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ANALYSIS OF A METHOD FOR SEPARATION OF RARE METALLS GOLD AND SILVER FROM ACIDIC THOUREA SOLUTIONS

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Abstract: The article analyzes various methods for the extraction of gold and silver from thiourea solutions (cementation, alkaline precipitation, electrolysis, activated carbon and extraction). The chemical processes, advantages and disadvantages of each method are considered. Although cementation is simple, the quality of the precipitate is low, while electrolysis and extraction provide high-quality precipitates, but are resource-intensive. The optimal method depends on the composition of the raw materials and economic factors.

Keywords: rare metals, gold, silver, thiourea, cementation, electrolysis, extraction, alkaline precipitation, activated carbon, regeneration.

As a result of gold desorption, regenerated raw material is obtained, the gold content of which is 0.5 -2 g/l. Copper, iron and other metals are found in regenerated raw material as additional metals.

There are several methods for the precipitation of gold and silver from thiometallurgical solutions: cementation, alkaline precipitation, electrolysis in the presence of an anode. The first method is the separation of rare metals from TM solutions with metals that are more active than them (zinc, lead, and aluminum).

Gold and silver can be precipitated from thiourea solutions using several methods. These include the following methods:

1) Lead deposition. The essence of the process is that lead displaces gold, since its oxidation energy is lower than that of gold. When lead powder is added to the solution, the following reaction occurs:

 $2Au[SC(NH_2)_2]Cl + Pb = 2Au + Pb [SC(NH_2)_2]_4C1_2$

according to the same reaction. The consumption of lead powders is 20-30g of lead per 1g of gold. The disadvantage of this process is the contamination of the solution with lead. This does not allow the TM solution to be recycled, and at the same time, lead is ineffective for TM solutions with sulfuric acid;

2) Zinc precipitation. First, the solution is neutralized with soda until the pH is 6-7, then 3-4 g of zinc powder is added to 1 g of gold. The solution is stirred for 2-3 hours. Gold precipitates according to the following reaction:



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 $Au[SC(NH_2)_2]_2 \}_2 SO 4 + Zn = {}_{2Au} + Zn [SC(NH_2)_2]_4 SO_4$

of gold and silver, soda is added to the solution and the pH of the medium is brought to 9-10. The purpose of adding soda is to precipitate part of the zinc in the form of hydroxide. The filtered precipitate contains up to 6-10% gold and is treated with sulfuric and hydrochloric acid. The solution is returned to the desorption process. The disadvantages of the process are the low-quality composition of the precipitate, the high consumption of reagents (soda, zinc powder, acid) and the contamination of the return solution with zinc, soda, sodium chloride salts;

3) Aluminum deposition. In the process, aluminum powder is crushed to a size of 0.074 mm with a particle size of up to 95%. The deposition proceeds according to the following reaction:

$$3[Au(TM)_2]_2SO_4 + 2Al = 6Au + 12TM + A1_2(SO_4)_3.$$

The consumption of aluminum in the reaction is 3 g of aluminum per 1 g of gold. The duration of the reaction is 4 hours at $20^{\circ C}$. The concentration of gold in the precipitate is up to 25%. The amount of gold remaining in the solution is 2-5 ml/g. To separate the aluminum in the precipitate, it is treated with a 5% solution of sodium hydroxide for 3 hours, as a result of which the gold content in the precipitate reaches 85%. The disadvantages of the process are the low-quality composition of the precipitate, the high consumption of reagents (aluminum powder, acid) and contamination of the reflux solution with aluminum sulfate salts;

4) Alkaline precipitation of gold. In this method, the HCN in the solution is removed by treating with compressed air for an initial 4-6 hours , otherwise, in the presence of alkali, it forms NaCN, which prevents the complete precipitation of gold. The solution is heated to 40-50 $^{\circ}$ C and 40% NaOH is added until the pH of the medium is 10-12 . In this way, the formation of gold hydroxide occurs according to the following reaction:

$$Au[SC(NH_2)_2]_2 Cl + NaOH = Au(OH) + 2SC(NH_2)_2 + NaCl$$

The precipitation of silver is similar. The duration of the precipitation process is 2-4 hours. The precipitate contains 10-15% gold in the form of hydroxides, which are filtered in filter presses, washed with boiling water, treated with compressed air and calcined at 300^{°C} to remove sulfur. The resulting soot is dissolved in sulfuric acid to remove impurities, and the resulting ^{30-45%} gold concentrate is sent to refining . Disadvantages of the process: poor filtration of precipitates, additional consumption of sulfuric acid and the production of low-quality precipitates;



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5) Precipitation of gold using activated carbon. When sorbing gold with coal, the selectivity of coal to gold is high, and it is preferable for sorbing gold from solutions with many additives. In a reverse 4-5-step process, the gold is completely separated, and the gold content in the coal precipitate is 15-20%. They are burned and smelted to obtain ferrous metal. Disadvantages of the process: the difficulty of the coal burning process, and the loss of the thiomachevina solution;

6) In this method, a gold-containing solution is mixed with an extractant, an organic substance that is insoluble in itself and "absorbs" gold by ion exchange in accordance with its electric ionic charge. As a result of extraction, 2 different products are obtained. One of these is a gold-containing, organic phase (extract) and a solution (raffinate) that does not contain gold, but may contain other elements. If the raffinate (solution) does not contain gold and does not contain other necessary elements, it can be sent to a waste disposal site as waste. The organic phase-extract containing gold is re-extracted to extract gold from it. The solution that dissolves gold from the extract is called a "re-extract". The extractant from which gold is extracted is reused. Rare metals are in the form of complex anions in cyanide solutions. Therefore, anion-exchange organic substances are used to extract them. Quaternary ammonium salts with such extractant properties are used - trialkylbenzisnammonium chloride, abbreviated as "TABAX".

according to the following reaction :

 $(R_{3}C_{7}H_{7}N)Cl + Au(CN)_{2} = (R_{3}C_{7}H_{7}N)Au(CN)_{2} + Cl$

silver and copper and zinc anion complexes is similar to the above reaction. To ensure good extraction, the gold solution and the extractant are fed in countercurrent.

The extractant can be carried out in an acidic solution of the gold thiourea substance. The re-extractant contains 8% CS(NH_2) ₂ It can be thiourea, 5-10% H ₂ SO ₄, or 20-35% sodium rhodanite solution. First, gold forms a complex salt with a stable cation:

$$(R_{3}C_{7}H_{7}N)Au(CN)_{2}+2CS(NH_{2})_{2}+2HCl=(R_{3}C_{7}H_{7}N)Cl+Au[CS(NH_{2})_{2}]_{2}Cl+2CN$$

the second case, anion exchange can be observed:

 $(R_{3}C_{7}H_{7}N)Au(CN)_{2}+CNS = (R_{3}C_{7}H_{7}N)CNS +Au(CN)_{2}$

By changing the concentration of the re-extractant, gold can be collected in one re-extractant and silver in another. During the re-extraction process, the organic phase can be regenerated and used again in the extraction.

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more saturated with gold, can be electrolyzed with an insoluble anode. During electrolysis, the amount of rare metals separated at the cathode is 90-95%, and 98-99% of the gold can be separated from the solution;

Electrolytic deposition of gold and silver. The second method of gold deposition is electrolytic deposition of a gold-containing solution with an anode. The anodes are made of graphite, and the cathodes are made of titanium or stainless steel, with a regenerated product acting as the electrolyte. The electrolysis process is carried out at a current density of 25-30 A/m². The voltage in the bath is about 1 V. As a result of the electrolysis of gold, the following reactions can occur:

The cathode is made of carbon graphite | [Au(TM) $_2$] $_2$ SO $_4$, TM, H $_2$ SO $_4$, H $_2$ O additives | Ti (anode). The following main reduction reactions take place at the cathode:

Au[SC(NH₂)₂]₂+ e = Au + 2SC(NH₂)₂
Au[SC(NH₂)₂]₃⁺+ e = Ag + 3SC(NH₂)₂
$$2 H^{+}+2 e = H_{2}.$$

Other additives such as copper, lead, and additives can also be recycled in this way.

At the anode, the following reactions occur and the H⁺ion is formed:

$$2 H_2 O - 4 e = O_2 + 4 H^+$$

In addition, TM is oxidized at the anode:

$$SC(NH2)_2 - 2e = CNNH_2 + S + 2 H^+$$

Over time, cyanide combines with water and converts to thiomachevine:

$$CNNH_2 + H_2O = CO(NH_2)_2$$

At the anode, thiomachevina is oxidized according to the following reaction :

$$SC(NH_2)_2 + N_2O - 2e = CO(NH_2)_2 + S + 2H^+$$

During electrolysis, the oxidation of thiourea at the anode increases significantly. As a result, the cost of this valuable reagent increases. In addition, the elemental sulfur formed is mechanically mixed with the cathode deposit, which degrades the quality of the cathode gold. To eliminate this situation, it is better to block the cathode area from the anode with a porous barrier, or better yet, with an ion exchange membrane. (The membrane is a thin membrane made of ionic resins).



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Cation membranes only pass cations, while anions pass anions . When the electrolysis time is 24 hours, 98% of the gold is deposited in the solution, and 60% more.

To keep the ionite in the electrolyzer in suspension and to continuously drive away the cyanic acid that may be released, forced air is sent through the electrolyzer. To prevent the gold particles deposited on the cathode from being damaged by the ionite impact, the cathode is screened with a filter cloth. The main admixture of the 60-90% rare metal precipitate of gold and silver washed from the resin by the action of a constant current is elemental sulfur oxidized around the cathode by thiourea. By blocking the anode and cathode surroundings with an ionite (membrane) curtain, it is possible to obtain a somewhat cleaner precipitate.

During electrolysis, the current density is 8-10 A/m², the bath voltage is 2-3 V, the electrolyte temperature is 50-60 0 C, and the oxidation energy is 0.3-0.4 V. The main part of the gold is deposited within 2-3 hours of electrolysis. After the concentration of gold in the deposit reaches 100-120 mg/l, the process duration can be extended to 6-12 hours, since 10-20 mg/l remains. The content of gold in the cathode deposit is 70-85%, silver is 10-25%, copper is 0.5 -5%, zinc is 0.1-0.2%, and iron is 0.1-0.4%. Non-rare additional metals remain in the electrolyte and return to the desorption process. The output of the electrolyte for the extraction of gold and silver is 30%. It is advisable to increase the current density to 15-20A/^{m2}, which will increase the level of additional copper deposition, but reduce current consumption.

The spent electrolyte, i.e. the acid, is enriched by concentration and reused to extract gold from subsequent ion exchange resins. The regenerated (restored, purified) resin is sent for reuse in sorption.

The released cyanic acid is pumped into acid absorbers filled with alkali with a vacuum pump. The resulting cyanic solution can be used for selective dissolution of the raw material.

In conclusion, electrolysis and extraction methods are effective in obtaining high-quality precipitates, but they are resource-intensive. Cementation is simple, but the quality of the precipitate is poor. The optimal method depends on the composition of the feedstock and economic factors. Devices such as EU-1 increase efficiency.

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