PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Thermodynamic Modeling of Phase Formation Conditions in The System CuO-CO_2-H_2O-NH_3

T. M. Bublikova[a,*], T. V. Setkova[a], V. S. Balitsky[a]

[a]*Korzhinskii Institute of Experimental Mineralogy of the Russian Academy of Sciences, Chernogolovka, 142432 Russia*

Received August 07, 2024
Revised September 27, 2024
Accepted for publication September 28, 2024

Phase formation in the $CuO–CO_2–H_2O–NH_3$ system has been studied using thermodynamic modelling in the temperature range of 20–100°C, $p^o = 0.1$ MPa and ammonia concentrations of 0, 0.01 and 2.0 mol/kg. The stability fields of tenorite [CuO], malachite [$Cu_2CO_3(OH)_2$], azurite [$Cu_3(CO_3)_2(OH)_2$] were determined and the compositions of the solutions in equilibrium with the solid phases were calculated. The effect of temperature and ammonia concentration on the change in phase relations in the system was shown. It was found that during the interaction of tenorite, malachite and azurite with ammonia solutions 1.0–3.0 mol/kg, the copper content in the solution increased with increasing ammonia concentration and decreased with increasing temperature. The results presented provide a basis for understanding the mechanism of mineral formation in aqueous copper-carbonate systems, as well as for solving a number of environmental problems and developing technological processes for ammonia leaching.

Keywords: thermodynamic modeling, tenorite, malachite, azurite, ammonia solutions

DOI: 10.31857/S0044457X250110e3

INTRODUCTION

The study of phase formation conditions in aqueous copper-carbonate systems is relevant because it is directly related to solving important theoretical and practical problems: determining the conditions for the formation of copper-containing minerals in nature, creating new technologies for the synthesis of basic copper carbonates, predicting the environmental situation and assessing environmental risks in areas where copper deposits and mining and processing plants are being developed, and choosing the composition of solutions used in hydrometallurgical processes of ammonia leaching.

The solid phases of the tenorite (**Tnr**) [CuO], malachite (**Mlc**) [$Cu_2CO_3(OH)_2$] and azurite (**Azu**) [$Cu_3(CO_3)_2(OH)_2$] system are widely distributed minerals in the oxidation zone of copper sulfide and polymetallic deposits. The general scheme of formation of the so-called "index" copper minerals with the participation of sulfate and carbonate solutions was proposed in [1] based on the study of geochemistry and mineralogy of the most important elements found in the oxidation zone. The most complete results of studying the conditions for the formation of tenorite, malachite and azurite are presented in [2]. Noting the large discrepancy in the values of thermodynamic quantities of minerals in existing databases, the authors experimentally determined the solubility constants of malachite and azurite. The obtained results are in good agreement with data from other researchers [3, 4]. The calculated stability fields of copper oxide and carbonates are presented on the stability diagram of compounds in the Cu^{2+}–CO_2–H_2O system at temperatures of 280–350 K. In general, the experimental and theoretical data available to date allow us to judge the stability of tenorite and malachite at temperatures of 280–373.15 K, azurite at 293.15–323.15 K in a wide range of solution pH. It should be noted that phase diagrams are usually given at a constant molar fraction of copper: 10^{-4} [2] and 10^{-6} mol/kg [5]. Quantitative data on the chemical composition of solutions in which crystallization of tenorite, malachite and azurite occurs are absent in the literature. The available results of analyses for copper content in mine waters of copper sulfide deposits differ by an order of magnitude or more. Thus, the concentration of copper in mine waters of the Southern Urals deposits ranges from 46.1 mg/l at Uzelginskoye to 1920 mg/l at the Gayskoye deposit. In the area of direct mining in mine workings at the Uzelginskoye deposit, the copper content in water reaches 175 mg/l. The distribution of dissolved ionic forms of copper has not been studied experimentally [6].

Investigation of phase formation conditions in aqueous copper-carbonate systems in the presence of low concentrations of NH_4^+ is of particular practical importance in connection with the study of corrosion resistance of containers in planned spent nuclear fuel storage facilities. Copper is considered as one of the possible structural materials for containers for high-level radioactive waste disposal [7]. Using the method of chemical thermodynamics, the authors of [5] evaluated the influence of groundwater on the copper corrosion process. The composition of the model solution corresponded to the composition of waters in Swedish granites at a depth of ~500 m. According to calculations, when the walls of copper containers contact with the pore waters of granites containing 0.01 mol/kg of total nitrogen, at temperatures of 25 and 100°C, the formation of oxides and basic copper salts is possible.

The study of the behavior of solid phases in the $CuO–CO_2–H_2O–NH_3$ system with the participation of concentrated ammonia solutions (up to 13.0 m NH_3) is directly related to improving the technology of hydrometallurgical copper extraction, since malachite, tenorite, and azurite are among the 15 copper-containing minerals of industrial importance. The set of factors affecting the conditions for using complex solutions of ammonia with ammonium salts in hydrometallurgical processes for extracting copper from depleted ores, tailings, and industrial wastes has been considered in a fairly large number of publications [8–14]. The effectiveness of using ammonia solutions without adding ammonium salts in the malachite leaching process is shown in [9]. Using a geochemical modeling program, the authors calculated and experimentally determined the copper concentration during the dissolution of malachite in 0–3.0 m NH_3 solutions. However, calculations and experiments were conducted at 25°C, although the ammonia leaching process is often carried out at elevated temperatures [10, 15]. There is very little data on the interaction of azurite with ammonium hydroxide. Nevertheless, azurite is an important representative of copper oxide minerals, and its reserves are second only to those of malachite.

The purpose of this study is to solve the following tasks using thermodynamic modeling:

1) investigation of conditions for the formation of solid phases in the $CuO–CO_2–H_2O–NH_3$ system under conditions typical for oxidation zones of copper sulfide

deposits (0 *m* NH_3), technogenic and industrial processes (0.01 and 2.0 *m* NH_3); temperature range 25–100°C, pressure 0.1 MPa;

2) determination of copper speciation and composition of solutions in equilibrium with tenorite, malachite, and azurite (0, 0.01 and 2.0 *m* NH_3);

3) establishing the influence of temperature on phase relationships in the CuO–CO_2–H_2O–NH_3 system (0.01 and 2.0 *m* NH_3) with temperature increase from 20 to 100°C;

4) calculation of dissolved copper concentration during interaction of tenorite, malachite, and azurite with 1.0–3.0 *m* ammonia solutions in the temperature range of 20–100°C.

CALCULATION METHODS

Phase relationships in the CuO–CO_2–H_2O–NH_3 system were determined using the "HCh" geochemical modeling software package [16]. The main thermodynamic parameter used in the "HCh" software package for modeling geochemical processes is the change in Gibbs free energy of system components (solid phases, complexes, and aqueous solution particles) from basic components [17]. For the stated tasks, the application of this package allows calculation of the concentration of all system components, the bulk composition of the solution in equilibrium with solid phases, ionic strength, and solution pH. When forming the database for calculations, special attention was paid to the consistency of thermodynamic values. The Gibbs free energy values for solid phases, aqueous solution particles, and copper complexes are presented in Table S1. In calculating the Gibbs energy of aqueous solution particles at elevated temperatures, the equations of Ryzhenko [18] and Helgeson–Kirkham–Flowers [19] were used, while experimental data on heat capacity we obtained earlier [20] were used in calculating the thermodynamic functions of malachite and azurite. Phase diagrams of copper compounds solubility were calculated for temperatures of 25–100°C and pressure of 0.1 MPa. The total amount of water in the solution was constant and equal to 1 kg, with component concentrations in the solution expressed in mol/kg H_2O. To solve the stated problems, sections of the composition space of the system with ammonia concentrations of 0, 0.01, and 2.0 mol/kg were selected.

RESULTS AND DISCUSSION

Phase Formation in the $CuO–CO_2–H_2O–NH_3$ System, $C_{NH3} = 0$ mol/kg

Under atmospheric conditions ($t = 25°C$, $p_{CO2} = 10^{-3.45}$ atm), as seen from Fig. 1, the formation of tenorite is most probable; tenorite and malachite are stable relative to azurite. In natural processes, the sources of additional carbon dioxide necessary for the formation of copper carbonates are groundwater, atmospheric CO_2, and bicarbonate solutions. Lowering the partial pressure of CO_2 in the atmosphere and decreasing the saturation of carbon dioxide in solutions circulating in the oxidation zone lead to a decrease in the content of carbonate-bicarbonate copper ions, which promotes the replacement of malachite with tenorite.

Investigation of the composition of mine, under-dump, and mine lake waters by membrane analysis showed that 92.4–99.5% of copper is transported in dissolved form [6]. According to our calculations, $CuOH^+$ and Cu^{2+} particles dominate in a solution in equilibrium with tenorite (Fig. 2a). With increasing CO_2 concentration (decreasing pH) in the solution, the content of aqueous particles $CuOH^+$, $Cu_2(OH)_2^{2+}$ and $Cu(OH)_2$(aq) decreases, while that of carbonate-bicarbonate particles $CuHCO_3^+$ and $CuCO_3$(aq) increases. The total concentration of particles CuO_2^{2-}, $Cu(OH)_3^-$, $Cu_3(OH)_4^{2+}$, $Cu(CO_3)_2^{2-}$ and $Cu(OH)_4^{2-}$ in the solution is <0.1% and does not make a significant contribution to the total amount of dissolved copper. The total copper concentration increases with increasing partial pressure of CO_2. Its content in a solution in equilibrium with malachite is 2.69×10^{-5}–4.38×10^{-4} mol/kg, with azurite – 4.38×10^{-4}–2.04×10^{-3} mol/kg.

At a temperature of 100°C, the form of the isotherm and the general character of changes in the concentration of copper particles in solution do not change significantly

(Fig. 1, 2). In a solution in equilibrium with malachite and azurite, the copper concentration is higher than at 25°C (with malachite – 1.15×10^{-4}–4.86×10^{-4} mol/kg, with azurite – 4.86×10^{-4}–1.87×10^{-3} mol/kg, decreasing towards the equilibrium boundary with copper carbonate). Thus, at elevated temperatures, malachite formation occurs from solutions more saturated with copper. The obtained data do not contradict the results of the study of mine water mineralization at the Levikha copper-pyrite deposit (Middle Urals). Depending on the horizon lowering from 85 to 205 m, the copper content in water increases from 125 to 2548 mg/l [21].

The stability fields of malachite and azurite shift to the region of higher partial pressure of CO_2 (lower pH values) with increasing temperature. The effect of temperature on the stability of phases in the system under consideration is to increase the stability of tenorite relative to malachite and malachite relative to azurite.

The obtained results help explain the formation process of the so-called "copper patina" on the surface of copper roofs of buildings and archaeological bronze objects [22]. According to [1], atmospheric precipitation is highly enriched with carbonic acid; air dissolved in rainwater contains 10 vol. % of carbon dioxide. The dashed line *2* in Fig. 1 ($t = 25°C$) indicates the partial pressure of carbon dioxide corresponding to its concentration in rainwater of 1.34×10^{-4} mol/kg. Analysis of the diagram shows that under atmospheric conditions, when copper contacts rainwater, the formation of malachite phase is natural.

It has been established and experimentally proven that as a result of the interaction of copper with water under atmospheric conditions, an X-ray amorphous analog of malachite is formed – georgeite $Cu_2(CO_3)(OH)_2 \cdot 6H_2O$ [23]. In the present study, the conditions for georgeite formation are not considered. There are very few reports in the literature about its properties due to its extremely rare occurrence in nature.

Phase Formation in the $CuO–CO_2–H_2O–NH_3$ System, $C_{NH3} = 0.01$ mol/kg

In Russia, geological isolation of high-level radioactive waste is planned to be carried out in the Krasnoyarsk Territory at the "Yeniseysky" site of the Nizhnekansky massif [24]. Deep disposal facilities are located in rock formations at a depth of ~500 m. According to chemical analyses, ammonia is present in the underground waters of the site, solutions of which are a typical environment that promotes stress corrosion cracking of copper under mechanical load [25]. Copper is considered as a possible construction material for containers. The concentration of NH_4^+ ion in waters is 0.24–0.85 mg/l [26]. The expected temperature of the container surface in the initial period of placement will reach 80°C and gradually decrease to 15°C after the repository closure [5]. To assess the influence of ammonia on the formation process and behavior of solid phases, as well as to understand the mechanism of interaction of groundwater with the surface of copper containers, we have adopted the $CuO–CO_2–H_2O–NH_3$ system as a model, with ammonia concentration of 0.01 mol/kg, at temperatures of 25 and 100°C.

In work [5], it was established that copper oxidation in a humid environment occurs with the formation of an oxide layer and basic copper salts, mainly with carbonate. As our calculations show (Fig. 3), at temperatures of 25 and 100°C, tenorite, malachite, and azurite have fairly wide stability fields. The concentration of copper in equilibrium with tenorite in solution at 25°C is higher than at 100°C. The total copper concentration is determined mainly by the content of the hydroxo complex $CuNH_3OH^+$ (Fig. 4a). The main contribution to the total copper concentration in solution, equilibrium with malachite, comes from the aqueous species $CuCO_3$(aq), with azurite – Cu^{2+} and $CuHCO_3^+$. The concentration of copper in solution in equilibrium with malachite and azurite at a temperature of 100°C is higher than at 25°C (Fig. 4), the stability fields of tenorite, malachite, and azurite shift to the area of higher CO_2 values, i.e., to a more acidic region (Fig. 4b).

Most of the dissolved inorganic carbon in natural waters is present in the form of the HCO_3^- anion [27], which corresponds to the data from chemical analyses of groundwater at a depth of ~500 meters. The concentration of bicarbonate ion in groundwater, as reported in studies [5, 26], reaches 450 mg/L (dashed line *1* in Fig. 3a;

lg m_{CO2} = -2.13). According to our calculations, the concentration of dissolved CO_2 at the tenorite-malachite-solution equilibrium point is 8.71×10^{-3} (lg m_{CO2} = -2.06) mol/kg, which is necessary and sufficient for the formation of malachite at a temperature of 25°C. Thus, when copper comes into contact with water containing 0.01 *m* NH_3, tenorite formation is more likely. A slight increase in the concentration of bicarbonate ion in water creates conditions for malachite formation. At a temperature of 100°C, the calculated concentration of carbon dioxide is higher – 1.78×10^{-2} mol/kg (lg m_{CO2} = -1.75). The most favorable conditions for malachite formation occur as the temperature decreases during container cooling. According to calculations, the formation of azurite is unlikely.

Obviously, the successful use of copper as a material for container manufacturing depends on the behavior of tenorite and malachite under the given conditions. To determine possible phase changes in the system with increasing temperature, the solubility of tenorite and malachite was calculated in solutions of 0.01 *m* NH_3 in the temperature range of 20-100°C. The dependence of tenorite solubility on temperature has a nonlinear character (Fig. 5). As the temperature increases to 70°C, its solubility decreases to minimum values and then increases up to 100°C. At the minimum point, a qualitative change in the solution composition occurs due to changes in the ratio of copper particles: the concentration of copper hydroxo complexes $Cu(NH_3)OH^+$ and $Cu(NH_3)_2(OH)_2$(aq) decreases with increasing temperature, while the concentration of $CuOH^+$, $Cu(OH)_2$(aq), $Cu(OH)_3^-$ particles increases.

Copper content in solution during malachite dissolution increases with temperature rise from 20 to 100°C, and the solubility dependence on temperature is close to linear. Throughout the entire temperature range of 25-100°C, tenorite is more stable, with copper concentration in solution during tenorite dissolution being 1-1.5 orders of magnitude lower than during malachite dissolution.

Malachite dissolution in 0.01 m NH_3 occurs incongruently with the formation of tenorite phase (Fig. 6). The incongruent nature of malachite dissolution in 0.01 *m* NH_3

has great practical significance for understanding the corrosion mechanism of copper containers. When groundwater containing 0.01 *m* NH_3 possibly contacts the surface of copper containers covered with a film of malachite, the latter begins to dissolve with the formation of the more stable tenorite phase. It is assumed that a layer of bentonite will be used as one of the protective engineering barriers of the repository. The pressure of bentonite swelling in a humid environment [28] will lead to a decrease in the layer porosity and compaction of the formed phases of malachite and tenorite, contributing to the passive behavior of copper. Under the considered conditions, malachite and tenorite are passivating phases on the container wall surface.

As a result of tenorite dissolution in 0.01 *m* NH_3, the concentration of free ammonia NH_3 (aq) in solution remains practically unchanged with temperature decrease from 100 to 20°C; during malachite dissolution, it increases from 0.0008 to 0.0012 mol/kg, which increases its negative impact on the container surface. However, the critical concentration of ammonia at 70°C is 0.05 mol/l and higher at lower temperatures [25]. Thus, such a slight increase in ammonia concentration in the solution does not lead to an increased risk of stress corrosion cracking of copper. To assess the corrosion rate of copper as a structural material for radioactive waste storage containers, thermodynamic modeling is insufficient, and additional experimental work is needed.

Phase Formation in the $CuO–CO_2–H_2O–NH_3$ System, $C_{NH3} = 2.0$ mol/kg

The main factors affecting the efficiency of hydrometallurgical copper extraction processes include ammonia concentration and temperature. Depending on the composition of the initial ore, the technological process is carried out both under atmospheric conditions and when heated to 135°C using ammonia solutions with concentrations up to 13 mol/l [10, 15].

To determine the stability fields of solid phases in the system and the composition of solutions in equilibrium with solid phases during leaching, isothermal solubility diagrams of compounds in the $CuO–CO_2–H_2O–NH_3$ system at temperatures of 25, 100°C and ammonia concentration of 2.0 mol/kg (Fig. 7) were constructed based on thermodynamic calculations.

The nature of the curve corresponding to the copper concentration at the solid phase-solution equilibrium boundary (Fig. 7a) at 25°C is determined by changes in the quantitative ratios of aqueous particles and copper complexes in the solution (Fig. 8a). The main contribution to the total concentration of dissolved copper comes primarily from copper-ammonia complexes $Cu(NH_3)_n^{2+}$ (n = 2–5). With decreasing pH, the concentration of $Cu(CO_3)_2^{2-}$, $CuCO_3$(aq), $CuOH^+$ and $CuHCO_3^+$ particles increases, but has practically no effect on the change in the total copper concentration in the solution. At the same time, the proportion of free ammonia NH_3(aq) decreases, while that of NH_4^+ ion increases; at the maximum point (lg m_{CO2} = –0.15, lg m_{Cu} = –0.43 in Fig. 7a; pH 9.42 in Fig. 8a), their concentrations become equal. Further decrease in the pH of the solution leads to a significant reduction in the proportion of NH_3(aq) in the solution; its deficiency results in a decrease in the concentration of copper-ammonia complexes.

At a temperature of 100°C, the absolute values of copper concentration in equilibrium with tenorite and malachite in an alkaline environment (pH ≥ 8.3) are higher than at 25°C, which is associated with the decrease in stability of copper-ammonia complexes with increasing temperature (Fig. 8, Table S2). The optimal range of dominance for the $Cu(NH_3)_4^{2+}$ complex at pH 7.1-11.5 is consistent with the data presented in the Pourbaix diagram [29]. At a temperature of 100°C, the largest domain also belongs to the $Cu(NH_3)_4^{2+}$ complex, but the dominance region shifts to a range of lower pH values (6.2-9.7). It is evident that the pH of the solution is an important indicator that allows determining the region where copper exists in dissolved form.

To clarify the behavior and mechanism of interaction between solid phases of the system and concentrated ammonia solutions, the copper concentration was determined during the dissolution of tenorite, malachite, and azurite in solutions of 1.0, 2.0, and 3.0 m NH_3 in the temperature range of 20-100°C (Fig. 9).

With increasing temperature from 20 to 100°C, the solubility of copper oxide and basic carbonates decreases. The main form of copper during the dissolution of tenorite, malachite, and azurite in 1.0 and 3.0 *m* NH_3, as well as in 2.0 *m* NH_3, is copper-ammonia complexes. The most pronounced change in solubility is observed for tenorite in 3.0 *m* NH_3, where the copper content during Tnr dissolution decreases 5-fold as the temperature increases from 20 to 100°C (Fig. 9a). In less concentrated solutions, the temperature dependence is less pronounced. The dependence of copper content in solution on temperature during the dissolution of malachite and azurite in solutions of 1.0-3.0 *m* NH_3 is close to linear and is less dramatic than for tenorite (Fig. 9b, 9c).

The absolute values of dissolved copper concentration during the dissolution of malachite and azurite are very close and also increase with increasing ammonia concentration. The copper concentration during the dissolution of malachite and azurite exceeds that during tenorite dissolution by tens of times at 20°C and by more than two orders of magnitude at 100°C. The obtained data on malachite solubility are in full agreement with the experimental data of the authors [9] (Fig. 9b).

Dissolution of malachite in 1.0–3.0 *m* solutions of NH_3 occurs incongruently with the formation of tenorite phase (Fig. 10a). With an increase in temperature from 20 to 100°C, the proportion of tenorite increases from 19 to 29% in 1.0 *m* NH_3 and more prominently with increasing ammonia concentration: from 65 to 98% in 3.0 *m* NH_3. Dissolution of azurite also occurs incongruently. When interacting with 1.0 *m* NH_3 azurite dissolves with the formation of 100% malachite, with 2.0 and 3.0 *m* solution of NH_3 – with the formation of malachite and tenorite phases. The proportion of tenorite is greater the higher the solution concentration and temperature (Fig. 10b). The significant influence of temperature on the phase ratio during dissolution of malachite and azurite can be traced up to 70–80°C. Thus, in aqueous 1.0–3.0 *m* ammonia solutions, tenorite limits the solubility of copper during the leaching of malachite and azurite.

Overall, the established high copper content (0.16–0.60 mol/kg at 20°C) during dissolution of malachite and azurite in 1.0–3.0 *m* NH_3 shows, that the use of aqueous ammonia solutions is highly effective: 1) for extracting copper from ores with high carbonization, when acid leaching is economically impractical due to high acid consumption; 2) when leaching ores with high content of dispersed copper.

CONCLUSION

The conditions of phase formation in the system $CuO–CO_2–H_2O–NH_3$ were studied using the method of thermodynamic modeling. The stability fields of solid phases of the system were determined and the compositions of solutions equilibrium with tenorite (Tnr), malachite (Mlc), and azurite (Azu) were calculated.

It has been shown that under conditions close to those of the oxidation zone, with an increase in temperature from 25 to 100°C, the stability fields of tenorite, malachite, and azurite shift to the region of higher partial pressure of CO_2 (lower pH values of the solution). The effect of temperature on the stability of phases in the system under consideration consists in increasing the stability of tenorite relative to malachite and malachite relative to azurite. Crystallization of malachite and azurite with increasing temperature occurs from solutions containing copper in higher concentrations than at 25°C.

The influence of ammonia solution (C_{NH3} = 0.01 mol/kg; t = 25, 100°C) on the formation process and behavior of solid phases during the interaction of groundwater with copper containers intended for radioactive waste disposal was evaluated. The conditions and mechanism of tenorite and malachite formation, which create a passivating layer on the surface of copper containers, were considered.

The dependence of copper concentration in solution during dissolution of tenorite, malachite and azurite on temperature (20-100°C) and ammonia concentration of 1.0-3.0 mol/kg was established. It was shown that high copper concentration in solution is achieved with increasing ammonia solution concentration and decreasing temperature.

The copper concentration during tenorite dissolution is 1.5-2 orders of magnitude lower than during malachite and azurite dissolution. Tenorite, formed during the incongruent dissolution of malachite and azurite, limits the solubility of copper in ammonia solutions. Using the results of thermodynamic modeling, including data on dissolution of Tnr, Mlc and Azu in ammonia solutions, allows selecting optimal parameters for the leaching process, modeling the composition of the working solution and changing it depending on the composition of the original ore.

In general, the application of the thermodynamic modeling method significantly expands the possibilities for studying natural and complex technogenic systems [30] and can significantly supplement the available data on the conditions of copper mineral formation.

ACKNOWLEDGMENT

The authors express their gratitude to V.N. Zyryanov for critical comments during the discussion of the results, and to A.F. Redkin and A.V. Plyasunov for consultations on thermodynamic calculations. We are grateful to the reviewers for the discussion and useful recommendations, as well as to the journal editorial board for their attention to our publication.

FUNDING

The work was carried out within the framework of the research topic of IEM RAS No. FMUF-2022-0002.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

SUPPLEMENTARY MATERIALS

Table S1 contains Gibbs energy values of the components of the $CuO–CO_2–H_2O–NH_3$ system used for calculations. **Table S2** shows copper concentrations in solutions in equilibrium with solid phases of the $CuO–CO_2–H_2O–NH_3$ system, C_{NH3} = 2.0 mol/kg at temperatures of 25 and 100°C.

REFERENCES

1. *Smirnov S.S.* Oxidation zone of sulfide deposits. L.: Publishing House of the USSR Academy of Sciences, 1955. 231 p.
2. *Preis W., Gamsjäger H.* // J. Chem. Thermodyn. 2002. V. 34. P. 631. http://dx.doi.org/10.1006/jcht.2002.0928
3. *Schindler P., Reinert M., Gamsjäger H.* // Helv. Chim. Acta. 1968. V. 51. P. 1845. https://doi.org/10.1002/hlca.19680510805
4. *Symes J.L., Kester D.R.* // Geochim. Cosmochim. Acta . 1984. V. 48. P. 2219. https://doi.org/10.1016/0016-7037(84)90218-7
5. *Puigdomenech I., Taxén C.* Thermodynamic data for copper. Implications for the corrosion of copper under repository conditions. Technical Report SKB-TR-00-13. Stockholm, 2000. 96 p.
6. *Orekhova N.N., Shadrunova I.V.* Formation and complex processing of natural and technogenic waters during the exploitation of copper-zinc-pyrite deposits. Magnitogorsk: Publishing House of Magnitogorsk State Technical University named after G.I. Nosov, 2015. 185 p.
7. Review of foreign practices for disposal of SNF and RW / Eds. Linge I.I., Polyakov Yu.D. M.: Komtekhprint Publishing House, 2015. 208 p.
8. *Arzutug M.E., Kocakerim M.M., Copur M.* // Ind. Eng. Chem. Res. 2004. № 43. P. 4118. https://doi.org/ 10.1021/ie0342558
9. *Wang Xi, Chen Qiyuan, Huiping Hu et al.* // Hydrometallurgy. 2009. № 99. P. 231. https://doi.org/ 10.1016/j.hydromet.2009.08.011
10. *Radmehr V., Koleni S.M.J., Khalesi M.R. et al.* // J. Inst. Eng. India Ser. D. 2014. V. 94. P. 95. https://doi.org/10.1007/s40033-013-0029-x
11. *Aracena A., Vivar Y., Jerez O., Vásquez D.* // Miner. Process. Extr. Metall. Rev. 2015. V. 36. P. 317. https://doi.org/ 10.1080/08827508.2015.1004404
12. *Aracena A., Pino J., Jerez O.* // Metals. 2020. № 10. P. 833.

https://doi.org/10.3390/met10060833

13. *Turan M.D., Ramazan O., Turan M. et al.* // Mining, Metallurgy & Exploration. 2020. P. 1. https://doi.org/10.1007/s42461-020-00241-6
14. *Velásquez-Yévenes L., Ram R.* // Cleaner Eng. Technol. 2022. V. 9. P. 100515. https://doi.org/10.1016/j.clet.2022.100515
15. *Panayotova M., Panayotov V.* // J. Scient. Appl. Res. 2017. V. 11. P. 10.
16. *Shvarov Yu.V., Bastrakov E.* HCh: a Software Package for Geochemical Equilibrium Modeling: User's Guide (AGSO RECORD 1999/y). Canberra: Austr. Geol. Surv. Organisation; Dept. Industry, Science and Resources. 1999. 57 p.
17. Rusanov A.I. // Russian J. Gen. Chem. 2022. V. 92. № 4. P. 539. https://doi.org/10.1134/S1070363222040016
18. *Ryzhenko B.N.* Thermodynamics of Equilibria in Hydrothermal Solutions. Moscow: Nauka, 1981. 191 p.
19. *Helgeson H.C., Kirkham D.H., Flowers G.C.* // Am. J. Sci . 1981 . № 281. P. 1249. https://doi.org/10.2475/ajs.281.10.1249
20. *Bublikova T.M., Balitsky V.S., Timokhina I.V.* Synthesis and Basic Properties of Jewelry-Ornamental Malachite. Synthesis of Minerals. Vol. 1. Alexandrov, 2000. 662 p.
21. *Rybnikova L.S., Rybnikov P.A., Tyutkov O.V* . // Water Management in Russia. 2014. № 6. P. 77.
22. *Nienhuis J., Robbiola L., Giuliani R. et al.* // e-Preservation Sci . 2016. V. 13. P. 23.
23. *Lytle D.A. , Wahman D., Schock M.R. et al.* // Chem. Eng. J. 2019. V. 355. P. 1. https://doi.org/ 10.1016/j.cej.2018.08.106
24. *Kochkin B.T., Malkovsky V.I., Yudintsev S.V.* Scientific Basis for Safety Assessment of Geological Isolation of Long-Lived Radioactive Waste (Yeniseysky Project). Moscow: IGEM RAN, 2017. 384 p.
25. *Suzuki Y., Hisamatsu Y.* // Corros. Sci. 1981. V. 21. P. 353.
26. *Zuev V.A., Bukaty M.B., Khafizov R.R.* // Geoecology. Engineering Geology, Hydrogeology, Geocryology. 2008. No. 6. P. 531.
27. *Cole J.J., Prairie Y.T.* // Reference Module Earth Systems Environ. Sci. 2014. https://doi.org/10.1016/b978-0-12-409548-9.09399-4
28. Alekseeva O.V., Smirnova D.N., Noskov A.V. et al. // Russ. J. Inorg. Chem. 2023. V. 68. № 8. P. 953. https://doi.org/10.1134/S0036023623601071
29. *Künkül A., Kocakerim M.M., Yapici S. et al* . // Int. J. Miner. Process. 1994. V. 41. P. 167.

https://doi.org/ 10.1016/0301-7516(94)90026-4

30. *Rudskoy A.I., Kuznetsov N.T., Ivanov V.K. et al.* // Russ. J. Inorg. Chem. 2023. V. 68. No. 5. P. 694. https://doi.org/ 10.31857/S0044457X23600068

FIGURE CAPTIONS

Fig. 1. Isothermal solubility diagrams of compounds in the $CuO\text{-}CO_2\text{-}H_2O$ system: *t* = 25, 50, 75, 100°C; p^o = 0.1 MPa; Tnr - tenorite, Mlc - malachite, Azu - azurite; *1* - partial pressure of CO_2 under atmospheric conditions; *2* - CO_2 content in rainwater [1].

Fig. 2. Concentration of copper particles in solution in equilibrium with solid phases of the $CuO\text{-}CO_2\text{-}H_2O$ system, depending on pH; *t* = 25 (a), 100°C (b); p^o = 0.1 MPa.

Fig. 3. Isothermal solubility diagrams of compounds in the $CuO\text{-}CO_2\text{-}H_2O\text{-}NH_3$ system: C_{NH3} = 0.01 mol/ kg; *t* = 25 (a), 100°C (b); p^o = 0.1 MPa.

Fig. 4. Concentration of aqueous particles and copper complexes in solution in equilibrium with solid phases of the $CuO\text{-}CO_2\text{-}H_2O\text{-}NH_3$ system, depending on pH. C_{NH3} = 0.01 mol/kg; *t* = 25 (a), 100°C (b); p^o = 0.1 MPa.

Fig. 5. Dependence of copper concentration in solution on temperature during dissolution of tenorite (Tnr) and malachite (Mlc) in 0.01 *m* NH_3 solution.

Fig. 6. Ratio of solid phases during incongruent dissolution of malachite (Mlc **)** in 0.01 *m* NH_3 solution.

Fig. 7. Isothermal solubility diagrams of compounds in the $CuO\text{-}CO_2\text{-}H_2O\text{-}NH_3$ system. C_{NH3} = 2.0 mol/kg; *t* = 25 (a), 100°C (b); p^o = 0.1 MPa.

Fig. 8. Concentration of aqueous particles and copper complexes in solution in equilibrium with solid phases of the $CuO\text{-}CO_2\text{-}H_2O\text{-}NH_3$ system, depending on pH. C_{NH3} = 2.0 mol/kg; *t* = 25 (a), 100°C (b); p^o = 0.1 MPa.

Fig. 9. Dependence of copper concentration in solution on temperature during dissolution of: a - tenorite, b - malachite, c - azurite in solutions 1.0 (*1*), 2.0 (*2*), 3.0 *m* NH_3 (*3*). Black triangles in Fig. 9b - experimental data from work [9].

Fig. 10. Ratio of solid phases during incongruent dissolution of: a - malachite (Mlc); b - azurite (Azu) in solutions 1.0 (*1*), 2.0 (*2*), 3.0 *m* NH_3 (*3*).

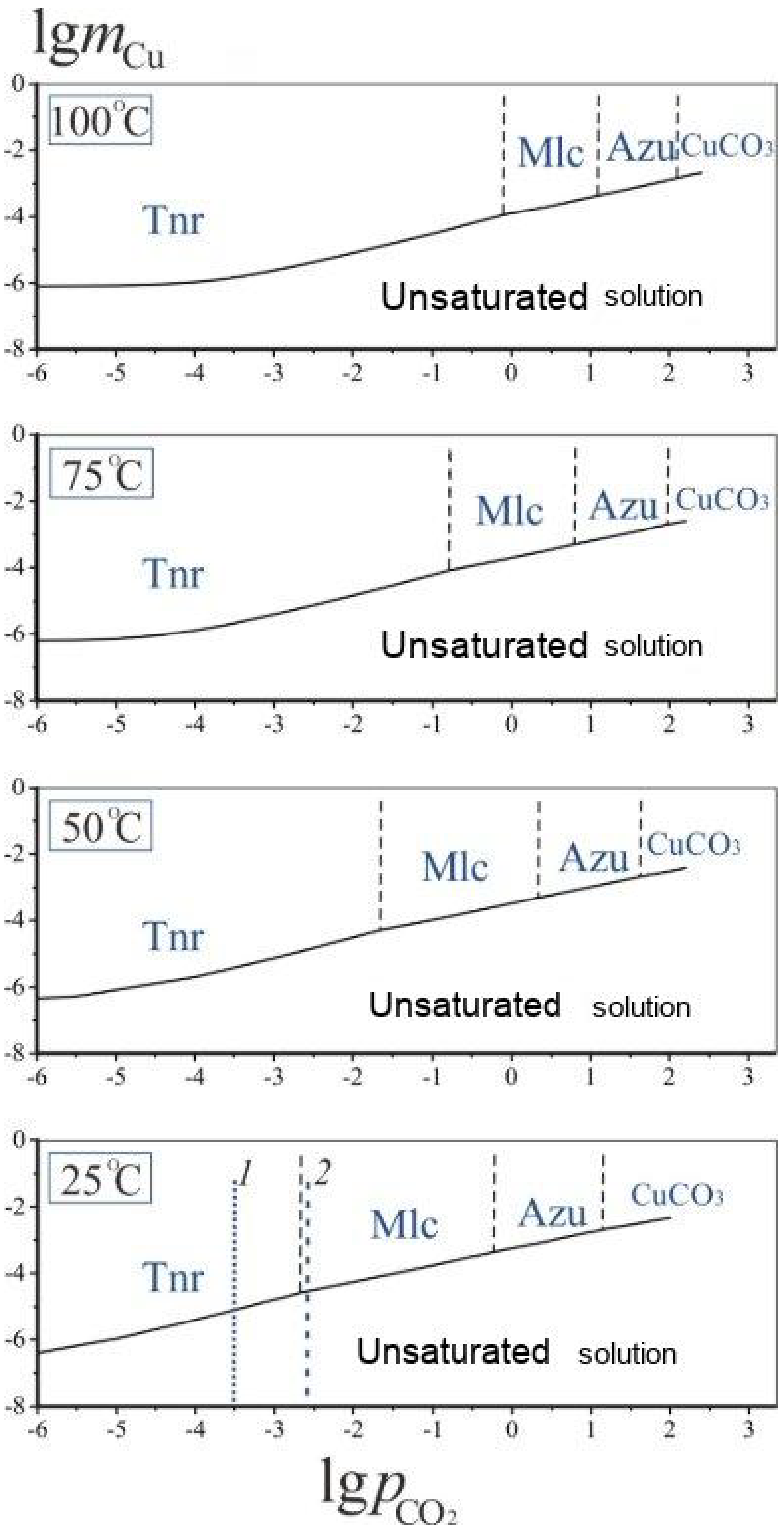

Fig. 1. Bublikova

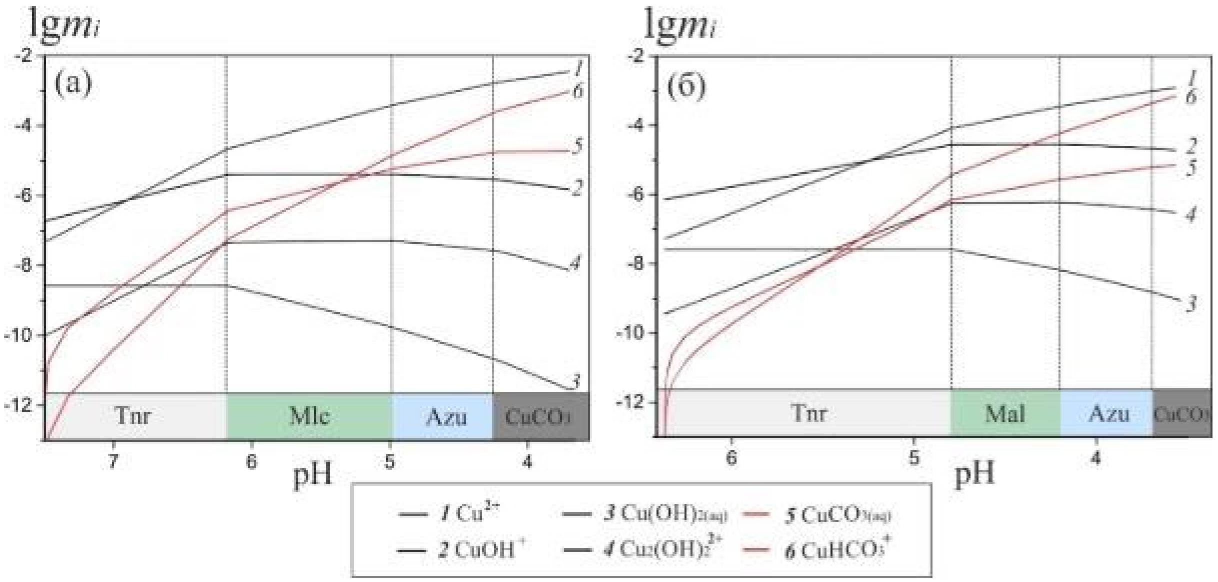

Fig. 2. Bublikova

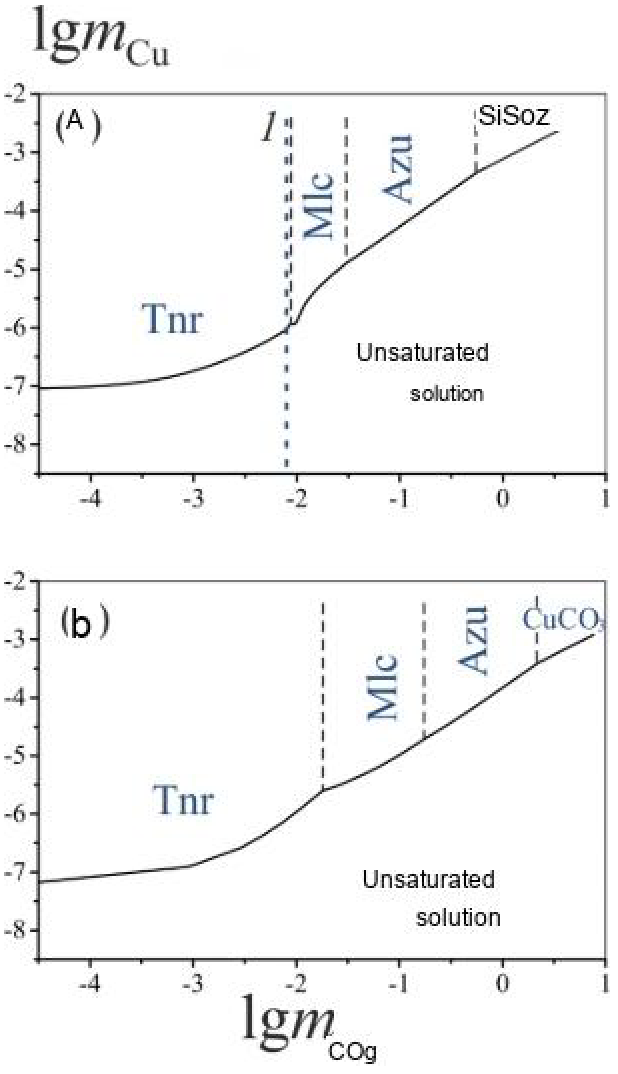

Fig. 3. Bublikova

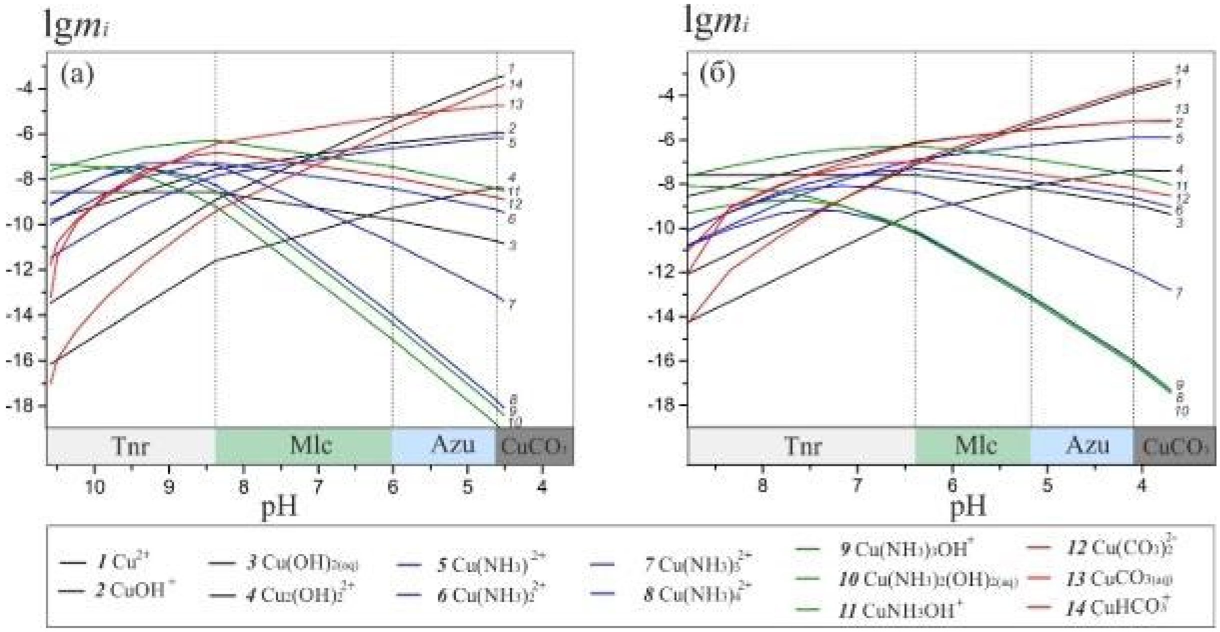

Fig. 4. Bublikova

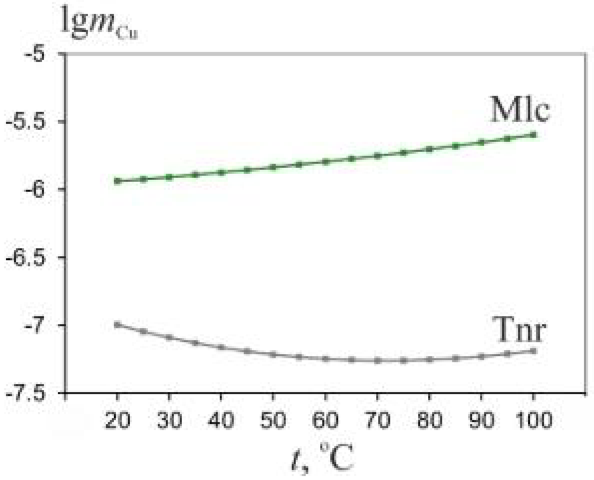

Fig. 5. Bublikova

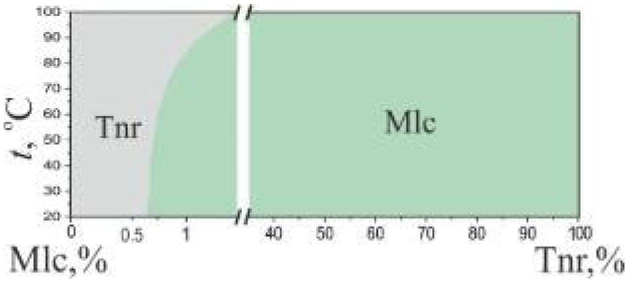

Fig. 6. Bublikova

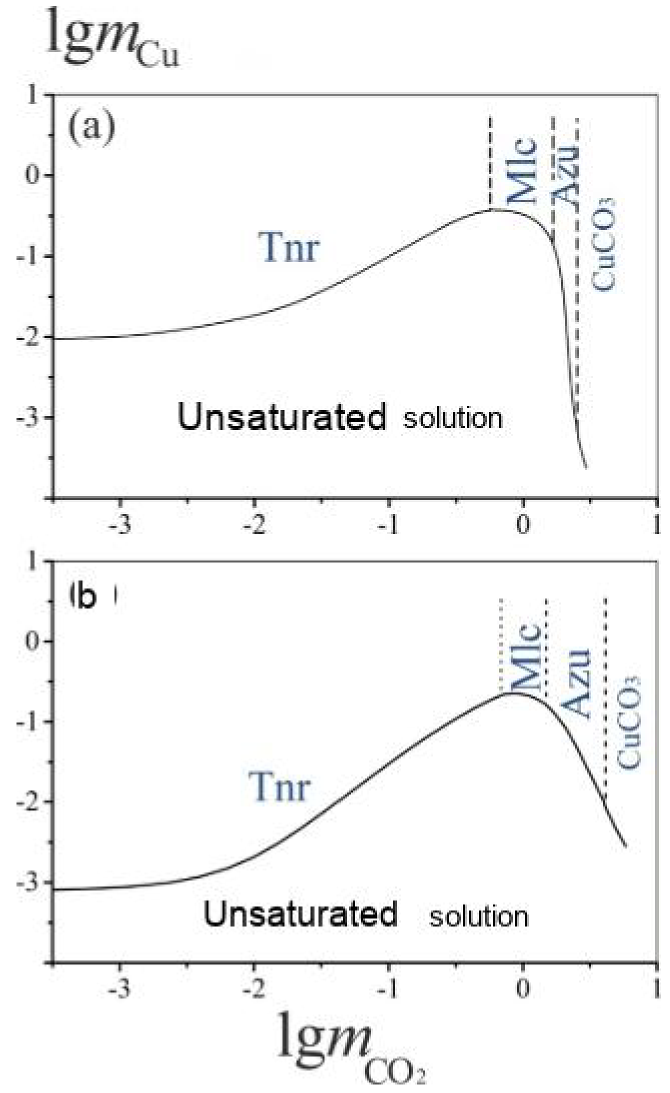

Fig. 7. Bublikova

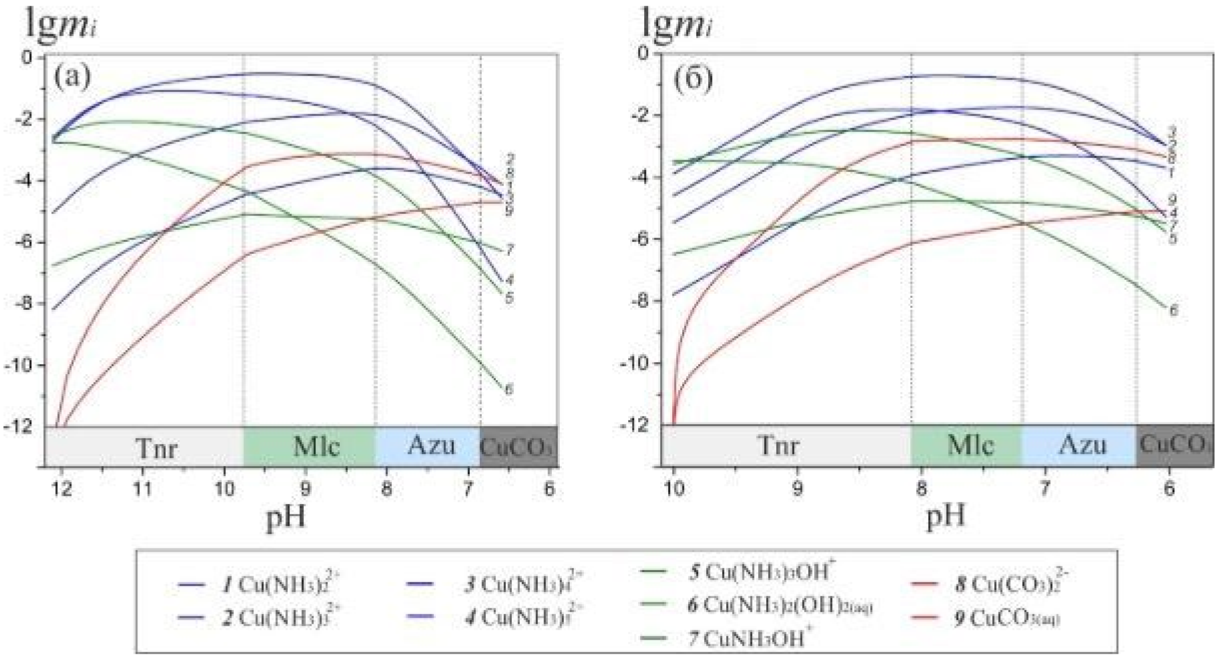

Fig. 8. Bublikova

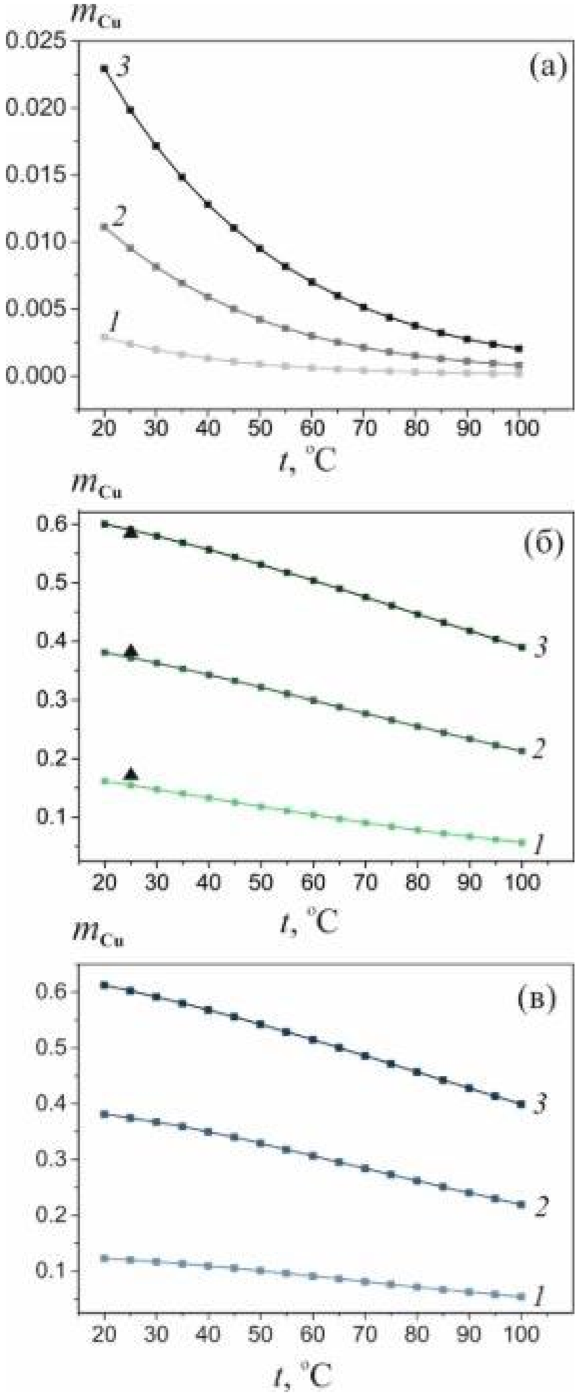

Fig. 9. Bublikova

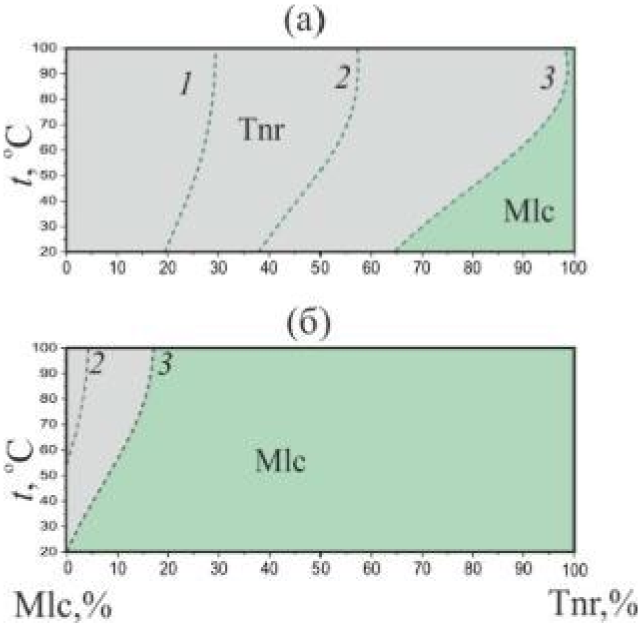

Fig. 10. Bublikova