Specifics of disseminated gold leaching from oxidizable and non-oxidizable mineral matrices by activated water-and-gas emulsions

AG Sekisov*, AV Rasskazova** and TG Konareva***
Institute of Mining, Far East Branch, Russian Academy of Sciences, Khabarovsk, Russia
E-mail: *sekisovag@mail.ru, **abbot87@mail.ru, ***tat_konareva@mail.ru

Abstract. The article gives theoretical and experimental substantiation of features of finely dispersed gold leaching from oxidizable and non-oxidizable mineral matrices by water-and-gas emulsions which are photo- and electro-chemically activated. Alternative compositions of agents used to prepare rebellious ore for leaching and, specifically, for gold leaching are considered.

1. Introduction
Dispersed and encapsulated gold used to accumulate in ores: either siliceous and aluminosilicate matrices or sulfide, sulfoarsenide and sulfosalt mineral matrices [1]. Gold nanoparticles encapsulated in sulfides in mineral ores is an important argument to survey deposits of commercial significance. Nano-size gold is also associated with secondary supergenic concentrated zones, it participates in formation of surface geochemical anomalies and gold-bearing concentrated occurrences. Comprehensive investigation into forms of nano-size gold in an ore makes the ground to revise the rating of some known deposits in view to expand their commercial potential and to update ore processing techniques, as well as to explore new deposits by using the latest prospecting techniques [2].

The recovery of nano-size gold implies, firstly, necessity of preliminary super-fine ore grinding down to 20–30 µm and less [3, 4], secondly, ore processing and oxidation of flotation concentrates in autoclaves or bioreactors [5–7]. Combination of superfine grinding and pre-oxidation also gives good results, but at substantial costs [8]. The pretreatment of rebellious ores is reviewed in details in [9]. The reported techniques provide a rather high gold recovery in follow-on adsorption cyanidation, but high capital and operating expenditures do not allow their application to process poor ore or mining waste.

2. Features of disperse-type gold leaching
The most prospective direction in search for solution to this problem can be the application of compounds containing active forms of oxygen as basic oxidizers in working solutions at an ore-preparation stage before leaching of productive mineral matrices bearing dispersed gold [10, 11]. Such compounds provide high-rate chemical reactions at relatively low temperature of the solution, possibility to oxidize not only respective mineral-forming elements, but dispersed gold included in crystalline lattice of mineral-carriers [12].

The active oxidizers can be produced by radiation of air or chemically pure diatomic oxygen with UV-spectrum light or by electrodischarge treatment with follow-on bubble aeration of the pulp, but the
process is accompanied with appreciable gold loss because of recombination of gold particles prior to transition from the gas phase to aqueous one.

The use of integrated electrochemical [13] and photochemical synthesis of oxidizers [14] and chelating complexes directly in concentrated leaching solutions, viz., preparation of reactive-active water-and-gas emulsions to treat the gold-bearing mineral mass at low consumption (L : S = 1 : 10 – 1 : 12) would enable to overcome the available complexities.

It is known that such high-active oxidizers as ozone, atomic oxygen, and hydroxyl-radical can form diatomic oxygen and water vapor under action of hard ultra-violet radiation in the range of electromagnetic wave length of 180–250 nm. In electrolysis of a solution of readily dissociating alkali and oxygen-bearing acids the bubbles of oxygen with water content evolve onto an anode. In the subsequent photochemical reactions water molecules in the volume of evolved bubbles are excited as a result of adsorption of UV radiation and electrolytic diatomic oxygen and decompose into active atoms and radicals or are subjected to ionization. The decomposition products interact with other excited molecules and produce secondary active radicals, ions, ion-radicals and strong molecular oxidizers:

\[ O_2^{\text{UV}} \rightarrow 2O^* \quad \text{O}_2 + O^* = O_3, \quad H_2O^{\text{UV}} \rightarrow H_2O^+ + e^- \quad H_2O_2^{\text{UV}} \rightarrow H^+ + HO_2^-, \quad H_2O^+ + HO_2^- = 3OH^* \quad (1) \]

Under coalescence the bubbles of oxygen and hydrogen evolved onto cathode are involved into mutual diffusion, the UV-radiation of the resultant water-and-gas emulsion provokes more intensive yield of active oxygen and hydrogen compounds. As bubbles of electrolytical gases are surrounded with water, then ozone, atomic oxygen, hydroxyl-radical and other active compounds formed in photochemical reactions tend to diffuse into water in the film and can manage to form active hydrate complexes prior of recombination. Thus photoelectrochemical synthesis allows a high yield of such strong oxidizers as \( H_2O_2, OH^* \) along with their hydrated forms in the solution. Using proper initial soluble substances and the integrated electrochemical and photochemical treatment of soda and chloride-sodium solutions, it is possible to synthesize reactive-active oxygen and hydrogen compounds with other elements: carbon and chlore: \( C_2O_4^*, C_2O_2^*, HClO^* \), if required.

Treatment of rather simple and cheap initial reagent solutions by the new technique makes it possible to produce water-and-gas emulsions, containing both high-active oxidizers and chelating agents. Hydroxyl-radicals, synthesized under photoelectrochemical treatment of the solution, are capable to concentrate in water the film and small-cracks and also to get rid of hydrate membrane on the internal boundary of the double electric layer, to diffuse into internal layers of crystalline lattice of ore minerals. In this connection, the chemical oxidation reactions with participation of hydroxyl-radicals can proceed not only in near-surface layers of mineral matrices, but also inside of them. The redox potential of hydroxyl-radicals amounts to 2800 mW [15], this makes it possible to oxidize iron and sulfur, as well as clustered atoms of dispersed gold and platinoids, therefore, transition of them into ionic form and growth of diffusion activity in the volume of the crystalline lattice of minerals. In these processes other active components in solutions resulted from photoelectrochemical treatment under electrodissociation of water or acids can play an important role.

They are cations of hydrogen–protons \( H^+ \) and metastable hydrogen \( (H^) \) anions, capable to differentiate periodically under dissociation from hydroxyl-ions \( OH^- \) or hydroxyl-ion-radicals \( OH^* \), \( OH = O + H, \quad OH^* = O^- + H^+ \). Hydroxyl-ion-radicals are formed in photoactivated hydrolisis of hydroxyl-radicals: \( OH^* + nH_2O = H^+ + OH^* + OH(n – 1)H_2O. \) As the points of crystalline lattice of mineral-carriers acquires impulses from diffusing hydrogen ions and hydroxyl ions and displaces periodically at distance exceeding the equilibrium level, then there is a high probability for precious metal ions to tunnel through interstitial lattice site.

Hydroxyl radicals are capable to form hydrate metastable complexes of \( Au*OH*OSIO \) type with atoms of silicium and aluminum associated directly in crystalline mineral lattice, with atoms of dispersed gold, thus gold gets an opportunity to realize intercrystalline migration as a component of compound \( AuOH \). “Internal” dissociation \( OH^* = (O^*H) \) can proceed periodically in hydroxyl-radical. Hydrogen atom in hydroxyl-radical periodically displaces to a nominal boundary of electron shell and becomes a free proton-particle of a rather high energy. Respectively, its location is not limited.
exclusively with electron shell of oxygen ion-radical associated to it. So, system (\(\text{O}^*\cdot\text{H}^+\)) can be considered as a meta-stable ion-radical pair \(\text{O}^*\cdot\text{p}^+\), capable to function on the one hand as proton acceptor and on the other hand as electron acceptor. Initial proton \(\text{p}^+\), detached from radical \(\text{OH}^*\), penetrates into electron shell of the neighboring atom of other element, gold, in particular. This can initiate appearance of mobile metastable \(\text{AuH}\)-type compounds. Ion pairs \(\text{H}^*\cdot\text{H}^+\) induce re-dislocation of impurity atoms in crystalline lattice and transit impulses to them with formation new defects in crystalline lattice and form metastable compounds \(\text{Au}_2\text{H}_2\), thus breaking gold bonds with silicium and oxygen. It is well known that even in natural water there are stable gold form \(\text{AuOH(H}_2\text{O})^6\) in a wide range \(\text{Eh}--pH\). Under certain conditions in the mineral medium– technological solution system the gold declustering by active hydrate complexes is possible with dislocation of atomic (ionic) gold in the composition of compounds \(\text{AuOH}^*\) and/or \(\text{AuH}^*\) from internal layers of crystalline lattice to surface of microcracks and pores of a mineral-concentrator. Later metastable gold compounds react with respective chelating components of the active water-and-gas emulsion with formation of more stable gold complexes directly or through formation of its secondary hydrated clusters. The active reagent medium, containing ion-radical clusters \((\text{H}^*\cdot\text{nH}_2\text{O}\cdot\text{HO}^*)\), associated with hydrated cyanide complexes with base \([\text{(Na}^+)\text{OHH}^*(\text{CN})]\) intensifies leaching of gold accumulated nearby free internal and external surfaces of crystalline lattices:

\[
\text{Au}_n + 2[\text{H}^+\cdot\text{nH}_2\text{O}^*\cdot\text{OH}^*\cdot\text{(Na}^+)\text{OH}^*\cdot\text{H}^*(\text{CN})] \\
\text{Au}_n + [\text{Au}_3(\text{CN})_2\cdot\text{(OH})_2]^{-} \quad \text{2mH}_2\text{O} \cdot \text{H}^+ + 2[\text{NaOH(n} - \text{m} + \text{1})\text{H}_2\text{O}].
\]

Thus, water-and-gas emulsions prepared in photoelectrochemical reactors on the basis of alkali and soda solutions can be used to leach ores containing conventionally non-oxidizable mineral-concentrators for dispersed gold.

In leaching the preparation of ores, bearing dispersed gold with high content of sulfide minerals with sulfide sulfur more than 5 % and arsenopyrite as well as 0.1--1 % content of carbonaceous matter can be based on the application of water-and-gas emulsion, containing containing sulfuric-peroxide as well as chloride compounds along with hydroxyl complexes and percarbonic acids. Sulfide-carbonic gold-bearing ores contain adsorption-active organogenic carbon and residual organic compounds, leading to re-precipitation of gold dissolved in leaching process. These ores are distinguished for really low gold recovery parameters, as a rule, no more than 20 %. Moreover, in this-type ores gold can be present in bielement Au–S, Au–S–C, and Au–C clusters, resisting to cyanidation. The use of water-and-gas emulsions, containing active oxygen, to prepare rebellious ores for leaching makes it possible to apply the percolation-leaching process.

In this case interaction of \((\text{O}^*\cdot\text{H}^*)\) pair with carbon can result in the process:

\[
\text{C} + (\text{O}^*\cdot\text{H}^*) = \text{CO} + \text{H}^*.
\]

Oxidation of sulfur and carbon in sulfuric-peroxide medium proceeds at the expense of their interaction with metastable permonosulfuric and persulfuric acids \(\text{H}_2\text{SO}_2\text{O}_8\), \(\text{H}_2\text{SO}_5\), which can be obtained by treating the initial solution in electrochemical and photochemical reactors.

In treatment of rebellious ores with water-and-gas emulsions the carbon in ore is oxidized by metastable permonosulfuric acid to monoxide in reaction:

\[
\text{H}_2\text{SO}_5 + \text{C} = \text{H}_2\text{SO}_4 + \text{CO}
\]

Next carbon monoxide is further oxidized by hydrogen peroxide or hydroxyl-radical:

\[
\text{CO} + \text{H}_2\text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}.
\]

Dispersed gold with a carbon bond preserved after its oxidation can interact with hydroxyl-radical with formation of metastable complexes of \(\text{Au}--\text{Au (OH, HCO}_3\) type.
In geotechnological evaluation of mineral materials, bearing dispersed goldmainly associated with sulfide sulfur and carbon the investigation was undertaken on gold-bearing carbonaceous-clayey carbonated ore of Southern Ural origin. The pre-oxidation of the ore was performed with pelletization of 5 mm ground fraction batches with cement, followed with irrigation with photoelectroactivated solutions with sulfuric-peroxide and carbonate-peroxide base. The pelletized batches were mixed and fed to percolation columns (figure). This integrated ore preparation scheme provided an appreciable increase in gold recovery with subsequent percolation-leaching by active cyanide-hydroxide solutions at 52% gold recovery into the production solution as compared to the routine gold recovery level of 18%.

3. Conclusions
The investigation into leaching of the study-type ore batches is in progress with active hydroxochloride solutions, subjected to integrated oxidation (direct activated hydrochloration). Hydroxochloride solutions obtained in electrophotochemical treatment of the initial sodium-chloride solutions provided additional oxidation of carbonaceous matter and suppression of its sorption activity as well as gold recovery at 70% level.

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