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THERMODYNAMIC ANALYSIS OF HEAVY METALS PRECIPITATION FOR THEIR RECOVERY FROM INDUSTRIAL WASTEWATERS

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Abstract

This work seeks to develop a suitable heavy metals precipitation modeling approach that could give reasonable results in mainstream use with industrial wastewater treatment. This paper is devoted to the thermodynamic analysis of the degree of precipitation of slightly soluble hydroxides and salts in industrial wastewaters in order to optimize the technological schemes of extraction and reuse of heavy metals from industrial waste. Based on the notion of the solubility product, the equations describing the dependence of the precipitation degree of the metal ion γ in the form of slightly soluble salts and hydroxides on the initial concentrations of the components, including complexing agents, and the pH of the solution, have been deduced. The thermodynamic meaning of the quantity γ has been revealed. Possibility of forming stable complexes between the metal ion and complexing agents in galvanic wastewater is taking into account**.** Degree of precipitation (in parentheses, %) and distribution of chemical species of metal ions (*Al* (43), *Cr* (0), *Fe* (100), *Zn* (0), *Sr* (100) and *Ba* (100)) from the multicomponent industrial effluents of an engineering company (electroplating units of the Tactical Missiles Corporation, Dubna, Russia) were analyzed at pH 6.

Key words: complex formation reaction, degree of precipitation, industrial wastewater, ion metal hydrolysis, slightly soluble compounds

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1. Introduction

The pollution of the environment with heavy metals ions pose a serious danger to the biosphere. One of the main sources of the environment pollution with heavy metals are industrial wastewater, which enter surface water courses (Ayangbenro and Babalola, 2017; Duca and Covaliova, 2017; Malschi et al., 2018; Marzougui et al., 2017; Wu et al., 2018; Zinicovscaia et al., 2015). The greater part of heavy metals enters the environment with wastewater from machine-building enterprises, galvanic units, mining enterprises and non-ferrous metallurgy (Khalturina and Bobric, 2018). In addition to pollution of natural and artificial water ecosystems with heavy metals, these industrial processes are characterized high water consumption (Makisha and Yunchina, 2017; Sofińska-Chmiel and Kolodynska, 2017).

In most cases, metal-containing wastewater are purified by conventional techniques, using chemical reagents, the effectiveness of which cannot be considered always satisfactory (Fu and Wang, 2011; Gunatilake, 2015). The reagent method of galvanic wastewater treatment is relatively common due to

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several advantages: relative simplicity, reliability, ease of automatic pH control (Luptáková et al., 2012; Ubaldini et al., 2013). However, complex chemical composition of the wastewater makes unattainable the reduction of metal concentration till maximum admissible levels, since it is almost impossible to define such pH range in which all ions of heavy metals could precipitate simultaneously (Kanamarlapudi et al., 2018). In addition, the presence in solution of complexing agents complicates the task (Gogina and Makisha, 2014). In this regard, the scientific development and improvement of both reagent and non-reagent methods for the neutralization of metal-containing wastewater from machine-building enterprises and mining, is an actual problem (Gaikwad and Gupta, 2008; Nancucheo, 2017). Review on removal of heavy metals from acid mine drainage.

Therefore, a new approach for evaluation of this method, based on the physicochemical analysis of not previously considered factors is needed.

The main objective of the paper is to derive the equations for the evaluation of the effectiveness of the reagent method used in the wastewater treatment, based on the calculations of the residual concentrations and degree of precipitation of heavy metal hydroxides and salts in an aqueous medium. The obtained expressions allow the determination of the pH range of hydroxides precipitation in the presence of complexing agents (organic or inorganic ligands), which ensures a minimum residual concentration of heavy metal ions in the wastewater (Aljerf, 2018). On other hand, it becomes possible to find the optimal conditions for the deep and complete extraction of metals, achieving high purity of the final products due to the joint and selective extraction and separation of elements with close properties, which is a main object for the next paper.

2. Theoretical considerations

For quantitative estimation of the precipitation process of compounds from aqueous solutions different characteristics are used, the most commonly used being the solubility S. Solving the problem of this kind is related to certain difficulties, because under real conditions, the ions of the solid phase participate in conjugated reactions with both the solvent (water) dissociation products and other substances present in the solution (as impurities), which leads to the reduction of the precipitated metal fraction in the form of slightly soluble compounds (Povar, 1994; Povar and Spinu, 2014a; Povar and Spinu, 2015; Povar and Spinu, 2016). At the same time, in many technological schemes and analytical procedures, a pre-estimation of the fraction or metal ion part precipitated as slightly soluble compounds, which depends on a series of parameters (the ratio of the initial concentrations of the components, the pH of the solution etc.) is strictly necessary. As a characteristic of the precipitated metal ion fraction, the degree of precipitation was introduced in (Povar and Spinu, 2016) study:

$$\gamma = \frac{C_M^0 - C_M^r}{C_M^0}, \tag{1}$$

where: C_M^0 and C_M^r are the total concentration of the metal ion in the mixture and its residual concentration in solution. In the cited above paper the following set of reactions in the "$M_mA_{n(S)}$ - *saturated aqueous solution*" system were considered:

$$M_mA_{n(S)} = mM + nA, \qquad K_S = [M]^m[A]^n \cdot \tag{2}$$

$$iM + jH_2O = M_i(OH)_j + jH, \quad K_{ij} = [M_i(OH)_j][H]^j/[M]^i \tag{3}$$

$$A + kH = H_kA, \quad \beta_k = [H_kA]/([H]^k[A]). \tag{4}$$

In Eqs. (2 - 4), the corresponding expressions of the law of the mass action are included next to the reaction equations. For the evidence of metal ion hydrolysis and anion protonation the α coefficients are used:

$$\alpha_M = C_M^r/[M] = 1 + \sum_{i=1}\sum_{j=1} iK_{ij}[M]^{i-1}[H]^{-j}$$

$$\alpha_A = C_A^r/[A] = 1 + \sum_{k=1}\beta_k[H]^k.$$

As it was mentioned, in paper (Povar and Spinu, 2016) only the equilibria (2 - 4) were taken into account. But multicomponent wastewater contains beside many inorganic ions and many organic compounds, which can act as complexing agents forming thermodynamically stable complexes with heavy metal ions. Their presence could transform essentially the whole picture of complex chemical equilibria and distribution of soluble and insoluble metal ion species. If the complexing agents, capable to form polydentate *ML* or stepwise complexes of the ML_i type are present in the system, the polynuclear complexes practically cannot be formed. Consequently, in addition to the hydrolysis of the metal ion to form $M(OH)_j$ mononuclear complexes, dependent on the pH and the total concentrations of the ligands C_L^0 or /and C_Y^0, the following side reactions are possible (for simplicity the charges of species are omitted):

$$M + kL = ML_k, \qquad \beta_k = [ML_k]/([M][L]^k) \tag{5}$$

$$M + sY = MY_s, \qquad \beta_s = [MY_s]/([M]Y]^s) \tag{6}$$

$$L + qH = H_qL, \qquad \beta_q = [H_qL]/([L][H]^q) \tag{7}$$

$$Y + rH = H_rY, \qquad \beta_r = [H_rY]/([Y][H]^r) \tag{8}$$

The last two Eqs. (7-8) take into account the possibility of protonation of corresponding ligand. Here just two complexing agents (ligands) will be considered, *L* and *Y*, but our thermodynamic analysis proves that the form of deduced equations remains the same for any numbers of ligands. For the system considered, the mass balance conditions take the form:

$$C_M^r = [M] + \sum_{i=1}[M(OH)_i) + \sum_{k=1}[ML_k] + \sum_{s=1}[MY_s] + ... = [M]\alpha_M \quad (9)$$

where the coefficient α_M is defined by the expression:

$$\alpha_M = 1 + \sum_{i=1} K_i [H]^{-i} + \sum_{k=1} \beta_k [L]^k + \sum_{s=1} \beta_s [Y]^s + ... \quad (10)$$

$$C_L^0 = [L] + \sum_{q=1}[H_q L] + \sum_{k=1} k[ML_k] = [L]\left(1 + \sum_{q=1} \beta_q [H]^q + \sum_{k=1} k\beta_k [L]^k\right) \quad (11)$$

$$C_Y^0 = [Y] + \sum_{r=1}[H_r Y] + \sum_{s=1} s[MY_s] = [L]\left(1 + \sum_{r=1} \beta_r [H]^r + \sum_{k=1} s\beta_s [L]^s\right) \quad (12)$$

When $C_L^0 >> C_M^0$ and $C_Y^0 >> C_M^0$ (condition *A*), in the Eq. (10) instead of the equilibrium concentrations of ligands *L* and *Y* can be used their total (analytical) concentrations C_L^0 and C_Y^0. Furthermore, under the condition *A,* in the Eqs. (11 - 12) the terms, associated with complex formation reactions, may be neglected.

Between the total concentration of the metal ion C_M^0 and its residual concentration in the solution C_M^r there is a mutuality relationship

$$C_i^0 = \Delta C_i + C_i^r, \quad (13)$$

where ΔC_i is the amount of precipitated metal ion (in moles) in a volume unit of the solution.

Consequently, the expression for the conditional solubility product can be presented as follows (Fishtik et al., 1986; Fishtik et al., 1987; Povar and Spinu, 2014a):

$$K_S^{cond} = \left(C_M^r\right)^m \left(C_A^r\right)^n = K_s \alpha_M^m \alpha_A^n. \quad (14)$$

By marking through *P* the amount of precipitated salt in a volume unit of the solution, with the evidence of precipitate stoichiometry, the mass balance conditions can be rewritten as follows:

$$C_M^0 = mP + C_M^r, \qquad C_A^0 = nP + C_A^r. \quad (15)$$

Joint solution of relations (1) and (15) with respect to γ gives:

$$\gamma = \frac{mP}{C_M^0}. \quad (16)$$

From Eqs. (15 - 16), it follows:

$$\gamma = \frac{m}{n}\left(\frac{C_A^0 - C_A^r}{C_M^r}\right), \qquad C_A^r = C_A^0 - \frac{n}{m}\gamma C_M^0. \quad (17)$$

Finally, by combining Eqs. (1, 14, 17), the following expression is obtained:

$$K_S^{cond} = \left(C_M^0 (1-\gamma)\right)^m \left(C_A^0 - \frac{n}{m}\gamma C_M^0\right)^n. \quad (18)$$

Eq. (18) is a non-explicit equation of the function γ of the total concentration of ions in the mixture C_M^0, C_A^0, C_L^0 and the pH of the environment. Taking into account the relation (14), the last equation can be converted in relation to γ:

$$\gamma = 1 - \frac{\left(K_S^{cond}\right)^{1/m}}{C_M^0 \left(C_A^r\right)^{n/m}}. \quad (19)$$

By solving the system of Eqs. (16 - 18), the calculation formula of function $\gamma = f(pH)$ for fixed values C_M^0, C_A^0 and C_L^0 is derived. For example, *for m = 1, n = 2* and $C_A^0 = 2C_M^0$, it is obtained:

$$\gamma^3 - 3\gamma^2 + 3\gamma + \frac{K_S \alpha_M \alpha_A^2}{2\left(C_M^0\right)^2} - 1 = 0$$

In the case of the stoichiometric ratio of the total concentrations of the solid phase components in the mixture, i.e. $nC_M^0 = mC_A^0$ (condition *B*), Eq. (18) takes the form:

$$\gamma = 1 - \frac{1}{C_M^0}\left(\frac{K_S^{cond} m^n}{n^n}\right)^{\frac{1}{m+n}} \quad (20)$$

Thus, if condition *B* is met, the degree of precipitation of the metal ion is calculated using a single Eq. (20). It should be mentioned that Eqs. (19 - 20) are applicable only when, from a thermodynamic point of view, it is impossible to convert the salt precipitate into a less soluble hydroxide $M(OH)_{n(S)}$, which usually takes place in the alkaline medium at high metal ion concentrations in solution.

In a series of papers (Povar and Spinu, 2014a; Povar and Spinu, 2016) the thermodynamic relationship between the expression for the Gibbs energy change of the summary process (2 - 4) ΔG_S^{tot}

and the residual concentrations C_M^r and C_A^r was revealed (Eq. 21):

$$\Delta G_S^{tot} = -mRT \ln \frac{C_M^r}{C_M^0} - nRT \ln \frac{C_A^r}{C_A^0} \cdot \qquad (21)$$

Our thermodynamic analysis shows that the expression (21) is valid for the summary process (2 - 8), when the metal ion forms stable complexes with ligands present in the studied systems. Therefore, taking into account the above mentioned expressions between residual concentrations and the degree of precipitation, one can be concluded - the quantity γ has a rigorously thermodynamic meaning.

Table 1 gives the values for slightly soluble salts $M_mA_{n(S)}$ of different composition in case of condition *B* satisfactory, obtained from Eq. (20). The last equation also allows an explicit determination of the γ dependence on the stoichiometric $M_mA_{n(S)}$ salt composition. Thus, with the increase of the coefficient *n*, according to Eq. (20), the degree of precipitation will increase under the conditions of invariance of the other parameters. In some analogous considerations, the increase in *m* will result in the precipitation diminution. Analogously, the relationship for calculating the degree of precipitation of the metal ion in the form of slightly soluble hydroxide with the formation of the hydroxocomplexes Eq. (3) and stable complexes Eqs. (5 - 6), has been deduced

$$M(OH)_{n(S)} + nH^+ = M^{n+} + nH_2O, \qquad K_{Sh} = [M][H]^{-n},$$
$$\gamma = 1 - \frac{K_{Sh}\alpha_M [H]^n}{C_M^0} \qquad (22)$$

where α_M is described by the Eq. (10).

Previously (Povar and Spinu, 2014a), it was deduced the expression (23) for the Gibbs energy change of the summary process (2 - 8):

$$\Delta G_S^{sum} = -RT \ln K_S \alpha_M + RT \ln\left(C_M^0\right)[H]^{-n}. \qquad (23)$$

Using the Eqs. (21 - 22) and taking into account the relationship between C_M^0, C_M^r and γ it is easy to found the expression (24):

$$\Delta G_S^{tot} = -RT \ln \frac{C_M^r}{C_M^0} = -RT \ln(1-\gamma) \qquad (24)$$

For both Eqs. (21 - 23) or Eq. (24), the solid-phase is stable if $\Delta G_S^{tot} > 0$. Depending on the ΔG_S^{tot} value, precipitation conditions and the plenitude of the precipitate can be determined. The condition $\Delta G_S^{tot} = 0$ corresponds to the beginning of its dissolution and (or) sedimentation.

For metal ions, which form stable anionic soluble hydroxyl complexes, the function γ (pH) passes through the maximum as the precipitation degree decreases in the range of alkaline solutions.

3. Materials and methods

Industrial effluents

The chemically complex wastewater with pH 6.0 was obtained from electroplating units of the Tactical Missiles Corporation (Dubna, Russia). The composition of wastewater was determined using atomic absorption spectrometry (AAC-spectrometer, Russia). Measurements were done in triplicate and obtained values ± SD are given in Table 2.

Table 1. Equations for the degree of precipitation γ for different composition salts $M_mA_{n(S)}$, $nC_M^0 = mC_A^0$

m/n	***1***	***2***	***3***
1	$1-\left(K_S^{cond}\right)^{1/2}/C_M^0$	$1-\left(K_S^{cond}/4\right)^{1/3}/C_M^0$	$1-\left(K_S^{cond}/27\right)^{1/4}/C_M^0$
2	$1-\left(2K_S^{cond}\right)^{1/3}/C_M^0$	$1-\left(K_S^{cond}\right)^{1/4}/C_M^0$	$1-\left(8K_S^{cond}/27\right)^{1/5}/C_M^0$
3	$1-\left(3K_S^{cond}\right)^{1/4}/C_M^0$	$1-\left(9K_S^{cond}\right)^{1/5}/C_M^0$	$1-\left(K_S^{cond}\right)^{1/6}/C_M^0$

Table 2. Industrial effluent chemical composition at pH = 6 and MPC values

Metal	***Concentration in wastewater, mg/L***	***MPC for Russia, mg/L***	***MPC established by WHO, mg/L***
Al	0.2±0.006	0.2	0.2
Cr	0.1±0.0025	0.5 (Cr^{3+}) 0.05 (Cr^{6+})	0.05
Fe	3.0±0.075	0.3	0.2
Zn	0.2±0.006	1.0	3.0
Ba	0.1±0.005	0.7	0.7
Sr	0.5±0.015	7.0	-
SO_4^{2-}	10000±500	-	-
NH_4^+	3000±270	-	-

4. Results and discussions

Using atomic absorption spectrometry, six elements were determined in analysed wastewater. In Table 2, the chemical composition of the studied effluent along with values of maximum permissible concentration (MPC) for elements in effluent established in Russia (Anonymous, 2003) and by World Health Organization (Anonymous, 2011) are given. The concentrations of Al, Ba, Sr and Zn in the effluent are lower than MPC, while Cr and Fe concentrations exceed MPC values.

In order to determine the quantities of of soluble and insoluble firstly, the function ΔG_S^{tot} was computed. For this purpose, the Gibbs energy values for this complex process, where the reactions (2 - 8) proceed concomitantly, was calculated by the Eq. (21) for slightly soluble salts and Eq. (24) for slightly soluble hydroxides. Then the partial molar fractions (γ_i) of all the heavy metal species containing the metal ion were calculated taking into consideration the obvious relation:

$$\gamma + \gamma^{tot} = 1$$

where γ^{tot} is the sum of the partial molar fractions of all metal soluble species, calculated from the system of Eqs. (9 - 12), taking the restriction (13), by the well-known expressions (Butler and Cogley, 1998). The total (analytical) experimental concentrations of heavy metal, C_M^0, were taken from Table 2. All the equilibrium constants needed for calculation were taken from (Ball and Nordstrom, 2001).

4.1. Chemical species of iron in wastewater

The hydroxide of iron as ferrihydrite *Fe(OH)3(S)* is stable in the region of pH 4.4 – 12.0, $\Delta G_S^{tot} .> 0$. The degree of precipitation has been calculated by the Eq. (22). At the experimental pH = 6 all iron precipitates. The complexes $FeSO_4^+$ and $Fe(SO_4)_2^+$ diminishes the stability of the solid phase in the region of pH 4.4 – 5.2, while in alkaline media the anionic hydroxocomplex $Fe(OH)_4^-$ competes with ferrihydrite (Fig. 1). Other iron hydroxomplexes, including polynuclear complexes $Fe_2(OH)_2^{4+}$ and $Fe_3(OH)_4^{5+}$ have a insignificant influence on the stability of solid phase (Smith et al., 2004).

4.2. Chemical species of chromium in wastewater

At the pH 6.0 all chromium (III) is present in wastewater in form of soluble complex $CrSO_4^+$. The pH of the beginning of precipitation of $Cr(OH)_{3(S)}$ is 7.4, while when pH is > 7.8 the solid phase is a predominant species. The hydroxocomplexes of *Cr(III)* practically do not contribute under studied conditions on the weakening of the thermodynamic stability of the chromium (III) hydroxide (Fig. 2).

4.3. Chemical species of aluminium in wastewater

The slightly soluble hydroxide of aluminium (as Gibbsite) is found to be thermodynamically stable in the region of pH 6.0 (experimental value) – 8.4 (Fig. 3). At the experimental pH 6 the following aluminium-containing species exist (in terms of their partial molar fractions): $\gamma\left(Al(OH)_2^+\right) = 0.04$, $\gamma\left(AlSO_4^+\right) = 0.12$, $\gamma\left(Al(SO_4)_2^-\right) = 0.41$, e.g. $\gamma^{tot} = 0.57$ and $\gamma\left(Al(OH)_{3(S)}\right) = 0.43$. Then the contribution of soluble species decreases with increasing pH. In the alkaline media the solid phase dissolves due to formation of thermodynamically more stable anionic hydroxocomplex $Al(OH)_4^-$ (Povar and Spinu, 2014b). This result correlates with the finding of authors that aluminum precipitated best at pH 7.0 with aluminum recovery 97.2% (Wei et al., 2005).

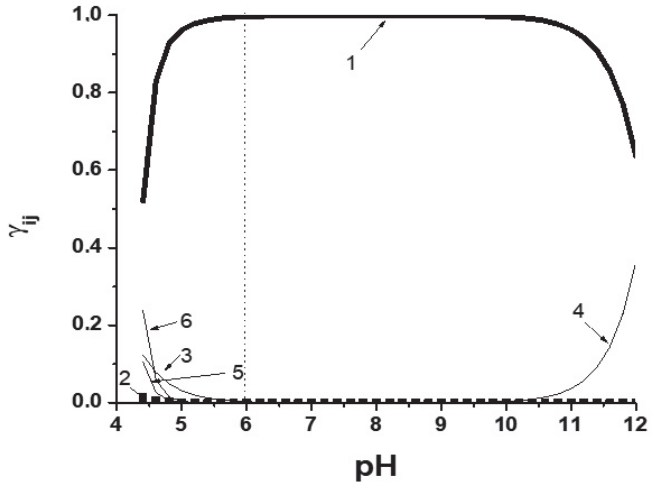

Fig. 1. Distribution curves of the soluble species and solid phase in the wastewater contaning 3 mg/L of iron and 10000 mg/L SO_4^{2-}: 1 – $Fe(OH)_{3(S)}$, 2 - $Fe(OH)^{2+}$, 3 - $Fe(OH)_2^+$, 4 - $Fe(OH)_4^-$, 5 - $FeSO_4^+$, 6 - $Fe(SO_4)_2^+$

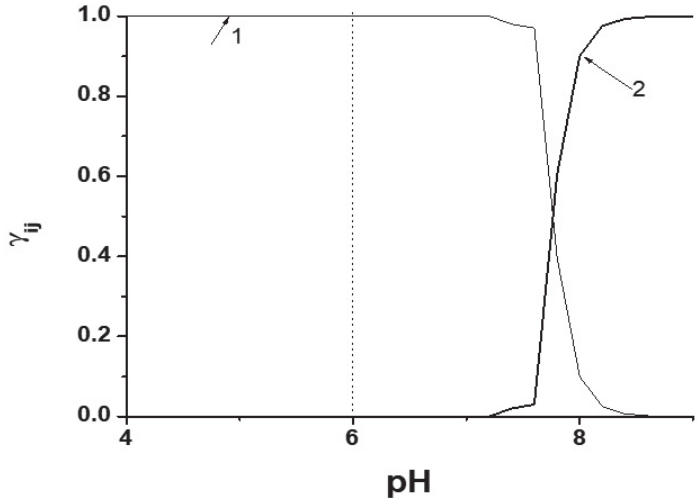

Fig. 2. Distribution curves of the soluble $CrSO_4^+$ chrome species (1) and insoluble chrome species $Cr(OH)_{3(S)}$ (2) in the wastewater contaning 0.1 mg/L of chrome and 10000 mg/L SO_4^{2-}

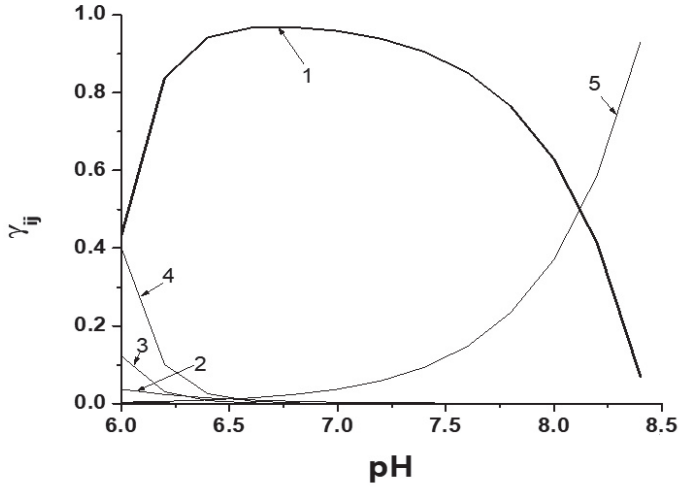

Fig. 3. Distribution curves of the soluble and insoluble aluminium species in the wastewater contaning 0.3 mg/L of chrome and 10000 mg/L SO_4^{2-}: 1 - $Al(OH)_{3(S)}$, 2 - $Al(OH)_2^+$, 3 - $AlSO_4^+$, 4 - $Al(SO_4)_2^+$, 5 - $Al(OH)_4^-$.

4.4. Chemical species of zinc in wastewater

Our thermodynamic analysis shows that for the wastewater of given composition within the pH range 2.0 – 9.0, under the excess of sulfate ions, the quantity ΔG_S^{tot}, calculated by Eq. (23), takes the negative values over all pH range. For this homogeneous solution, the partial molar fractions are computed by the usual equations used for the construction of distribution diagrams (Butler and Cogley, 1998). In this case, under conditions of only mononuclear complex species formation, the partial molar fraction values do not depend on the initial concentration of the components. Therefore, all the containing zinc species are soluble due to formation of stable complexes $ZnSO_4^0$ and $Zn(SO_4)_2^{2-}$, which prevent the formation of the precipitate of $Zn(OH)_{2(S)}$, $\gamma^{tot} = 1$ and $\gamma = 0$ (Fig. 4). At the experimental pH 6 there is a following distribution of soluble zinc-containing species (in terms of partial molar fraction): $\gamma(Zn^{2+})$=0.02, $\gamma(ZnSO_4)$ = 0.53 and $\gamma(Zn(SO_4)_2^{2-}$ = 0.45. Zinc ammonia complexes practically do no influence the chemical equilibria due the formation of NH_4^+ stable ion and therefore instable complex formation under the studied conditions.

4.5. Chemical species of barium and strontium in wastewater

Due to the large amounts of sulfate ions in wastewater, all the barium and strontium precipitated in the form of $BaSO_{4(S)}$ and $SrSO_{4(S)}$, respectively. The Gibbs energy of the process (2 - 6), calculated by the Eq. (21), gives constant positive value over all the pH range. The quantity γ has been calculated from the formula taken from the Table 1. For all the pH range, $\gamma = 1$ and $\gamma^{tot} = 0$.

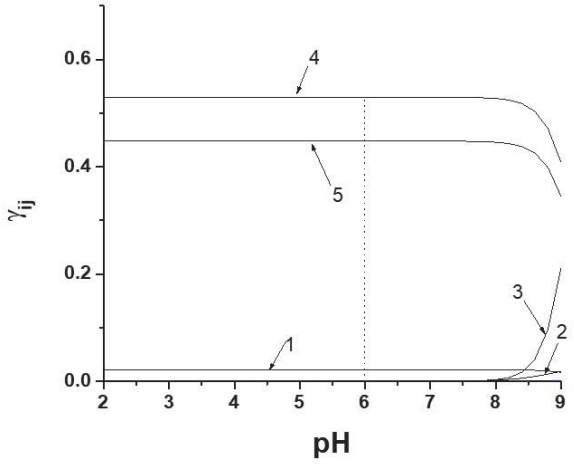

Fig. 4. Diagram of distribution of the soluble zinc species in the wastewater contaning 0.3 mg/L of chrome and 10000 mg/L SO_4^{2-}: 1 - Zn^{2+}, 2 - $ZnOH^{+}$, 3 - $Zn(OH)_2^0$, 4 - $ZnSO_4^0$, 5 - $Zn(SO_4)_2^{2-}$

5. Conclusions

The expressions of the dependence of the precipitation degree of the metal ion in the form of slightly soluble salts and hydroxides on the initial concentrations of the components and solution pH, including complexing agents have been deduced. The possibility of forming stable complexes between the metal ion and complexing agents in galvanic wastewater is taking into account. The thermodynamic meaning of the degree of precipitation for slightly soluble hydroxides and salts has been revealed.

The degree of precipitation and distribution of chemical species of metal ions (*Al, Cr, Fe, Zn, Sr* and *Ba*) in the complex industrial effluents of an engineering company (electroplating units of the Tactical Missiles Corporation, Dubna, Russia), under large amounts of sulfate ions, were analyzed. It has been shown that pH values, which ensure minimum solubility of metal hydroxides are very different from each other and are within the pH range from 5 to 11, which in principle does not allow optimizing the process of precipitation of hydroxides at simultaneous presence of various metals in solution. At pH 6.5-8.5, allowed for discharge of sewage into water bodies, only iron hydroxide can be precipitated to the maximum extent.

The efficiency of the method of precipitation depends on the chemical composition of wastewater that contains complexing agents, capable to bind the heavy metals in thermodynamically stable complexes. Additionally, it is necessary to take into account the co-precipitation and competitive processes. The iron hydroxide precipitated can act as sorbent and remove other heavy metals present in wastewater.

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