Efficiency of using peroxide-carbonate compounds in reagent complexes for leaching gold hard to recover from placer

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Abstract. The article deals with the data of theoretical and experimental studies of the processes of activation gold leaching using reactive peroxide carbonate compounds, obtained by electrophotochemical treatment of solutions of initial reagents of the corresponding composition, in the composition of reagent complexes. The obtained results of the experiments on the interaction of various carbonate and peroxide-carbonate compounds with sodium cyanide in the process of mixing activated and non-activated solutions with aqueous cyanide solutions in different order definitely prove that supramolecular percarbonate-cyanide compounds are being formed in them. It has been established that these activated solutions, prepared on the basis of the initial hydrocarbonate ones, contain metastable compounds that provide a higher rate of gold extraction from crude minerals than standard aqueous cyanic solutions of the same initial concentration.

1. Introduction
In spite of having been depleted significantly by intensive exploitation for more than a century, placer gold deposits still remain an important source of obtaining this precious metal in Russia. In this context, it is quite natural that the gold placers being developed at the present time are characterized by a much more difficult mode of productive layers occurrence, lower content of gold and, most importantly, more complicated forms of its occurrence in the sands as compared to already abandoned gold deposits. Besides, the increase of commercial importance of man-made sources containing gold (gale-lixiviation waste dumps and tailings left by gold mining plants) and pillar-drawing workplaces, formed during the previous years of exploiting placer deposits, is being observed. In these potential exploitation plays, gold has forms predominantly difficult to recover by means of traditional gold recovery techniques, such as free particles of fine-dispersed gold, flake or dust gold and intracrystalline inclusions in the crystal lattices of mineral concentrators (both encapsulated and dispersed) or oxide-hydroxide filmy formations on their surface. Such gold deportments should be recovered effectively by means of leaching techniques in combination with the traditional gravel and / or flotation gold recovery processes. Meanwhile, in many cases, standard leaching methods do not allow to extract intracrystalline (both encapsulated and dispersed) and occluded (reprecipitated) gold
in a fairly complete manner. As a result, it is necessary to develop new reagent complexes and technological schemes for leaching gold from placer sands.

2. Theoretical foundations of the processes occurring during oxidizing of productive mineral matrices of placer sands and selective dissolution of gold

For low-grade gold, rusty gold and, most importantly, encapsulated and dispersed gold localized inside the crystal lattices of wash pan concentrates and quartz as well as in films of ferrous oxides and hydroxides covering it to be extracted from placer sands, it seems obvious to use the system of reagents that chemogenically transform mineral carriers of gold. Chemogenic transformation of alluvial sand crystal lattices as gold concentrators can be accompanied by both parallel and sequential formation of a soluble gold-bearing complex. The most acceptable in this case is the peroxide-carbonate complex that, being combined with both cyanides and chlorides, forms supramolecular structures interacting with dispersed gold through the cluster mechanism.

The proposed leaching method is based on the use of electrochemical and photochemical treatment of the initial hydrocarbonate solutions, during which peroxide-carbonate complexes are produced.

Supraperoxide carboxy-containing compounds (monopercarbonic H$_2$CO$_3$ and percarbonic H$_2$C$_2$O$_6$ acids) can be synthetically produced in the process of treating an aqueous solution of sodium hydrogen carbonate in electrochemical and photochemical reactors. Such supraperoxide compounds are metastable; therefore, they dissociate within the cluster structures producing highly active OH$^*$ hydroxyl radicals (through an intermediate stage of hydrogen peroxide evolution): H$_2$CO$_3$= H$_2$O$_2$+CO$_2$, H$_2$C$_2$O$_6$= H$_2$O$_2$+2CO$_2$, H$_2$O$_2$+OH = H$_2$O+O$^*$+OH*, or hydroxyl radical ions and carboxyl cations – (2OH$^*$+C$_2$O$_2^*$, 2OH$^*$+ C$_2$O$_4^*$). Experimental evidence of supramolecular carbonate-cyanide structures being formed will obviously be temporary cyanide content decrease in the activated combined solution and its subsequent return to the initial value, as well as the difference in the kinetics and dynamics of gold leaching from parallel sub-samples according to the standard scheme of leaching cyanide of the same concentration with an aqueous solution.

2.1. Targets of research

Targets of the research were the processes occurring in combined carbonate-cyanide and percarbonate-cyanide solutions as well as the processes of activation leaching of forms of gold difficult to recover from placer sands and their placer fraction.

2.2. Experimental research

To confirm tentatively that percarbonates in coordination with cyanides form a supramolecular metastable complex, experiments with various solutions of blend composition were carried out.

The formation of metastable supramolecular complexes in such solutions can obviously be confirmed by the decrease and the subsequent increase of the cyanide content.

Changes in the content of sodium cyanide in mixed solutions containing different carbonate bases were carried out according to the following possible options for their composition and preparation sequence.

1. Check (zero) test. A sub-sample of 0.5051 g NaCN was placed in a flask with 100 ml of water, then 100 ml of water were added to it and mixed.
2. A sub-sample of 0.5053 g NaCN was placed in a 100 ml flask, then 100 ml of an activated NaHCO$_3$ solution (10 g L$^{-1}$) were added.
3. A sub-sample of 0.5226 g NaCN was placed in a 100 ml flask, then 100 ml of an aqueous solution of NaHCO$_3$ (10 g L$^{-1}$) were added.
4. A sub-sample of 0.5027 g NaCN was placed in a 100 ml flask, then 100 ml of an aqueous solution of Na$_2$CO$_3$ (10 g L$^{-1}$) were added.
5. 0.5052 g of NaCN was placed in a 100 ml flask, the sub-sample was dissolved in 50 ml of water, and 50 ml of an activated NaHCO$_3$ solution (10 g L$^{-1}$) were introduced into the resulting mixture.
6. 0.5109 g of NaCN were placed in a 100 ml flask, 50 ml of water were added, and another 50 ml of an aqueous solution of NaHCO$_3$ (1 g) were added to the resulting mixture.
7. 0.5125 g of NaCN were placed in a 100 ml flask, the sub-sample was dissolved in 50 ml of water, and 50 ml of an aqueous solution of NaHCO\(_3\) (1 g) were introduced into the mixture.

Then, all the flasks with the obtained solutions were left in a dimly lit place and aliquots with argentometric titration were taken at variable amounts of time.

As table shows, the cyanide concentration in the control flask remained practically unchanged (the only insignificant deviation was recorded in the 4th measurement, which may be attributed to a local temporary decrease in air temperature and the permissible measurement error).

**Table 1.** Empirical data of assessing the stability of carbonate-cyanide and percarbonate-cyanide.

|                  | 16.03.2021 | 18.03.2021 | 22.03.2021 | 26.03.2021 | 30.03.2021 | 19.05.2021 |
|------------------|------------|------------|------------|------------|------------|------------|
| **Control 0.5 g NaCN** |            |            |            |            |            |            |
| CN, g L\(^{-1}\) | 1.20       | 1.2        | 1.2        | 1.16       | 1.20       | 0.96       |
| CN, %            | 0.12       | 0.12       | 0.12       | 0.12       | 0.12       | 0.10       |
| NaCN g L\(^{-1}\) | 2.27       | 2.27       | 2.27       | 2.18       | 2.27       | 1.82       |
| **Active NaHCO\(_3\)+0.5 NaCN** |            |            |            |            |            |            |
| CN, g L\(^{-1}\) | 1.20       | 1.20       | 1.16/1.25  | 1.20/1.20  | 1.20       | 1.10       |
| CN, %            | 0.12       | 0.12       | 0.12/0.13  | 0.12/0.12  | 0.12       | 0.11       |
| NaCN g L\(^{-1}\) | 2.27       | 2.27       | 2.18/2.36  | 2.27/2.27  | 2.27       | 2.07       |
| **NaHCO\(_3\)+0.5 NaCN** |            |            |            |            |            |            |
| CN, g L\(^{-1}\) | 1.20       | 1.01       | 1.01       | 0.91       | 0.89       | 0.48       |
| CN, %            | 0.12       | 0.10       | 0.10       | 0.09       | 0.09       | 0.05       |
| NaCN g L\(^{-1}\) | 2.27       | 1.91       | 1.91       | 1.72       | 1.68       | 0.91       |
| **Na\(_2\)CO\(_3\)+0.5 NaCN** |            |            |            |            |            |            |
| CN, g L\(^{-1}\) | 1.25       | 1.20       | 1.20       | 1.20       | 1.20       | 1.02       |
| CN, %            | 0.13       | 0.12       | 0.12       | 0.12       | 0.12       | 0.10       |
| NaCN g L\(^{-1}\) | 2.36       | 2.27       | 2.27       | 2.27       | 2.27       | 1.93       |
| **0.5 NaCN + active NaHCO\(_3\)** |            |            |            |            |            |            |
| CN, g L\(^{-1}\) | 1.25       | 1.25       | 1.20/1.30  | 1.16/1.20  | 1.20       | 1.08       |
| CN, %            | 0.13       | 0.13       | 0.12/0.13  | 0.12/0.12  | 0.12       | 0.11       |
| NaCN, g L\(^{-1}\) | 2.36       | 2.36       | 2.27/2.45  | 2.18/2.27  | 2.27       | 2.03       |
| **0.5 NaCN + NaHCO\(_3\)** |            |            |            |            |            |            |
| CN, g L\(^{-1}\) | 1.16       | 1.01       | 1.01       | 0.91       | 0.89       | 0.48       |
| CN, %            | 0.12       | 0.10       | 0.10       | 0.09       | 0.09       | 0.05       |
| NaCN, g L\(^{-1}\) | 2.18       | 1.91       | 1.91       | 1.72       | 1.68       | 0.91       |
| **0.5 NaCN +Na\(_2\)CO\(_3\)** |            |            |            |            |            |            |
| CN, g L\(^{-1}\) | 1.25       | 1.20       | 1.25       | 1.25       | 1.25       | 1.04       |
| CN, %            | 0.13       | 0.12       | 0.13       | 0.13       | 0.13       | 0.10       |
| NaCN, g L\(^{-1}\) | 2.36       | 2.27       | 2.36       | 2.36       | 2.36       | 1.96       |

Notably, over the next 4 days, the sodium cyanide content returned to its previous value. Also, the cyanide content in the sodium carbonate solution remained practically unchanged, while the cyanide content in the sodium hydrocarbonate solution dropped sharply. This can be explained by the fact that carbonic acid forming volatile hydrocyanic acid when interacting with sodium cyanide is not intensively produced in carbonate solutions, as compared to hydrocarbonate solutions, due to the higher concentration of sodium ions, stepwise dissociation and hydration of sodium carbonate. The cyanide content remained unchanged in the activated hydrocarbonate solutions for 2 days, and sediment began to appear on the fourth day. At the same time, the cyanide content in the pure fraction of the aliquot comparatively decreased as relating to its initial value but it also increased, within the measurement accuracy, due to the solid fraction of the sediment.

Thus, we can assume that, generally, the electrophotochemical activation of hydrocarbonate solutions before sodium cyanide being introduced into them significantly changes their physical and chemical properties towards the positive direction. Experiments with gold leaching have shown high efficiency of percarbonate-cyanide solutions obtained on the basis of a sodium hydrocarbonate
solution treated by the electrophotochemical method relative to cyanide solutions of the same initial concentration. The increase in its recovery comprises from 15 to 55% for placer sands with different proportions of its encapsulated and dispersed forms of occurrence.

References
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