

Cluster chemical reactions at mineral–liquid interface in metal leaching by photo-electroactive water-and-gas emulsions

AG Sekisov

Chita Division, Chinakal Institute of Mining, Siberian Branch, Russian Academy of Sciences, Chita, Russia

E-mail: sekisovag@mail.ru

Abstract. Possibility of cluster (inter-cluster) reactions at the interface of mineral and liquid phases in leaching of metals mainly in dispersed cluster form by photo-electrically activated water-and-gas emulsions is theoretically evaluated. The governing role of active clusters of water and clustered hydrate envelopes generated under dissolution of active oxygen forms is determined. The scope of the study covers possible processes of transformation of clustered gold in mineral substance under direct interaction with the components of the active water-and-gas emulsions.

According to findings of many Russian and foreign researchers in geology and geochemistry, gold occurs in gold-bearing minerals in the form of micron and submicron particles and in dispersion form of poly- and mono-element clusters. Dispersed gold particles are geochemically associated in gold-bearing minerals with such metals as silver, copper, iron, lead, bismuth, and with anion formers such as sulfur, silicium, arsenic, antimony and tellurium. Metals and gold particles are in metallic bonding, while chemical bond of gold and anion formers is much more complex and is at the early stage of being explained theoretically.

Inasmuch as, first, it is known on the existence of such natural minerals as petrovskaita (AuAgS), utenbogaardtite (Ag_3AuS_2), calaverite (AuTe_2), aurostibnite (AuSb_2) and montbreite ($(\text{AuSb}_2)\text{Te}_3$), and, second, it is experimentally been found to be feasible to obtain cluster compounds of gold with sulfur (Au_mS_m) and with sulfur and hydrogen, it can be supposed that sulfide mineral can contain poly-element cluster nanostructures with a mono-element “core” with the gold–gold bond and a “shell” composed of atoms either of basic mineral-forming elements (iron, copper, sulfur, arsenic) or atoms of antimony, tellurium, silver, hydrogen, i.e. doping elements that indirectly connect gold with basic atoms (ions) of lattices of the host mineral.

In view of high degree of geochemical bonding between silicium and gold, the evidence of clustering of silicium with alkali metals (fullerene-like clusters of silicium and encapsulated atoms of alkali metals: NaN_{10}Si , K_{10}Si , Rb_{10}Si , Cs_{10}Si), which are to a certain degree the analogs of gold, it can be supposed that metal minerals can contain gold–quartz and gold–sulfide–quartz assemblages, and gold–silicium bi-element clusters (Au_mSi_m). Similar gold–carbon nanostructures (Au_mC_m) could appear in the course of bio-geo-chemical recycling of gold (upon disintegration of organometallic complexes in zones of orogenic activity, a part of gold migrates in solid-phase medium, and another part strengthens bonding with carbon). So, hydroxyl radicals and sodium and hydrogen ions can



dissociate dispersed gold clusters, i.e. break both excitonic bonds between gold atoms and, for instance, silicium atoms, and metallic gold–gold bonds in the core of a cluster. As the atoms of “shell”-making elements are also clustered, they, when in contact with aqueous medium and, consequently, in the interaction with outside hydrated complexing agents, which are actually cluster structures, can form “above-cluster” compounds with the “core” of gold atoms. It is assumable that clusters contain “collective-state electrons” according to Little, which conditions chemical interaction between them as a single particle and another object of similar structure. In this manner, the first stage of dissolution of cluster gold may be single-step interaction between a complex of atoms, making the “shell” of the gold cluster, and hydrated clusters of complexing agents of solution followed by indirect passing into film water in the form of an aggregate hydrated complex with the preserved bonding of the “core” of gold atoms and the “shell” atoms. Naturally, probability of this process depends on energy and structural conformity of hydrated complexes making the “shell” of the gold clusters. Therefore, these hydrated complexes, containing molecules of water and ions and/or radicals of certain elements or their compounds interacting with the atoms in the gold cluster “shell,” should have a cluster structure, as well. Clustering of water molecules can take place during formation of hydrated shells around molecules (atoms, ions) of soluble solids, clathrates of molecules (atoms) of soluble gases, or under interaction with inoculating ions of hydrogen and oxygen, e.g. H^+ , OH^- [1, 2], as well as with radicals OH^* or ion radicals, e.g. high-active oxygen ion radical (O^{*-}). Proton and hydroxyl ions of neighbor molecules can make metastable bonds ($H+H^-$ or $H^*(e+e^-)H^*$), which results in clustering. Energy of a cluster, e.g. $H+(H_2O)_n$, $OH^*(H_2O)_n$ (where $n = 2-30$), and, accordingly, its reactivity depend both on the energy of the inoculating center and the energy of water molecules and their dissociates (H^+ , OH^- , OH^*).

Such ionized and radical reactive components of water clusters can be obtained using different methods of treatment of aqueous solution of initial reagents, though the most suitable methods are electrolysis, photolysis and photoelectrolysis. Electrolysis of solutions of some salts and acids greatly intensifies dissociation of water molecules, which increases energy of hydrated shells of ions in water, and can produce compounds with polymeric structure and/or with high concentration of oxygen, which can result in formation of high-energy water clusters connected with these compounds.

In particular, electrolysis of sulfuric acid (H_2SO_4) produces in the anode zone metaspulfuric and persulfuric acids (H_2SO_5 , $H_2S_2O_8$); azotic acid—pernitric acid (HNO_4); sodium bicarbonate ($NaHCO_3$)—metacarbonic and percarbonic acids (H_2CO_4 , $H_2C_2O_6$) in the anode zone and superoxides of alkali metals ($Na_2C_2O_6$, $K_2C_2O_6$) in the interelectrode space. Electrolysis of sodium chloride solution produces hypochloric acid ($HClO$) perhypochloric acid ($H_2Cl_4O_4$) in the anode zone and sodium hyperchlorine ($NaClO$) in the interelectrode space. UV irradiation of water-and-gas emulsion after the electrolysis generates such highly active oxidizers in the gas bubbles as atomic oxygen, superoxide radical ion (O^{*-}), ozone and hydroxide radical (OH^*), which, under interaction with film water around the gas bubbles, create ion radical and radical-bearing clusters.

When such hydrated cluster appeared after photo-electrochemical treatment of an initial solution contains a few complexing radicals and/or ions, it can be a reaction entity with the structural and energy parameters complementary to the structure and energy of the “shell” of a gold-bearing cluster.

The active clusters and clathrates—clusters in treated solutions can support passing of gold-bearing cluster in water phase both directly and indirectly as is described below.

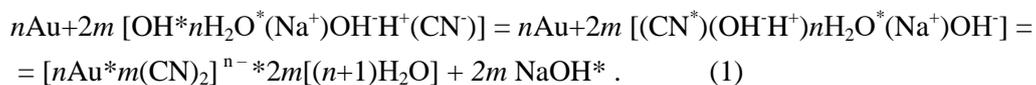
Periodic dissociation of water molecules making an active cluster (or cluster shell of clathrate) may generate secondary active particles: H^+ and OH^- , OH^* “fixed” ionic pares of H^+H^- type, active (excited) molecules and/or ions: H_2O^* , H_2O^+ , H_2O^- , which can diffuse inside lattices of dispersed gold-containing minerals and induce breaking of bonds between atoms (ions) of mineral-forming elements and nano-cracks in the lattices. Moreover, active ions and radicals of hydrogen and oxygen and their compound can join together inside a crystal of a metallic mineral and generate meta-stable reactive complexes of the type of $nH_2O^*H^+H^-$, supporting clustering of atoms of such elements and silicium, sulfur, oxygen, iron, etc., making a ‘shell’ around the clustered atoms of gold. The “shell” elements make bonds with water oxygen and break bonds with the “core” gold atoms. Sodium and/or

potassium ions diffusing into the double electric layer at the contact with the surface of mineral particle can liberate from the hydrated shell owing to oxidation of negatively charged hydroxyl ions in the shell by protons and can also enter lattices. Sodium cation, being high active and having smaller ionic radius, can replace gold in silicium clusters. The similar effect can be created by hydrogen ions (protons) as they also can make clusters with silicium of the type of [3].

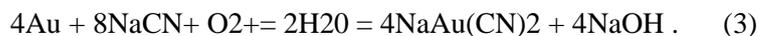
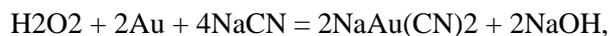
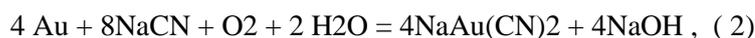
Later on, ionic pairs $H^+ \cdot H^-$ and hydroxyl radicals, diffusing through the double electric layer to the lattice, excite sharing electron shells (including hybrid, at levels 5d-6s) of clustered gold atoms. This results in the exponentially growing probability of break of the chemical bonds between gold atoms and surrounding atoms of mineral-forming elements. The liberated mono-elements clusters of gold and/or individual gold atoms are permitted to migrate inside the lattice of a mineral and reach micro-cracks and pores, including in the form of meta-stable compounds with hydroxide radical. It is known that even natural water contains stable occurrence form of gold— $AuOH(H_2O)^0$ —in a wide range Eh–pH. So, during interaction of hydroxyl radicals and protons, which penetrate a metallic mineral lattice from process solution, with the dispersed gold atoms (including clustered), it is highly possible that mobile meta-stable compounds $AuOH^*$ and AuH^* will appear and can be moved to contact surface under heap leaching. Consequently, this ensures further complexing of gold and cyanide in leaching solution and diffusion of gold-and-cyanide complexes to pregnant solution.

To make secondary gold clusters at the surface of micro-cracks and pores and the “cores” of the primary poly-element gold-bearing clusters (after its separation from the “shell”) pass into solution, it is most efficient to use not individual hydrated anions $nH_2O^*CN^-$ or radicals $nH_2O^*CN^*$ but structurally and energy complimentary hydrated clusters including a few single compounds CN as complexing entities: $m[(CN^*)(OH^+H^+)nH_2O^*(Na^+)OH^-]$.

Ionic pairs $H^+ \cdot H^-$ in the composition of these reactive clusters transform ions CN^- into active meta-stable radicals CN^* and, at the same time, excite shearing electron shells of gold clusters and, consequently, open way for single-stage interaction and clustering of hydrated anions $[nAu^*m(CN)_2]^{n-} \cdot nH_2O$



The known models of gold cyanidation by Elsner (2) and Bodlander (3), as follows from the formulas below, also assume interaction of many sodium cyanide molecules in complexing but fail to expose physicochemical background of these reactions



The appropriateness of the proposed model (1), assuming dispersed gold leaching by photoelectrically activated solutions as the result of the cluster reaction with the active hydrated complexing agents, is approved both by the experimental evidence of clustering between water molecules and their dissociation products [3] and by the existence of a narrow range pH = 10–11.5 for efficient reaction of cyanidation. The latter fact implies a significant role of the joint presence of both ions H^+ (protons) and OH^- (and, consequently, meta-stable ions H^-) in the hydrated clusters, including complexing agents for gold, with the periodic generation of meta-stable pairs ensuring their reactivity.

Numerous experiments on photoelectric activation leaching of dispersed gold from rebellious metallic minerals and waste carried out at the Chita Division of the Institute of Mining, SB RAS, have proved the theoretical statements of the discussed model of cluster reactions. It has been found that leaching rate and extraction rate of gold depend on gold dissociation intensity and re-combination of water molecules, on mobility of hydroxyl ions and hydroxonium, on concentration of sodium cyanide and on its dissociation in photoelectrically activated solution. The most interesting proof of formation of cyanide-bearing clusters in photoelectrically activated solutions is the essential decrease in

concentration of “free” cyanide ions, which is determined by alkalimetric testing, in the first hours after preparation of the activated solution (water and gas emulsion) with the subsequent increase up to initial values that are close to estimated values. The same increase in the concentration of sodium cyanate, an oxidized form of sodium cyanide, is not observed. The main experimental finding to prove cluster behavior of chemical reactions during leaching of gold and associated silver is the stage-wise yield of these metals in pregnant solutions as against gradually descending kinetic curve in the test experiments on plain water solutions with equal concentrations of cyanides.

References

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