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Thermodynamic analysis of oxidized copper minerals interaction with modified reagent

Practicality of preliminary sulphidization of oxidized copper minerals for the purpose of oxidized ore concentration is shown in the paper. For the first time the thermodynamic analysis was carried out for interaction of modified sulphidizing reagent with major components of oxidized copper ore — malachite, azurite and chrysocolla. Ammonium polysulfide formed in the solution of sodium polysulfide and ammonium sulfate was used as modified sulphidizing reagent. Temperature dependence of standard Gibbs energy for the reaction of ammonium polysulfide with oxidized copper minerals was determined. It was noted that standard Gibbs energy for malachite and azurite interaction with modified reagent has negative values in the temperature range of 298,15–373 K, thus showing high probability of interaction, which grows together with temperature. Interaction with chrysocolla is less active than with malachite and azurite but is still possible at mentioned temperature, with interaction probability again proportional to temperature. Thus, the possibility of oxidized copper minerals sulphidization with modified sulphidizing reagent is determined in the research.

Keywords: oxidized minerals, chrysocolla, malachite, azurite, modified sulphidizing reagent, sulphidization, thermodynamic analysis, Gibbs energy.

Introduction

Cheap flotation enrichment methods, conventional for sulfide ore, are less effective for oxidized ore due to natural hydrophilicity of oxidized copper minerals surface [1–3].

One of feasible solutions is chemical modification of minerals via sulphidization resulting in transformation of oxidized minerals into sulfidized ones, which can improve the flotation enrichment efficiency [4–9].

The thermodynamic analysis of possible reactions with determination temperature dependence of standard Gibbs energy has been carried out in order to assess the possibility of sulphidization with modified reagent.

Ammonium polysulfide formed in the solution of sodium polysulfide and ammonium sulfate was used as modified sulphidizing reagent.

The objective of work was to find the temperature dependence of ammonium polysulfide interaction with major components of oxidized copper ore, such as malachite, azurite and chrysocolla.

Experimental

Three types of interaction of modified reagent with copper compounds — malachite, azurite and chrysocolla have been studied:

$$Cu_2CO_3(OH)_{2(solid)} + 2(NH_4)_2S_{5(solid)} = 2CuS_{(solid)} + 8S_{(solid)} + (NH_4)_2CO_{3(solid)} + 2NH_4OH_{(liquid)}; \quad (1)$$

$$Cu_3(CO_3)_2(OH)_{2(solid)} + 3(NH_4)_2S_{5(solid)} = 3CuS_{(solid)} + 12S_{(solid)} + 2(NH_4)_2CO_{3(solid)} + 2NH_4OH_{(liquid)}; \quad (2)$$

$$CuSiO_3(H_2O)_{2(solid)} + (NH_4)_2S_{5(solid)} = CuS_{(solid)} + 4S_{(solid)} + (NH_4)_2SiO_{3(solid)} + 2H_2O_{(liquid)}. \quad (3)$$

Probability of reactions was estimated by alteration of standard Gibbs energy.

Calculation of temperature dependence of standard Gibbs energy is based on Hess law [10] and was made using the formula

$$\Delta_r G^0_T = \sum \Delta_f G^0_T \,(\text{products}) + \sum \Delta_f G^0_T \,(\text{init.}), \quad (4)$$

where $\Delta_r G^0_T$ — standard Gibbs energy at temperature (T), $\sum \Delta_f G^0_T$ (products) — sum of standard Gibbs energy of reactions products formation at temperature (T), $\sum \Delta_f G^0_T$ (init.) — sum of standard Gibbs energy of initial components formation at temperature (T).

Temperature dependence of reaction velocity constant was calculated using the next formula:

$$\lg K_{P(T)} = -\Delta_f G^0_T/(2.303RT), \tag{5}$$

where R is the universal gas constant.

Temperature dependence of standard Gibbs energy of reactions products formation was determined by approximated method of Temkin-Schwartzman [11, 12], taking $\Delta Cp0$ = const, by the formula

$$\Delta_f G^0_T = \Delta_f H^0_{298.15} - T\Delta_f S^0_{298.15} - TM\Delta_f C_p{}^0_{298.15}, \tag{6}$$

where $\Delta_f H^0_{298.15}$ is the standard enthalpy of compound formation at 298.15 K; $\Delta_f S^0_{298.15}$ is the standard entropy of compound formation at 298.15 К; $\Delta_f C_p{}^0_{298.15}$ is the standard heat of compound formation at 298.15 К; M is the coefficient, equal to

$$M = 298{,}15/T - 1 + \ln(T/298.15). \tag{7}$$

Standard entropy was determined by formula

$$\Delta_f S^0_{298,15} = S^0_{298,15} - \sum S^0_{298,15}(\text{elementary substance}), \tag{8}$$

where $S^0_{298,15}$ is the standard entropy of compound at 298.15 K; $\sum S^0_{298,15}$(elementary substance) is the sum of standard entropies of substances forming the compound at 298,15 К.

Standard heat capacity of compound formation was determined by the formula:

$$\Delta_f C_p{}^0_{298,15} = C_p{}^0_{298,15} — \sum C_p{}^0_{298,15}(\text{elementary substance}), \tag{9}$$

where $C_p{}^0_{298,15}$ is the standard heat capacity of compound at 298,15 К; $\sum C_p{}^0_{298,15}$(elementary substance) is the sum of standard heat capacities of substances forming the compound, at 298.15K.

In case of insufficiency of the available literature data, the necessary values have been determined by proximate methods.

Standard heat capacity was estimated by the Kumok method [13] based on heat capacity increments system:

$$C_p{}^0_{298,15}(A_mB_n) = mC_p{}^i_{298,15}(A^{n+}) + nC_p{}^i_{298,15}(B^{m-}), \tag{10}$$

where $C_p{}^i_{298,15}(A^{n+})$ is the increment of cation heat capacity; $C_p{}^i_{298,15}(B^{m-})$ is the increment of anion heat capacity.

Results and Discussion

The standard enthalpy values of compound formation at 298.15 K are given in the Table 1. Values for $H_2O_{(liquid)}$, $NH_4OH_{(liquid)}$, $(NH_4)_2CO_{3(solid)}$, $CuS_{(solid)}$, $Cu_2CO_3[OH]_{2(solid)}$, $Cu_3[CO_3]_2[OH]_{2(solid)}$ compounds are from [6–8]. $S_{(solid)}$equals to $S_{8(g)}$ with enthalpy data by [14]. Standard enthalpy for $(NH_4)_2S_{5(solid)}$, $(NH_4)_2CO_{3(solid)}$ and $(NH_4)_2SiO_{3(solid)}$ was calculated by Kassenov method from ionic increments [12]. Lacking data on increment of $S_5{}^{2-}$ $SiO_3{}^{2-}$ ions were found by evaluation method using standard enthalpy of sodium pentasulfide and silicates of First Group metals [16]. Data for $CuSiO_3{\cdot}nH_2O_{(solid)}$ are from [18].

Table 1

Standard enthalpy of compound formation

Substance	$-\Delta_f H^0_{298,15}$, kJ·mol^{-1}
$H_2O_{(liquid)}$	285.829
$NH_4OH_{(liquid)}$	361.271
$S_{(solid)}$	12.735
$(NH_4)_2S_{5(solid)}$	94.9
$(NH_4)_2CO_{3(solid)}$	821.1
$CuS_{(solid)}$	53.136
$(NH_4)_2SiO_{3(solid)}$	1251.6
$Cu_2CO_3[OH]_{2(solid)}$	1051.020
$Cu_3[CO_3]_2[OH]_{2(solid)}$	1631.341
$CuSiO_3{\cdot}nH_2O_{(solid)}$	1747.3

There are standard entropy values of compound formation at 298.15 K in the Table 2.

Data for $H_2O_{(liquid)}$, $NH_4OH_{(liquid)}$, $S_{(solid)}$, $CuS_{(solid)}$, $Cu_2CO_3[OH]_{2(solid)}$, $Cu_3[CO_3]_2[OH]_{2(solid)}$, $CuSiO_3{\cdot}nH_2O_{(solid)}$ were calculated by formula (8) based on [14–17]. For chrysocolla accepted n = 2. Standard entropy at 298.15 К for $(NH_4)_2S_{5(solid)}$, $(NH_4)_2CO_{3(solid)}$, $(NH_4)_2SiO_{3(solid)}$ was determined using entropy data found by Kumok method [13].

Table 2

Standard entropy of compound formation

Substance	$\Delta_f S^0_{298,15}$, J·mol^{-1}·K^{-1}
$H_2O_{(liquid)}$	–162.955
$NH_4OH_{(liquid)}$	–359.004
$S_{(solid)}$	23.567
$(NH_4)_2S_{5(solid)}$	–579.1
$(NH_4)_2CO_{3(solid)}$	–841.3
$CuS_{(solid)}$	1.453
$(NH_4)_2SiO_{3(solid)}$	–857.5
$Cu_2CO_3[OH]_{2(solid)}$	–503.504
$Cu_3[CO_3]_2[OH]_{2(solid)}$	–671.479
$CuSiO_3·nH_2O_{(solid)}$	–629.305

Standard heat capacity of compounds formation at 298,15 К is shown in the Table 3.

For $H_2O_{(liquid)}$, $NH_4OH_{(liquid)}$, $S_{(solid)}$, $CuS_{(solid)}$, $Cu_2CO_3[OH]_{2(solid)}$ compounds the data were taken from [14–17]. Values for $(NH_4)_2S_{5(solid)}$, $(NH_4)_2CO_{3(solid)}$, $(NH_4)_2SiO_{3(solid)}$ compounds were found using Kumok method [13], those for $CuSiO_3·nH_2O_{(solid)}$ are from [19].

Table 3

Standard heat capacity of compounds formation

Substance	$\Delta_f C_p{}^0{}_{298.15}$.J·mol^{-1}·K^{-1}
$H_2O_{(liquid)}$	31.793
$NH_4OH_{(liquid)}$	53.576
$S_{(solid)}$	–2.594
$(NH_4)_2S_{5(solid)}$	–17.633
$(NH_4)_2CO_{3(solid)}$	–14.3
$CuS_{(solid)}$	0.712
$(NH_4)_2SiO_{3(solid)}$	–18.8
$Cu_2CO_3[OH]_{2(solid)}$	–5.309
$Cu_3[CO_3]_2[OH]_{2(solid)}$	4.203
$CuSiO_3·nH_2O_{(solid)}$	45.288

By means of the equation 6 the temperature dependence of standard Gibbs energy for every interacting compound have been calculated. The results are given in the Table 4.

Table 4

Temperature dependence of standard Gibbs energy of compounds formation

Substance	T, K					
	298.15	313	328	343	358	373
	$\Delta_f G^0_T$, kJ·mol^{-1}					
$H_2O_{(liquid)}$	–237.244	–234.836	–232.426	–230.038	–227.67	–225.323
$NH_4OH_{(liquid)}$	–254.234	–248.922	–243.595	–238.305	–233.05	–227.828
$S_{(solid)}$	5.708	5.359	5.009	4.660	4.313	3.967
$(NH_4)_2S_{5(solid)}$	77.759	86.365	95.070	103.788	112.517	121.258
$(NH_4)_2CO_{3(solid)}$	–570.266	–557.768	–545.133	–532.488	–519.834	–507.171
$CuS_{(solid)}$	–53.569	–53.591	–53.614	–53.637	–53.66	–53.684
$(NH_4)_2SiO_{3(solid)}$	–995.936	–983.196	–970.313	–957.417	–944.509	–931.589
$Cu_2CO_3[OH]_{2(solid)}$	–900.9	–893.423	–885.869	–878.301	–870.736	–863.167
$Cu_3[CO_3]_2[OH]_{2(solid)}$	–1431.139	–1421.166	–1411.09	–1401.01	–1390.928	–1380.843
$CuSiO_3·2H_2O_{(solid)}$	–1559.673	–1550.344	–1540.953	–1531.594	–1522.264	–1512.963

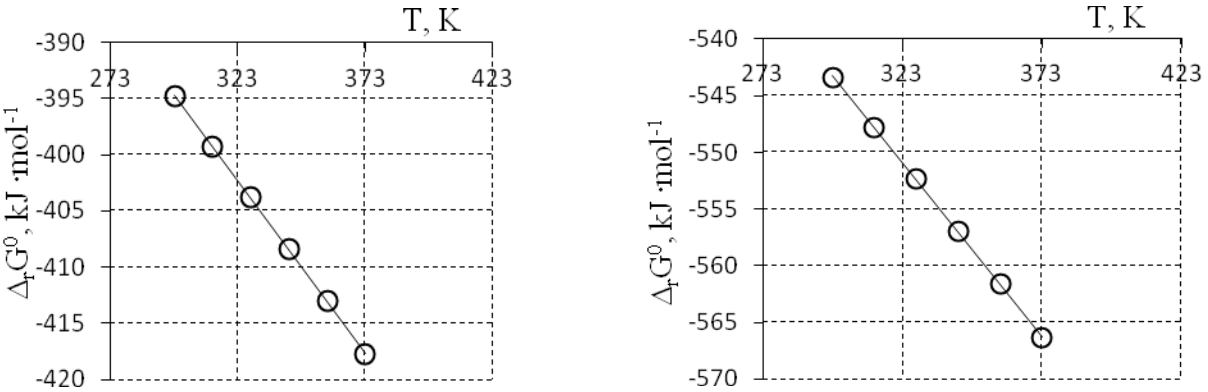
Using respective data from Table 4 in the equation (4) the temperature dependence of standard Gibbs energy for the reactions (1–3) was determined. Formula (5) was used to calculate temperature dependence of equilibrium constant for the reaction (Table 5).

Table 5

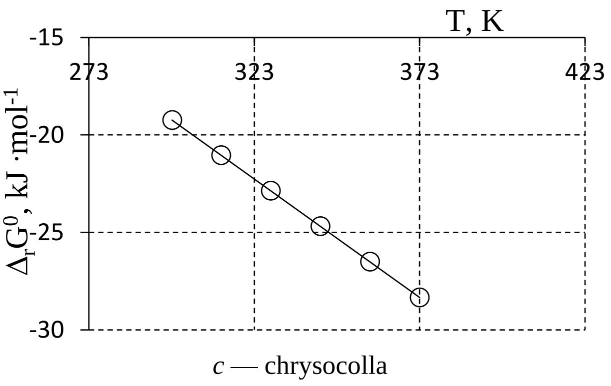
Temperature dependence of standard Gibbs energy and equilibrium constant

Reaction	T, K	298.15	313	328	343	358	373
10	$-\Delta_r G^0_T$.kJ·mol^{-1}	394.826	399.229	403.75	408.367	413.048	417.808
	Equation	$\Delta_r G^0_T = -0.307T - 303.1$					
	lgK$_P$	69.25	66.70	64.37	62.26	60.34	58.58
11	$-\Delta_r G^0_T$.kJ·mol^{-1}	543.349	547.774	552.31	556.931	561.615	566.377
	Equation	$\Delta_r G^0_T = -0.307T - 451.5$					
	lgK$_P$	95.30	91.52	88.06	84.91	82.04	79.41
12	$-\Delta_r G^0_T$.kJ·mol^{-1}	19.247	21.044	22.86	24.684	26.51	28.346
	Equation	$\Delta_r G^0_T = -0.121T + 16.99$					
	lgK$_P$	3.38	3.52	3.64	3.76	3.87	3.97

Based on Table 5 data, the temperature dependence diagrams were built for interaction of malachite, azurite and chrysocolla with modified reagent (Fig. 1).



a — malachite *b* — azurite



c — chrysocolla

Figure 1. Temperature dependence of standard Gibbs energy for interaction of copper minerals with modified reagent

As follows from Figure 1, standard Gibbs energy for malachite and azurite is negative in the whole temperature range, indicating high probability of interaction, growing with temperature. Interaction with chrysocolla is less active than with malachite and azurite but is still possible at mentioned temperature, with interaction probability again proportional to temperature growth.

Interaction of a modified reagent with chrysocolla in interval of 298.15–373 K is lower than for malachite and azurite. But also it can proceed in this temperature interval. Raise of temperature also is able to increase the probability of interaction.

Conclusions

Based on the results of thermodynamic analysis the modified reagent is recommended as oxidized copper minerals sulphidizer for flotation enrichment of oxidized copper ore. In particular, the possibility of sulphidizing the ore containing malachite, azurite and chrysocolla as major components, is demonstrated in the study.

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Тотыққан мыс минералдарының модификацияланған реагентпен әрекеттесуінің термодинамикалық талдауы

Тотыққан мыс кендерін байыту кезінде тотыққан мыс минералдарын алдын ала сульфидтеу керектігі көрсетілген. Алғаш рет тотыққан мыс кендерінің негізін құраушы — малахит, азурит және хризоколланың модификацияланған сульфидтеуші реагентпен әрекеттесуінің термодинамикалық талдауы жүргізілді. Модификацияланған сульфидтеуші реагент ретінде натрий полисульфиді мен аммоний сульфатының ерітіндісінде пайда болған аммоний полисульфиді қолданылды. Аммоний полисульфидінің тотыққан мыс минералдарымен реакциясының стандартты Гиббс энергиясының температуралық тәуелділігі айқындалды. Малахит пен азурит үшін 298,15–373 К аралығында модификацияланған реагентпен реакциясы кезінде стандартты Гиббс энергиясы теріс әсер көрсететіндігі анықталды. Сондықтан модификацияланған реагенттің малахит және азуритпен әрекеттесу ықтималдығы жоғары. Температураның жоғарылауы өзара әсер ету ықтималдығын арттырады. Модификацияланған реагенттің хризоколламен әрекеттесуі малахит пен азуритке қарағанда әлсіз көрсетілген. Алайда осы температура интервалында ағып кетуі мүмкін. Температураның жоғарылауы сонымен қатар өзара әсер ету ықтималдылығын арттырады. Осыған байланысты, тотыққан мыс минералдарының модификацияланған сульфидтеуші реагенті — аммоний полисульфидімен сульфидтенуінің мүмкіндігі көрсетілген.

Кілт сөздері: тотыққан минералдар, хризокола, малахит, азурит, сульфидтеуші модификацияланған реагент, сульфидтеу, термодинамикалық талдау, Гиббс энергиясы.

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Термодинамический анализ взаимодействия окисленных минералов меди с модифицированным реагентом

Показана необходимость предварительной сульфидизации окисленных минералов меди при обогащении окисленной медной руды. Впервые проведен термодинамический анализ взаимодействия модифицированного сульфидирующего реагента с основными составляющими окисленной медной руды — малахитом, азуритом и хризоколлой. В качестве модифицированного сульфидирующего реагента применен полисульфид аммония, образованный в растворе полисульфида натрия и сульфата аммония. Определена температурная зависимость стандартной энергии Гиббса реакции полисульфида аммония с окисленными медными минералами. Показано, что изменение стандартной энергии Гиббса реакции для малахита и азурита с модифицированным реагентом в интервале 298,15–373 К принимает отрицательные значения. Следовательно, высока вероятность взаимодействия модифицированного реагента с малахитом и азуритом. Повышение температуры способствует увеличению вероятности взаимодействия. Связь модифицированного реагента с хризоколлой выражена слабее, чем малахита и азурита. Однако она может протекать в данном температурном интервале. Повышение температуры также способствует увеличению вероятности взаимодействия. Таким образом, установлена принципиальная возможность сульфидизации окисленных медных минералов модифицированным сульфидирующим реагентом — полисульфидом аммония.

Ключевые слова: окисленные минералы, хризоколла, малахит, азурит, модифицированный сульфидирующий реагент, сульфидизация, термодинамический анализ, энергия Гиббса.

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