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STAGE-ACTIVATION LEACHING OF OXIDIZED COPPER–GOLD ORE: THEORY AND TECHNOLOGY

The article emphasizes the urgent need of heap leaching in the current geotechnical conditions. The application prospects for heap leaching are connected with preliminary oxidation of refractory ore. Another important requirement is geo-engineering typification of ore through geotechnical mapping. An alternative of cyanide in gold leaching is chlorine compounds. The article describes the theory of formation of active chlorine–oxygen complexes using electrochemical and photochemical effects. Iron acts as a catalyst of gold complexing by means of change in the oxidation rate +3/+2. The tests of agitation leaching are carried out on oxidized copper–porphyry–gold ore from the Malmyzh deposit. Efficiency of the best reagent scheme is proved by the results of percolation leaching. The laboratory experiment included primary processing of ore in peroxide–sulfuric solution prepared by electrochemical and photochemical treatment. After diffusion oxidation during ageing of treated samples for three days, the samples were irrigated with active hypochlorite–chloride solution for 15 days. The experiment proved recoverability of gold at a rate of 92–93% and copper at a rate of 55–60% without capital input and at minimized operating cost. The new-developed circuit of heap leaching includes layer-by-layer stockpiling. Selectivity of heap leaching is ensured by treatment of layers of qualitatively different ore types and grades by solutions of different reagents, at certain concentrations and in certain hydrodynamic modes of irrigation.

Key words: *copper–porphyry–gold ore, oxidized ore, leaching, geotechnical mapping, stockpiling, electro-photochemical activation, preparatory oxidation, reagents, peroxide–sulfuric solutions, hypochlorite–chloride leaching.*

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Introduction

As against many metals and minerals, the price of gold is governed not only by the demand and supply balance but also depends on numerous industrial, political and economic factors. In gold mines, despite the anticipated rise in the gold price, a sturdy characteristic of a final product is the capital and operating cost dependent on the mineral supplies, as well as on labor, power, material and technical resources. The complex-structure folded ore bodies, with highly heterogeneous distribution of gold per different scales and with varied ratio of gold occurrence forms, need differentiated quality requirements. This necessity was highlighted by such mining scientists as Academician M. I. Agoshkov, Professor Z. A. Terpogosov, Professor S. S. Reznichenko and other as early as the late 1980s. The complex composition of copper–gold ore gives rise to a high scatter of the recovery results and quality data of flotation concentrate. The difference in composition of chalcopyrite, chalcocite and oxidized minerals of copper allows dividing ore into processing types [1]. In this case, the economic performance of processing of various copper–porphyritic ore should be estimated in terms of gold and copper recovery in flotation and heap leaching. At the present time, percentage of gold and copper produced by heap leaching in the world exceeds 40%.

The subject of this research is the Malmyzh copper–gold deposit in the Khabarovsk Krai. The only economically expedient method to recover the low-grade copper and gold ore from the oxidation zone of this deposit is heap leaching [2, 3].

The prospects for gold heap leaching are connected with pre-oxidation of rebellious ore [4], with an increase in the rate and ratio of dispersed gold recovery in order to make this method comparable with the conventional production and processing efficiency reached with both low-grade and high-grade ore. It is advisable to assess applicability of flexible hybrid circuits in mining and processing of such ore, including selective extraction of their geological engineering subtypes with difficult to recover forms of gold occurrence and conventional pre-treatment with production of middling and/or tailings (separation by batches or lumps with subsequent additional recovery of gold by heap leaching). To this effect, it is required to use selective heap leaching circuits, with separate formation of piles or layers, and with processing of qualitatively different varieties (type and grades) of ore by solutions of different reagents of certain concentration and in specific hydrodynamic sprinkling modes. Furthermore, it is necessary to develop algorithms for automated geotechnical mapping of a deposit and for the optimization of open pit mining sequence and advance, with selection of mining schemes and parameters for different type and grade gold ore in cooperation with the sequence and parameters of stockpiling for heap leaching.

Theory of physicochemical processes in photochemical activation

The range of use of heap gold leaching in development of complex-structure deposits can be expanded by means of oxidation of gold-bearing sulphide, sulphur arsenide and carbonaceous minerals in order to ensure reverse adsorption of gold (preg-robbing) [5]. In treatment of rebellious ore, the best commercial gold solvent alternatives to alkali and alkali earth metal cyanides are chlorine compounds. Chlorine, similarly to other halogens, is a complexing agent for free gold and at the same time an oxidizing agent for most sulphide minerals and carbonaceous matter. In aqueous solutions, chlorine occurs in ionic form and in compounds with oxygen (the so called active chlorine). Active chlorine violently interacts with iron and some other mineral-forming metals, sulfur and metalloids. Accordingly, at the first stage of interaction with ore containing much sulphide minerals, chlorine sits out of complexing reaction with gold.

Gold complexing with chlorine is less stable than with cyanides and greatly depends on solution pH [6] and on reduction/oxidation potential [7]. Furthermore, chlorine–gold complexes experience reentrainment when contacting reducing agents such as sulphide minerals [6], silicates [8] and carbon [9]. This problem can be handled be means of active carbon introduction to slurry in carbon-in-chloride-leach (CICL). This approach provides high recovery of gold in nonaggressive environment [10].

Inefficient use of chlorine and (or) its compounds in ore pre-treatment can be eliminated owing to preliminary oxidation of sulphide minerals. During processing of ore from oxidation zone with low content of residual sulphides, feasibility of chloride leach of gold depends on the ratio of free and chemically bound gold. Gold tellurides, natural gold alloys, as well as gold–silicon, gold–sulfur, gold–carbon and more complex clusters are difficult to recover from oxidized ore with any complexing agent. Therefore, extraction of such gold from ore from oxidation zones needs a system of reagents capable of chemogenic transformation of productive mineral matrices with subsequent or concurrent formation of a soluble gold-bearing cluster. Dissolution of some shell structures in gold-bearing clusters inside crystalline lattices of minerals in ore from oxidation zone and complexing of gold atoms making the 'core' of the clusters is possible with active chlorine–oxygen complexes. Such complexes are created in electrolysis of sodium chlorine brine: in the interelectrode space—hypochloric acid $(HClO)^*nH_2O$, sodium hypochloride $NaClO$, and in the anode region with acidifying with salt acid—per-hypochloric acid $(H_2Cl_4O_4)\cdot nH_2O$.

Such activated solutions (water–gas emulsions) after electrolysis become meta-stable environments; in such environments, at certain values of Eh and pH, hypochloric acids and per-hypochloric acids form and periodically disproportionate:

$$HClO=(HCl+O),\ (H_2Cl_4O_4)\cdot nH_2O=2Cl_2\cdot O\cdot H_2O_2\cdot nH_2O. \quad (1)$$

Such astable processes in water solutions with peroxide compounds were experimentally proved by the research supervised by Professor and Doctor of Biological Sciences V. L. Voeikov at the Moscow State University [11].

UV irradiation (within the wavelength region of 180–300 nm) of a chloride–hyperchlorite solution after electrochemical treatment greatly intensifies these stable processes. Per-hypochloric acid within an appropriate pH range disproportionate with atomic oxygen yield and with formation of reaction complex $(H_2Cl_4O_2)\cdot nH_2O$, which, in interaction of clustered disperse gold, can form a meta-stable hydroxide–chloride complex: $Au_3[(OH)_2Cl_4]^-$.

It is expedient that preliminary oxidation of residual sulphide minerals of naturally oxidized copper–porphyry ore with disperse gold and, consequently, reduction of inefficient consumption of active chlorine compounds with oxygen and hydrogen for oxidation of iron, and depression of unwanted unbalance between ferrous iron and ferric iron (Fe^{2+}/Fe^{3+}) uses sulfuric–peroxide solution. In a water–gas emulsion produced in the electrolysis of sulfuric acid solution, in the volume of gas bubbles during absorption of UV radiation, highly active oxidizes appear, such as atomic oxygen, superoxide–radical ion (O^{*-}), ozone (O_3), hydroxyl radical (OH^*). These active forms of oxygen interact with film water surrounding gas bubbles and create ion-radical and radical clathrates and clusters with priming centers represented by active forms of oxygen [12]. Such meta-stable solutions, namely, water–gas emulsions, keep active for a comparatively long time (dozens of hours), while a hydroxyl radical in a free form exists not longer than 10^{-12} s. Incidentally, super-peroxide compounds can sufficiently long maintain activity of leaching solutions.

Leaching of oxidized ore containing oxide and oxide–hydroxide iron minerals in such solutions ensures transition of iron into oxide sulphates at their contact surfaces:

$$Fe_2O_3 + 2H_2SO_4\cdot nH_2O\cdot H_2O_2=2[Fe(OH)(SO_4)]O\cdot(n + 2) \times H_2O; \quad (2)$$

$$2[Fe(OH)(SO_4)]O\cdot(n + 2)H_2O + 2H_2SO_4 = Fe_2(SO_4)_3 \cdot (n + 5)H_2O. \quad (3)$$

The research into sulfuric–peroxide leaching of gold from copper–gold ore from oxidized ferruginous deposits reveal that variation in concentration of hydrogen peroxide in working solution has no essential influence on copper recovery. For another thing, sulphur deposit observed on the surface of minerals decelerates leaching [13]. Iron oxide sulphate in such crystalline hydrate is ill-susceptive to further hydrolysis, and iron ions (Fe^{3+}) remain in the solid phase therefore. Clustered oxygen integrates hydroxonium ions and, through their agency, clustered anions OCl^-. As acceptors of electrons and centers of clusters of oxygen atoms in sulphates, paired atoms of iron with oxidation rate of +3 in the conditional formula $Fe_2(SO_4)_3$, during transition to bivalent state, can form meta-stable compounds $Fe_2[(OH)_2Cl_2]$ or $Fe_4[(OH)_4Cl_4]$ with ion hypochlorite. In such a manner, it becomes highly probable that a clustering reaction can take place between a complexing chloride cluster and clustered disperse gold associated with iron within the composition of hydroxide–oxide, sulphate and residual sulphide minerals from oxidation zone. Thus, iron, through variation of oxidation rate (+3/+2), catalyzes the process of gold complexing in hypochlorite–chloride leaching. Copper in chloride solutions in bivalent state, as 3-valent iron, can catalyze clustering of hydrated chlorine ions, which increases probability of their interaction with clustered gold. In oxidized copper–porphyry ore, disperse gold mostly preserves geochemical bonding with copper [14], typical of primary ore; for this reason, chloride complexes of copper in certain conditions ensures extractability of gold from supergene copper minerals. The research findings [10] prove that admixtures of iron and copper in gold ore (1.6% Fe and 0.05% Cu) are self-initiating oxidizers.

Experimentation procedure

The first-stage experiments on hypochlorite–chloride leaching of gold with preliminary oxidation of residual sulphides were carried out on bulk sample of ore from oxidation zone of the Malmyzh deposit. For the comparative evaluation of the chloride complexing circuit, conventional leaching of gold from the same ore was performed, with cyanide complexing agent and with treatment of ore in the activated sulphate–peroxide and percarbonate solutions. The solutions were prepared, respectively, by preliminary electrochemical and photochemical treatment of sulfuric acid and sodium bicarbonate water solutions. The conventional cyanide circuit was tested with ‘theoretical’ admittedly over-estimated (considering interaction of the complexing agent with iron and copper) content of the main agent—sodium cyanide (0.7%) and with real (economically sound) consumption of sodium cyanide (content in solution NaCN = 0.05%). After treatment of ore sample in percarbonate solution, leaching of gold used cyanide–ammonium complex.

Results and discussion

The influence of sulphate–peroxide oxidation on gold leaching efficiency was compared with direct gold leaching by active chloride solution (See the **table**).

As seen from the test data in the table, the chloride–hypochlorite leaching circuit [15] features nearly total yield of copper and iron with liquid phase and gold recovery of 0.64 mg/l (after agitation leaching for 2 h).

The staged circuit of activated heap leaching of disperse gold from finely milled ore of the Malmyzh deposit was tested in the mode of percolation with the most promising scheme of reagents: first impregnation with peroxide–sulfuric solution and then sprinkling with activation hypochlorite–chloride solution.

The tests of percolation leaching of gold and copper used the ore sample left after the agitation tests and milled to the size of –10 mm. The lab-scale experiment included preliminary treatment of two similar ore samples until complete wetting with peroxide–sulfuric solution prepared by electrochemical and photochemical treatment of the initial sulfuric solution with addition of hydrogen peroxide before UV irradiation. After diffusion oxidation in the course of ageing of the treated samples for three days, the active hypochlorite–chloride solution was prepared by means of electrolysis of a two-percent sodium chloride solution with subsequent treatment in sulfuric acid solution. At the final stage, the active water–gas emulsion was subjected to UV irradiation under DRT-240 lamp for 5 min. The test ore samples were placed in percolators and dripped with the resultant chloride solution at an average flow rate of 100 ml/kg per day for 15 days.

Test data of gold leaching from bulk sample of oxidized ore of the Malmyzh deposit

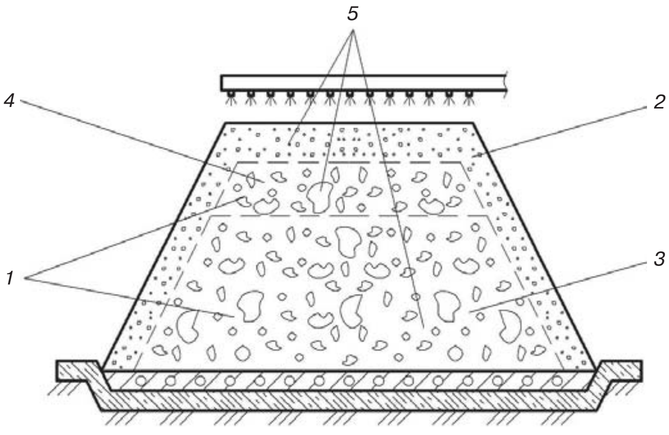
Leaching circuit	Recovery into solution, mg/l			
	Au	Ag	Cu	Fe
Leaching at high cyanide content ($C_{NaCN} = 0.7\%$)	0.93	0.42	32.3	390.7
Leaching at standard cyanide content ($C_{NaCN} = 0.05\%$)	0.65	0.30	29.8	32.9
Sulphate–peroxide activation and cyanide leaching	0.80		21.5	7.1
Sulphate–peroxide activation and chloride leaching	0.94		7.7	8.9
Carbonate activation and cyanide–ammonium leaching	0.81		13.5	34
Chloride leaching without preliminary treatment	0.64	0.33	0.45	0

The resultant gold recovery from both samples made 92–93%, i.e., it equaled the recovery in the tests with agitation leaching by the same reagent scheme and preparation of solutions. The subsequent peroxide–sulfuric leaching recovered not less than 50% of copper.

The experiments proved the efficiency of the proposed stage-wise extraction of gold and copper from low-grade oxidized copper–porphyry–gold ore. On this basis, the method of heap leaching was developed (see the **figure**). First, the low-grade ore with low copper and gold content ($C_{Au}<C_{Au\ min}$ and $C_{Cu}<C_{Cu\ min}$—the contents of gold and copper less than the minimum commercial content) is stacked into a pile *1* so that the bottom layer *3* is ore with low content of sulfuric acid and the intermediate layer *4* is the finely milled ore with higher content of sulfuric acid (more than the average content by 20–100%).

The leaching layer *2* is formed from the finely milled ore with standard gold content ($C_{Au} \geq C_{Au\ min}$ — the gold content higher than the minimum commercial content) and with low copper content ($C_{Cu} < C_{Cu\ min}$—the copper content lower than the minimum commercial content). All layers form the stockpile *5*. After stockpiling, differential extraction of useful components is started using solutions of different compositions.

The additional layer *2* and intermediate layer *4* are first sprinkled with sulfuric solution after photochemical treatment for the formation of peroxide complexes. The additional layer *2* is impregnated until complete saturation with active hypochlorite–chloride solution. Then a break is made in the



Schematic of heap leaching of copper–porphyry–gold ore: *1* — oxidized ore; *2* — additional layer; *3* — bottom layer; *4* — intermediate layer; *5*—stockpile

hydrodynamic penetration–diffusion process in order to ensure gold leaching from this layer. Then, the pile *1* of ore with standard copper content is prepared for the further leaching by oxidation of sulphide minerals and by total destruction. After the break, the pile *5* is intensely sprinkled with low-concentration hypochlorite–chloride solution or with water with gold leaching by percolation. After gold leaching, the second break is made to ensure natural oxidation of the whole pile *5* by atmospheric oxide and for formation additional sulfuric acid in the reaction between residual reagents with minerals in the intermediate layer *4* with increased content of sulfuric acid. After that, the pile *1* with the additional layer *2* is treated with the cycling aqueous weak-concentration solution of sulfuric acid for leaching of copper. The pregnant solutions are collected and processed separately.

The rough economic evaluation shows that the operating cost per 1 g of god is lower in the activation chloride circuit by 12–17% as compared with the cyanide leaching process.

Conclusions

The best commercially suitable solvent of gold as an alternative to cyanides of alkali and alkali earth metals in processing of rebellious ore is chlorine. Similarly to other halogens, chlorine is a complexing agent for free gold and at the same time an oxidizer for most sulphide minerals and carbon. The output of agitation leaching of valuable components from oxidized copper–gold ore of the Malmyzh deposit using different reagent schemes has demonstrated efficiency of activation sulphate–peroxide treatment and subsequent chlorine leaching (gold recovery 94%). The percolation leaching circuit with preliminary impregnation with peroxide–sulfuric solution and subsequent sprinkling with electrically and photochemically activated hypochlorite–chloride solution allows recovery of gold at 92–93%. The subsequent sulfuric leaching of copper provides copper recovery at 50%. The rough economic evaluation of operating cost per 1 g has shown that the operating cost of the activation chlorine circuit is less than in the cyanide leaching circuit by 12–17%. Based on the experimental results, the layer-by-layer stockpiling scheme is developed for heap leaching and efficient recovery of both gold and copper from low-grade ore of the Malmyzh deposit.

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