ISSN 0016-7029, Geochemistry International, 2007, Vol. 45, No. 3, pp. 298–301. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © S.V. Petrov, V.F. Petrov, 2007, published in Geokhimiya, 2007, No. 3, pp. 337–341.

SHORT COMMUNICATIONS

Study of the Removal of Water-Soluble Copper Compounds from Heap-Leaching Gold Wastes under the Influence of Natural Factors

S. V. Petrov and V. F. Petrov

OAO Irkutsk Research Institute of Noble and Trace Metals and Diamonds,
bul'v. Gagarina 38, Irkutsk, GSP-158, 664025 Russia
e-mail: svpetrov@mail.ru

Received July 20, 2005

DOI: 10.1134/S0016702907030081

The technology of heap leaching (HL) is characterized by low capital and exploitation costs and is presently widely applied in Russia for processing gold ores. In this method, the broken ore mass is piled (heaped) on a hydroisolated base and sprayed with Na cyanide solution to extract noble metals [1]. After the extraction of Au and Ag, considerable amounts of wastes are formed, including spent ores containing moisture with highly toxic components, such as cyanides, thiocyanates, and heavy metals. The long-term safe storage of these wastes requires their detoxication.

The wastes of heap leaching are traditionally detoxified by "chemical" methods, for example, oxidation by hydrogen peroxide [2], treatment with SO_2–air mixtures [3, 4], chlorination [5–7], etc. However, the practical application of these operations is limited by the high cost of reagents and construction and service of sewage treatment plants. In addition, their ecological effect may be minor, because the desired extent of removal of toxic substances cannot be reached or the secondary pollution of wastes by the products of chemical reactions can occur. Thus, there is a need to develop a more advanced technology for the detoxication of this waste type.

A promising technology devoid of these disadvantages is cyanide detoxication under the influence of natural factors ("natural" detoxication). The natural detoxication is low cost and does not lead to secondary pollution with "ballast" salts, because the process is reagent-free.

It is known that cyanides can be decomposed under the influence of natural factors [8, 9]. However, the physicochemical characteristics of the relevant processes are poorly understood, which prevents the development of a highly efficient and safe detoxication technology. The most difficult problem is studying the removal of heavy metals, which are present in neutralized cyanide-bearing wastes as cyanide-bearing complexes.

As was mentioned above, in addition to cyanides, a spent ore dump contains several other toxic components, including copper. The presence of this metal is related to the interaction between cyanides and mineral component of the ore [10]. Copper occurs in the liquid phase of wastes (moisture of ore mass) as complex species, $[Cu(CN)_4]^{3-}$or $[Cu(CN)_3]^{2-}$.

The removal of copper during natural detoxication was studied in a real ore material. A special technique was developed and applied; it is based on the following premises.

A spent ore dump is heterogeneous in terms of temperature and contents of water and free oxygen. The upper layer is prone to seasonal and daily variations. The lower layers bounded by the depth of freezing and have an almost constant temperature of no less than 0°C. The moisture content of the spent ore material after draining by productive solutions remains practically constant at 10–15%, with the exception of the upper layers exposed to the atmosphere. The content of free oxygen decreases with depth owing to geochemical reactions with minerals (e.g., with sulfides) and consumption by cyanides, other compounds, and bacterial populations contained in the wet ore.

Thus, in terms of temperature, oxygen, and water content, the ore dump can be conditionally subdivided into four zones (layers). The uppermost zone (layer 1) is directly exposed to the atmosphere. It is affected by seasonal temperature variations, and its moisture content depends on the rate of precipitation and evaporation. The layer has a minor thickness of 0.2–0.5 m. Its presence exerts no significant effect on the behavior of toxic compounds during neutralization.

The underlying zone, layer 2, extends to the depth of frost penetration (1.5–3.0 m) and can be characterized as an oxygen-saturated zone. This zone has almost constant moisture content owing to the hampering of water evaporation by the upper layer, but its temperature shows seasonal variations.

Layer 3 is located below the depth of frost penetration, where temperature variations are insignificant. The layer can extend to the base of the ore dump at the absence of oxygen-free zones, which is characteristic of the final stages of decomposition of toxic compounds. The temperature of ore in this layer is approximately 0–4°C. The material occurs under aerobic conditions.

The deepest zone (layer 4) is distinguished by the deficiency of oxygen, which is largely consumed by the overlaying ore material. These conditions can also be provided by the specific properties of ores, for example, high content of sulfides and clays, and by the applied technology of ore preparation. During the initial stage, after dump washing with technological waters, the development of natural detoxication can result in significant thickening of this zone, up to the replacement of layer 3. During subsequent detoxication, its thickness decreases up to zero values. The temperature of ore in this layer is estimated as 0–4°C.

In order to elucidate tendencies in the removal of water-soluble copper compounds from ore moisture, we studied their behavior in each of the described layers, except for the first one, which is thin and exerts no notable effect on the end result. Spent ore material after gold heap leaching at the Maiskoe deposit (Republic of Khakassia, ZAO ZDK Zolotaya Zvezda) was studied. It is characterized by the following properties [11].

The ore mass consists of a mixture of rubble and sandy–clayey material. The clastic material consists of limonitized porphyrites, quartz–carbonate–feldspar, feldspar–quartz, clay–carbonate–quartz metasomatites, and carbonaceous siliceous shales. The rocks are strongly altered, disintegrated, and brecciated. Iron oxides and hydroxides completely penetrate the rocks and fill interstices, fractures, and cavities. There are also lenslike aggregates and veinlets of quartz, up to 10–15 mm thick. Sulfides are completely oxidized and transformed to oxides and hydroxides. This indicates that the ore is completely oxidized and can be processed by heap leaching.

The material was chemically and mineralogically analyzed. The results of these investigations are shown in Tables 1 and 2.

The ore is enriched in tailing–forming minerals, which can hinder the free ore–atmosphere exchange during wet material storage. Clay minerals account for a considerable portion of the muddy fraction (grain size <0.074 mm), which is confirmed by the results of granulometric analysis presented in Table 3. In addition, the ores inevitably show some sorption capacity, which is related to the presence of clays and carbonaceous matter.

There is another important factor. In the plant, the crushed ore is agglomerated with the addition of cement, which results in the resistance of the solid phase to acidification through geochemical and atmospheric processes. The pH value of the ore moisture

Table 1. Results of the semiquantitative spectral analysis of the ore material used in this study

Component	Weight fraction, %	Component	Weight fraction, %
Silicon	10	Barium	0.003–0.01
Aluminum	10	Yttrium	0.003–0.01
Iron	1–10	Lead	0.001–0.003
Calcium	1–10	Tungsten	0.001–0.003
Sodium	0.1–1.0	Nickel	0.001–0.003
Magnesium	0.01–0,1	Chromium	0.001–0.003
Titanium	0.3–1.0	Gold	0.001–0.003
Manganese	0.03–0.1	Tin	<0.001
Vanadium	0.01–0.03	Gallium	<0.001
Copper	0.01–0.03	Molybdenum	<0.001
Cadmium	0.01–0.03	Silver	<0.001
Zirconium	0.01–0.03	Cobalt	<0.001
Arsenic	0.01–0.03	Ytterbium	<0.001
Strontium	0.003–0.01	Scandium	<0.001
Antimony	0.003–0.01	Beryllium	<0.001

Table 2. Results of the mineralogical analysis of the ore material used in this study

Minerals	Weight fraction, %
Quartz, chalcedony-like quartz	55.0
Calcite	14.0
Kaolinite	7.0
Chlorite, altered feldspar, hydromuscovite, talc, amphiboles, epidote	20.0
Apatite, magnetite, zircon, rutile, titanite	signs and single signs
Iron oxides and hydroxides (limonite, goethite, hematite)	3.0
Manganese oxide	0.1
Jarosite	signs
Pyrite, arsenopyrite, galena, antimonite	single signs
Graphite, carbonaceous matter	signs

Table 3. Results of the granulometric analysis of the ore material used in this study

Grain size fraction, mm	Weight fraction, %	Grain size fraction, mm	Weight fraction, %
+10	19.3	–0.2 + 0.16	1.0
–10 + 5	20.9	–0.16 + 0.1	1.7
–5 + 2	15.3	–0.1 + 0.074	1.8
–2 + 1	6.7	–0.074 + 0.063	1.5
–1 + 0.63	2.1	–0.063 + 0.056	0.3
–0.63 + 0.45	2.6	–0.056 + 0.032	4.0
–0.45 + 0.315	2.1	–0.032	18.0
–0.315 + 0.2	2.7		

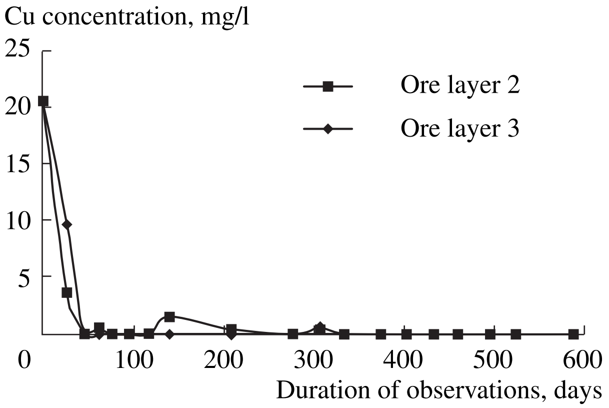

Fig. 1. Variations in the concentration of water-soluble Cu species in layers 2 and 3.

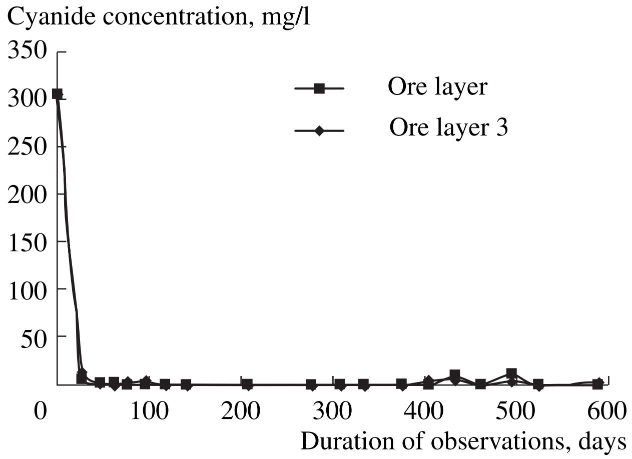

Fig. 2. Variations in the concentration of cyanides in layers 2 and 3.

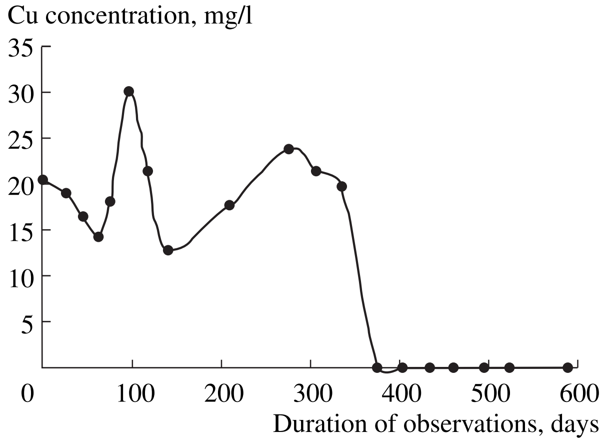

Fig. 3. Variations in the concentration of water-soluble Cu species in layer 4.

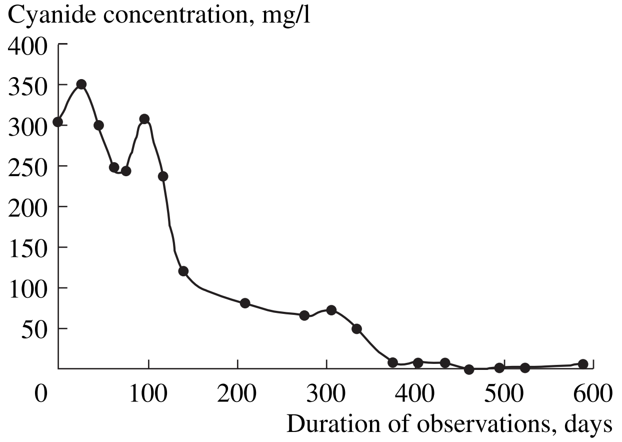

Fig. 4. Variations in the concentration of cyanides in layer 4.

remained practically constant at 9.0–9.2 during the entire period of our study.

Samples of leached ore material were collected for tests from a spent pad at a depth of 2 m (from a 4-m high ore dump). They were packed in hermetic packages and delivered to the test site within three days. The ore was immediately analyzed after arrival, and its liquid contained 19.0 mg/l Cu and 304.7 mg/l cyanides.

The ore samples were placed at conditions approaching the real conditions in each of the layers considered according to the following scheme.

Second ore layer. A 32-kg ore sample was loaded into a container, 0.4 × 0.225 × 0.25 m in size, with free air access and kept dark. The sample was maintained in a water-saturated state. The weight loss due to evaporation was compensated by distilled water sprayed over the entire open area of the ore material. The temperature of the sample was maintained at 20°C.

Third ore layer. A 32-kg ore sample was loaded into a container, 0.4 × 0.225 × 0.225 m in size, with free air access and kept dark. It was found that the moisture content of the ore remained practically constant during storage, which was caused by the specific conditions of this experiment. The temperature of sample storage was 4°C.

Fourth ore layer. An ore sample, 9.6 kg in weight, was divided into 48 200-g portions and loaded into polyethylene packages. The packages were evacuated, blown with Ar, sealed, and placed into a container with a constant temperature of 0–4°C. One package was used for each analysis.

The concentrations of the compounds of interest in the ore material were determined by the method of waste toxicity analysis USEPA Method 1311 TSLP. The results were recalculated to ore moisture.

The experimental results are shown in Figs. 1–4.

Soluble Cu was efficiently removed from ore layers 2 and 3, where its content decreased rapidly to zero. Further analyses did not detect Cu in the moisture (Fig. 1). The intense transition of Cu into a weakly mobile form is related to the high rate of degradation of cyanides, which are necessary for the formation of water-soluble Cu-cyanide complexes (Fig. 2).

The dynamics of removal of water-soluble Cu species from ore layer 4 is characterized by some specific features (Fig. 3). There is an area with high Cu content and no signs of detoxication, which is related to the high cyanide content in the liquid phase (Fig. 4). The subsequent destruction of the cyanic component leads to the complete removal of the metal from the solution.

The removal of soluble Cu compounds occurs most likely through the transition of Cu cyanide complexes into a lower-coordination state and eventually the formation of insoluble hydroxides and carbonates:

$$\mathrm{Cu(CN)_4^{3-}} \rightleftharpoons \mathrm{Cu(CN)_3^{2-}} + \mathrm{CN^-}, \quad (1)$$

$$\mathrm{Cu(CN)_3^{2-}} \rightleftharpoons \mathrm{Cu(CN)_2^{-}} + \mathrm{CN^-}, \quad (2)$$

$$\mathrm{Cu(CN)_2^{-}} \rightleftharpoons \mathrm{Cu(CN)} + \mathrm{CN^-}, \quad (3)$$

$$\mathrm{2Cu(CN)} + \mathrm{H_2O} \rightleftharpoons \mathrm{Cu_2O} + \mathrm{2HCN}, \quad (4)$$

$$\mathrm{2Cu(CN)} + \mathrm{H_2O} + \mathrm{CO_2} \rightleftharpoons \mathrm{Cu_2CO_3} + \mathrm{2HCN}. \quad (5)$$

In the presence of sulfide ions and iron cyanides in the liquid phase, weakly soluble salts can be formed, for instance, Cu sulfide and ferrocyanide:

$$\mathrm{4Cu(CN)} + \mathrm{Fe(CN)_6^{4-}} \rightleftharpoons \mathrm{Cu_4Fe(CN)_6} + \mathrm{4CN^-}, \quad (6)$$

$$\mathrm{2Cu(CN)} + \mathrm{S^{2-}} \rightleftharpoons \mathrm{Cu_2S} + \mathrm{2CN^-}. \quad (7)$$

We attempted to approximate the obtained experimental curves by first-order kinetic equations.

The values of the corresponding coefficients of reaction rate (k) determined for the above-described conditions of ore material storage are shown in Table 4.

Table 4. Coefficients of the reaction rate of first-order kinetic equations approximating the removal of water-soluble Cu compounds from the ore moisture (k)

No. of ore layer	Rate coefficient, 1/s
2	6.0×10^{-7}
3	6.7×10^{-7}
4	8.3×10^{-8}

As temperature decreases from 20 (layer 2) to 4°C (layer 3) in an aerobic environment, the constant of the rate of removal of water-soluble Cu compounds practically does not vary, which is suggested by the similar values of estimated k (6.0×10^{-7}–6.7×10^{-7} 1/s). The anaerobic conditions of the storage of ore material (layer 4) exert the strongest effect on the rate constant; the total rate of degradation decreases by a factor of about 10 as k decreases to 10^{-8}. It can be concluded that the intensity of removal of water-soluble Cu compounds from the wastes is practically independent of the temperature regime of their storage within the temperature range 4–20°C. The process is controlled by the presence of anaerobic zones in the ore dump.

The results reported here can serve as a basis for the development of the technology of removal of soluble Cu compounds from ore materials under the influence of natural factors. The transition of Cu into a weakly mobile state is a fairly intense process, which is accompanied by the formation of lower coordination metal complexes and eventually weakly soluble compounds, such as copper hydroxides and carbonates. The rate and completeness of the process depend on the oxygen regime in the spent dump and degree of cyanide degradation.

REFERENCES

1. G. G. Mineev and S. B. Leonov, *Heap Leaching of Gold Ores* (IrGTU, Irkutsk, 1997) [in Russian].
2. G. Vickell, "Degussas Cyanide Destruction Process. A Practical Technology," CIM Bull. **926** (1989).
3. R. V. Ferguson and H. E. Walker, RF Patent No. 1183617, Byull. Izobret., No. 443518.
4. G. J. Borbely, E. A. Devuyst, and V. A. Ettel, RF Patent No. 4537686, Byull. Izobret., No. 587611.
5. L. M. Milovanov, *Waste Water Treatment at the Works of Non-Ferrous Metallurgy* (Metallurgiya, Moscow, 1971) [in Russian].
6. H. Afsar, S. Kocaoba, and F. Turak, "Determination and Removal of Cyanides from Waste-Waters," in *Proceedings of 36th IUPAC Congress on Frontiers in Chemistry, New Perspectives for the 2000s, Geneva, Switzerland, 1997* (Geneva, 1997), No. 7, p. 405.
7. V. V. Barchenkov, "Cyclical Technology for the detoxication of Cyanic Wastes of the Mnogovershinnaya ZIF," Kolyma, No. 7, 21–23 (1992).
8. A. Smith and D. W. Struhsacker, "Cyanide Geochemistry and detoxication Regulations," in *Introduction to Evaluation, Design, and Operation of Precious Metal Heap Leaching Projects* (Littleton, Colorado, 1988), pp. 275–292.
9. P. Menling, "Fate of Cyanide in Abandoned Tailings Ponds," CIM. Bull, No. 926 (1981).
10. I. N. Maslenitskii and L. V. Chugaev, *Noble Metal Metallurgy* (Metallurgiya, Moscow, 1972) [in Russian].
11. V. E. Dement'ev, G. A. Stroganov, A. M. Shutov, et al., *Technological Guides for the Elaboration of the Project of an Industrial Set-Up for Heap Leaching of Gold Ores at the Maiskoe Deposit* (Irgiredmet, Irkutsk, 1993) [in Russian].