Study of the Technology for Gold Recovery from Gravity-Flotation Concentrate from Ore Beneficiation with the use of Oxidizing Reagents

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Abstract Gold-containing ore processing technology has been developed by using chemical, X-ray phase, mineralogical, X-ray fluorescence analyses. The results of experiments on the gold recovery from a concentrate with a particle size of 10 and 4 μm are presented, including options for direct cyanidation without preliminary oxygen oxidation, as well as with the use of preliminary oxidation of Trichloroisocyanuric acid (TCCA) and Sulfanol surfactant (SAS). It was found that the test sample contains 24.74 g/t Au; 11.66% S; 18.51% Fe. The content of sulfide minerals is 36.1%, the main sulfides are arsenopyrite (25.4%) and pyrite (10.7%). Microscopic examination of the combined gravity-flotation concentrate revealed ultrafine, fine and visible gold dust particles both in free form and in aggregations with waste rock. The particle size of Au in the product varies from 0.5 to 18.8 μm. 77.12% of gold is recovered from concentrate of 10 μm by direct cyanidation. “Sulfanol” was used to recover 83.71% of gold. Pre-treatment with TCCA yielded 85.61% of gold. Recovery of gold from the 4 μm concentrate was 75.38% for direct cyanidation, 78.79% for cyanidation with Sulfanol surfactant, 76.52% for cyanidation with TCCA.

Keywords Gravity flotation concentrate · Mineral composition · Phase composition · Gold recovery · Surfactant · Oxidizing agent (TCCA Trichloroisocyanuric acid)

Introduction

Kazakhstan has significant potential reserves of gold-bearing minerals. Most of the gold in Kazakhstan is traditionally mined from complex deposits. The largest gold ore object in Kazakhstan is the Vasilkovskoye deposit, 17 km northwest of the city of Kokshetau. The Vasilkovskoye deposit belongs to the gold-quartz moderately sulfide formation. The main ore minerals of primary ores are arsenopyrite, pyrite, bismuth minerals and native gold. Arsenopyrite sharply predominates of all the minerals. The main change in the production process was the abandonment of heap leaching to process gold-bearing ore and the introduction of a complex combined technology using traditional operations to recover gold from ore: flotation, gravitation and cyanidation. Gold in ores and concentrates is mostly in a free form and concentrated in small to very small particles, which affects the rate at which cyanide solutions dissolve [1, 2]. Non-traditional methods are required to involve refractory (hard-to-recover) minerals in processing. One of the promising technologies of mineral processing is chemical leaching with the use of oxidizing reagents, which does not require large material costs and does not pollute the atmosphere [2–4].

The gold content in ore material (free or chemically bound), the size and aggregate state of gold, the passivation films, the ore-bearing rocks genesis (altered or unaltered) and their structural characteristics (porosity, fracturing) determine the appropriateness of one or another gold processing method depending on the initial noble metal content and mineralogical composition [5–8].
The particle size of gold is one of its most important technological characteristics. The fine- and ultrafine-dispersed gold, associated in most cases with sulfide minerals, is revealed only insignificantly during ore crushing, its main mass remains in the minerals. Such gold is almost insoluble during cyanidation, but is recovered together with carrier minerals during gravitation and flotation [9, 10]. Consequently, a preparatory stage is necessary to improve further recovery rates to acceptable values, or an increase in gold recovery rates can be achieved by using different reagents. Preparation consists of opening up the dispersed gold inclusions in one way or another to provide access to the cyanide solution. The preparation usually consists of oxidizing the sulfide or arsenide matrix, if the main mineral carriers of gold are sulfides and arsenopyrite.

The majority of gold processing plants currently handle ores containing sulfide minerals. Gold in such ores is partially associated with sulfides and partially in a free state. Ores of this type are in most cases classified as refractory. The raw material for gold recovery is the gravity-flotation concentrate of ore enrichment. Technological mineralogy methods allow to reveal useful and harmful minerals and their associations in ores, to determine features of their real composition and structure, character of relations between each other and with rock-forming phases, to control, explain and predict behavior of ores in technological processes [11–13].

The raw material base of the gold mining industry of Kazakhstan is represented mainly by small (with reserves up to 25 tons) and medium (from 25 to 100 tons) deposits [14]. The leading position, however, is held by the deposits of Eastern, Northern and Central Kazakhstan. Search for the most effective integrated technology to recover gold from minerals is an urgent task for the gold mining industry in Kazakhstan.

Materials and Methods

Combined gravity-flotation concentrate was used as a feedstock in this study after ultrafine grinding from the processing of ore from the Vasilkovskoye deposit.

Chemical, X-ray phase, X-ray spectral, mineralogical analyses, as well as the standard method of sample preparation (GOST 14,180–80, 2021) were used for physicochemical studies. Gold content in the samples was determined by assay and atomic absorption analysis (HCAM 497-XC methodology).

X-ray phase analysis was performed on a D8 Advance (Bruker, Billerica, MA, USA) using Cu Kα radiation at 40 kV and 40 mA. Processing of the diffractograms was performed using EVA software, and phase identification was performed using Search/Match and the PDF-2 powder diffraction database.

X-ray fluorescence elemental analysis was performed using a Venus 200 wave-dispersive combined spectrometer (PANalytical B.V.), (Holland). Mineralsogical studies of thin sections and polished sections were performed on an optical microscope AxioScope. Agitation leaching method with agitator ES-8300, with overhead agitator is equipped with a built-in electronic stepless speed controller.

Results and Discussion

Initial specimens’ samples of 87–89% of the 10 µm and 4 µm size class of were taken-11.66%; Fe-18.51%; As 19.93%; SiO₂-30.12%; Al₂O₃-8.56%; CaO-2.685% to conduct experiments on leaching by the agitation method.

The composition of the sample, according to X-ray phase analysis (Fig. 1), included quartz (SiO₂ – 38.7%), arsenopyrite (Fe₃S₈), pyrite (FeS₂ – 10.7%), calcium aluminum silicate (Ca₀.₈₈Al₂₅S₄Si₂₃O₇₈ – 6.3%), microcline (K₆Si₃Al₆O₁₈ – 6.1%), kronsentenite (Fe₃Si₃O₁₂ – 5.6%), illit-2M2, glycosylated (NR) ((K₉H₃O)₆Al₆Si₆O₂₄(OH)₄ – 5.6%), calcium silicate (CaSiO₃ – 2.3%).

The mineralogical analysis of the concentrate sample was supplemented with an AxioScope A1 optical microscope. Thirty-six gold particles were found, of which: 30 particles in free form—83.33%, Au size from 0.5 to 18.8 µm, gold (Figs. 2, 3); 4 particles in intergrowths with waste rock—11.11%, with parameters—Au from 0.7 to 7.4 µm (Fig. 4); 2 facts of the gold particles occurrence in waste rock with thin phenocrysts of arsenopyrite particles in it – 5.56%, the size range of gold particles is within: Au from 0.5 to 6.8 µm. The particle size is within: Au (0.5–18.8 µm), i.e., ultrafine (0.1–1.0 µm) finely dispersed gold (1.0–10.0 µm) and visible pulverized gold (10.0–50.0 µm), (according to Petrovskaya’s classification “Native gold”).

Figure 2 shows gold particles in the free state, covered with oxidation films, probably goethite-limonite composition.

Figure 3 shows the facts of occurrence of gold particle “inclusions” in waste rock grains with thin phenocrysts of arsenopyrite in it.

Characteristics of Related Components

Ore components, presented in order of their occurrence:
Sulfides: arsenopyrite—Ars (FeAsS), pyrite—Py (FeS₂), chalcopyrite—Cp (CuFeS₂) and pyrrhotite—Pirr (Fe₁₋ₓS), bismuthine—Bi₂S₃;

Iron oxides: goethite—(HFeO₂), hydrogoethite—(HFeO₂/C₁ag)—g/g, magnetite—Mgt (Fe₃O₄), hematite—Hm (Fe₂O₃). The metallic scrap fragments—Fe (in the percentage of 2.5% of the total mass of the studied particles) are observed along with the studied ore components of the product (sulfides, oxides, hydroxides of iron) (Fig. 5, Table 1). The non-metallic components are represented by: prevailing quartz, feldspars, carbonates, chlorite, sericite, and mica (conventionally, the common designation “p.p.” is taken on the images).

Microscopic examination of the combined gravity-flotation concentrate revealed ultrafine, fine and visible gold dust particles both in free form and in aggregations with waste rock. The size of occurrence of Au particles in the product varies in the range: Au from 0.5 to 18.8 μm. The shape of gold grains is varied: spherical, rounded, monolithic, hooked, elongated not regular. The surface of Au grains is both even with clear contours and rough and relief.

The results of the rational (phase) analysis of the gold in the concentrate, regrid to a particle size of 90% of −0.071 mm class (Table 2), show that the content of free gold and in bundles (cyanide-bearing gold) is 9.0%.

The presence of thinly disseminated gold in sulfides is one of the main reasons for the technological persistence of minerals, 68% of gold is associated with sulfides, and 5.0% is associated with acid-soluble compounds. Higher gold content (4.32 g/t, or 18.0%) is noted in rock-forming minerals.

**Cyanidation**

The effect of different material sizes on the process parameters with the additional reagents was studied in order to determine the possibility of recovering gold from the combined gravity-flotation concentrate by cyanidation.

It has been used a surfactant sulfanol, which is known under various names, including sodium alkylbenzenesulfonate, and is a mixture of isomers of sodium salts of alkylbenzenesulfonic acids, with the general formula R-C₆H₄NaO₃S, where R — radical corresponding to the general formula CnH2n₊₁, as an activator reagent.

The main active ingredient in trichloroisocyanuric acid is chlorine, which makes up more than 90% of the total specific gravity of the finished product. It promotes the transfer of gold into a productive solution to obtain a water-soluble complex [11–13], when used as a leaching or oxidizing agent.

\[ \text{Au} + 0.5\text{Cl}_2 + \text{Cl} \rightarrow \text{AuCl}_2 \]  \hspace{1cm} (1)

\[ \text{AuCl}_2^- + \text{Cl}_2 \rightarrow \text{AuCl}_4^- + \text{Cl}_2 + \text{HCl} \]  \hspace{1cm} (2)
Fig. 2 Loose gold particles in polystyrene
2Au + 3Cl₂ + 2Cl⁻ = 2AuCl₄⁻

(3)

The influence of material grain size, cyanide concentration in the solution, and leaching time on key process parameters (gold recovery, reagent consumption) was studied using an initial concentrate sample.

The combined gravity-flotation concentrate leaching (the mode of obtaining products and their main indicators are shown in Table 3) was performed in direct mode at the initial material size and at a size of 87–89% 4 μm (0.004 mm) using various oxidizers. The combined gravity-flotation concentrate was subjected to ultrafine grinding in a bead mill to a particle size of P89 4 μm. Zirconium oxide balls are used as an abrasive fragment in the bead mill. The worn material was subjected then to oxidation and cyanidation in agitation mode.

Concentrate was milled to 4 μm in a laboratory bead mill with a wet milling process in preparation for hydrometallurgical studies. The coarseness of the crushed material was monitored using a laser granulometer—a versatile high-tech instrument for rapid and accurate particle size distribution of suspensions, emulsions and dry powders. A graph of the product particle size dependence on grinding time was plotted for the concentrate based on the test results, shown in Fig. 6.

Experiments on the concentrate cyanidation were performed on material of the following size: 87% 4 μm (0.004 mm), 89–90% 10 μm (0.01 mm). Leaching parameters, identical for all tests, are given in Table 3.

Tests results for cyanidation of the concentrate initial sample of various sizes are presented in Table 4 and Fig. 7.

Gold recovery during the combined gravity-flotation concentrate cyanidation using surfactants at a particle size of 89% 10 μm (−0.01 mm) is on average 81.6% compared with the use of TCCA—84.0% (average result for 3 tests). Reducing the concentrate size from 89−0.01 to 89%−0.004 mm does not improve gold recovery. Gold recovery with surfactant and TCCA leaching averaged 76.64 and 75.66%, respectively, compared to direct cyanide leaching recovered 75.38% of gold.

The studies therefore revealed data on the composition of the concentrate (cake) after leaching, obtained under optimal conditions with the use of additional reagents.

The data of X-ray phase analysis of the sample (cake) after leaching with preoxidation with TCCA and surfactant...
showed that the total arsenopyrite content is 35.8 and 31.7%, pyrite 13.0 and 11.2%, respectively. The studies revealed significant changes in the minerals, and it can be assumed that the gold recovery has increased due to a more

### Table 1 Form of gold particles in the combined gravity-flotation concentrate

| Form of gold location | Free gold | Gold in intergrowths with waste rock | Facts of Au particles occurrence in p.p. with thin Ars phenocrysts in it | Facts of occurrence of Au particles with p/p |
|-----------------------|-----------|-------------------------------------|-------------------------------------------------|-------------------------------------------|
|                       | Au (surface clean) | Au “in the shirt” | Edge intergrowth Au | Core inclusions Au | Facts of occurrence of Au particles with p/p |
| Number of particles, pcs | 26 | 4 | 1 | 3 | 2 |
| Percentage ratio, %    | 72.22 | 11.11 | 2.78 | 8.33 | 5.56 |
| Total quantity, pcs    | 26 | 4 | 2.78 | 8.33 | 5.56 |
| Dimension μm           | 0.5–18.8 | 0.7–7.4 | 0.5–6.8 |
| Total percentage ratio, % | 83.33 | 11.11 | 5.56 |
complete leaching of free gold and gold from inclusions in the waste rock. The results indicate that the process of concentrate leaching leads to oxidation of sulfides, uncovering of resistant gold and its recovery during the subsequent cyanidation of the oxidation residue.

**Table 2** Phase analysis results for gold of initial concentrate crushed sample with particle size of 90% grade $- 0.071$ mm

| Forms of gold in the concentrate | Gold distribution |
|---------------------------------|------------------|
| Free and in the form of intergrowth | 2.16 9.0 |
| Associated with acid-soluble minerals (carbonates, hydroxides, chlorites, etc.) | 1.2 5.0 |
| Associated with sulfides | 16.32 68.0 |
| Finely disseminated in rock-forming minerals | 4.32 18.0 |
| Total in the sample (according to the balance) | 24.0 100 |

**Table 3** Leaching mode of initial concentrate sample

| Parameter | Units of measurement | Value |
|-----------|---------------------|-------|
| Accelerator reagent oxidation: sulfanol | Hour | 6 |
| Laboratory bead mill with wet grinding SAS | Hour | 24 |
| Cyanide concentration | g/l | 2.0 |
| Cyanidation duration | % solid | 30 |
| pH | – | 10.5 |

IR Spectroscopic Analysis

The spectra were obtained on an Avatar 370 CsI IR-Fourier spectrometer in the spectral range 4000–400 cm$^{-1}$ from capillary layers of solutions in KRS-5 windows (Fig. 8). Experiment prefix: Transmission E.S.P. The analysis showed the presence in the sample of a productive solution after direct cyanidation of 0.2% NaCN concentrate with a size of 4 μm, compounds $[\text{Ag(CN)}_2]^{-}; [\text{Cu(CN)}_3]^{2-}; [\text{Ag(CN)}_4]^{3-}; [\text{Fe(CN)}_5 \text{SO}_3]^{5-}; [\text{CNO}]^{-}; (\text{CN})^{-}$, the solution contains complex compounds of silver, iron and copper and free cyanide.

The sample of the productive leaching solution with TCCA oxidation contains $[\text{Ag(CN)}_2]; [\text{Cu(CN)}_2]^{-} \text{cm}^{-1}; [\text{Fe(CN)}_5 \text{SO}_3]^{5-}$. Sulfate ion $[\text{SO}_4]^{2-}$ and the group $[\text{ClO}_4]^{-}$, which shows that the chlorination reaction is taking place. The sample of productive solution with sulfanol has the following cyanide complexes $[\text{Au(CN)}_2]^{-}; [\text{Cu(CN)}_2]^{-} \text{cm}^{-1}; [\text{Zn(CN)}_4]^{2-}; [\text{Fe(CN)}_6]^{3-} – \text{and valence variations of the bonds C=\text{N}.}$. The productive solution sample with the complex application of sulfanol and TCCA surfactants revealed cyanide complexes $[\text{Ag(CN)}_2]^{-}; [\text{Ag(CN)}_4]^{3-}; [\text{Cu(CN)}_3]^{2-}; [\text{Fe(CN)}_6]^{3-}; [\text{Fe(CN)}_5\text{SO}_3]^{5-}; [\text{NCS}]^{-},$ group $[\text{CNO}]^{-},$ cyanide ion $[\text{CN}],$ group $[\text{NCS}]^{-}$ which indicates a more complex composition. It can conclude from the studies that the productive solutions contain cyanide complexes of gold, silver, non-ferrous metals, and free cyanide ions; the difference in the forms of the compounds suggests different metal transfer mechanisms in the solution.

Thus, the raw materials structure peculiarities were confirmed and the variant of gold recovery from concentrate by cyanidation with the use of reagents—gas pedal of
Table 4 Results of concentrate leaching of different sizes

| Test number | Coarseness of material, mm | Au content, g/t | Extraction of gold, % | Leaching solution | Sample weight, g |
|-------------|---------------------------|-----------------|----------------------|-------------------|-----------------|
|             |                           | In the initial  | In the filter cake   | Reagent (% of sample weight) | NaCN, g/dm³ |
| 1           | Initial coarseness 89–90% cl 10 μm (0.01 mm) | 26.4          | 6.04                | 77.12              | –               | 2.0 100 |
| 1.1         |                           | 5.5            | 79.17               | SAS 0.2            |                 |                 |
| 1.2         |                           | 4.3            | 83.71               | SAS 0.8            |                 |                 |
| 1.3         |                           | 4.8            | 81.82               | SAS 1.2            |                 |                 |
| 2.1         |                           | 4.8            | 81.82               | TCCA 0.5           |                 |                 |
| 2.2         |                           | 4.04           | 84.70               | TCCA 1.0           |                 |                 |
| 2.3         |                           | 3.8            | 85.61               | TCCA 1.5           |                 |                 |
| After grinding in a bead mill | 87% cl 4 μm (0.004 mm) | 26.4          | 6.5                 | 75.38              | –               | 2.0 150 |
| 3.1         |                           | 5.6            | 78.79               | SAS 0.2            |                 |                 |
| 3.2         |                           | 6.8            | 74.24               | SAS 0.8            |                 |                 |
| 3.3         |                           | 6.1            | 76.89               | SAS 1.2            |                 |                 |
| 4.1         |                           | 6.8            | 74.24               | TCCA 0.5           |                 |                 |
| 4.2         |                           | 6.2            | 76.52               | TCCA 1.0           |                 |                 |
|             |                           | 6.28           | 76.21               | TCCA 1.5           |                 |                 |

Fig. 7 Kinetic curves for the leaching of Au from products at different sizes
leaching process—surfactant “Sulfanol” and chlorine containing reagent “trichloroisocyanuric acid” TCCA was proposed.

Conclusions

It has been performed experiments in gold recovery from 10 to 4 μm concentrate, including variants of direct cyanidation without pre-oxidation, as well as using pre-oxidation with TCCA and Sulfanol surfactant. All experiments were performed without the use of hydrogen peroxide or other reactive oxygen compounds.

The results showed that direct cyanidation recovered 77.12% of gold from concentrate of 10 μm in size. Recovery of 83.71% of gold (without oxygen) when using “Sulfanol” (without “an increase of 6.59%”). Pretreatment with TCCA produced 85.61% of gold (without oxygen), an increase of 8.49% compared to direct cyanidation.

The recovery of gold from a concentrate with a size of 4 μm was—75.38% with direct cyanidation (without oxygen), cyanidation with Sulfanol surfactant—78.79% (an increase of 3.41% compared to direct cyanidation), cyanidation with TCCA—76, 52, 1.14% increase.

The decrease in the gold recovery degree during the leaching of ultrafine grinding concentrate, finely ground to 4 μm using surfactants (compared to 10 μm), occurs due to oxidation and the formation of complex compounds on the surface of free gold. The main significance of the surface-active substances usage eliminates the sulfur films passivating effect, which contributes to an increase in the rate of sulfides oxidation.

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Declarations

Conflict of interest The article was sent for publication in the Journal. The authors have no conflicts of interest. This is the original work of the authors and has not been previously published in other publications.

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