100 rpm, 5 min), Coagulant (10.3 mg L⁻¹ppm FeCl₃, 100 rpm, 5 min)].

4. Conclusions

In this study, removal of mercury was investigated from cyanide leach solutions containing gold, silver and mercury by precipitation using Na₂S, Na-DDC and APDC. In the experiments, the molar ratio of Hg: precipitant as Precipitator 1: 4 was adjusted. In addition, the effect of coagulant (10.3 mg L⁻¹ ppm, FeCl₃) and flocculant (0.3 mg L⁻¹ ppm, Superfloc A130) addition on mercury removal efficiency was investigated.

APDC with 98.91% yield was found to be better than Na₂S and Na-DDC. Hg concentration was decreased from 8.0 mg L⁻¹ to 0.087 mg L⁻¹ ppb. It was observed that Au concentrations were not affected much and Ag concentrations decreased slightly. Coagulation and flocculation on Na₂S and Na-DDC increased Hg removal efficiency, whereas the efficiency decreased with APDC usage.

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