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Calculation of equilibria in the solution above the precipitate of a hydroxide of a metal capable forming hydroxycomplexes

ABSTRACT

The simple equations for the determination of pH range in which the precipitation with maximum amount of the sparingly soluble metal hydroxide and the minimum concentration of the metal in the solution occur were derived.

Keywords: metal hydroxide precipitate, metal hydroxycomplexes, equilibria, wastewater treatment.

1. INTRODUCTION

Precipitation of metals as hydroxides is widely used in hydrometallurgy [1], analytical chemistry [2] and especially in wastewater treatment [3,4] where many various practical modifications are proposed [5-8].

Many of heavy metal ions create not only insoluble hydroxides but soluble hydroxycomplexes too, and phase equilibria in the solution must be taken into account and they are intensively investigated [9]. An useful example present the paper of Jin et al. [10] where a method for calculation of ion distribution in reaction systems formed hydroxides was proposed, but it is relatively sophisticated.

In our previous paper [11] the equations for the determination of initial and final pHs of metal hydroxide precipitation as well as dissolution, due to the formation of hydroxycomplexes were derived.

It is a particular theoretical and practical interest to obtain an equation showing the dependence of the fraction of the metal ion forming a poorly soluble hydroxide and capable to dissolve through the formation of hydroxocomplexes, as well as an equation expressing the total metal ion concentration and its hydroxycomplexes over the sediment of metal hydroxide sludge, on the pH of the solution.

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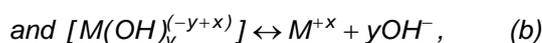
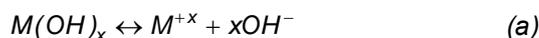
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2. THE PROBLEM STATEMENT

In the solution containing the ligand (OH⁻), capable of forming one complex with the metal ion $[M(OH)_y^{(-y+x)}]$ and the precipitate of metal hydroxide $(M(OH)_x)$ two equilibria are established:



which are described, according to [2], by the equations:

$$K_{sp} = [M^{+x}][OH^-]^x \quad (1), \text{ and}$$

$$K = \frac{[M^{+x}][OH^-]^y}{[M(OH)_y^{(-y+x)}]}, \quad (2)$$

where: K_{sp} - hydroxide solubility product, K - instability constant of a hydroxy-complex, x - valence of the metal, and y - the coordination number of the metal.

The metal ion concentrations $[M^{+x}]$ are equal to each other according to reactions (a) and (b). The solution of the equations (1) and (2) with respect to $[M(OH)_y^{(-y+x)}]$, leads to the following expression when the ionic product of water ($K_w = [H^+][OH^-]$) is taken into account.

$$[M(OH)_y^{(-y+x)}] = \frac{K_{sp}(K_w)^{y-x}}{[H^+]^{y-x}K}. \quad (3)$$

According to the material balance the sum of the amount of the metal in the precipitate, as a hydroxide (m/M), in the solution in the form of

hydroxide complexes $[M(OH)_y]^{y-x}$ and as the free ion $[M^{+x}]$ is equal to the initial amount of metal in solution:

$$c_M V = \frac{m}{M} + [M(OH)_y]^{y-x} V + [M^{+x}] V \quad (4)$$

where V represents the solution volume, m and M are the mass of sediment and molar mass of the metal hydroxide, respectively, and c_M is the initial metal ion concentration in the solution (mol/L).

Dividing both sides of the last equation by the initial amount of metal in solution ($c_M V$), and introducing concentration of hydroxycomplexes calculated from equation (3) as well as metal ion concentration calculated from equation (1) gives the following equation:

$$\alpha = 1 - \frac{K_{sp}(K_w)^{y-x}}{[H^+]^{y-x} K C_M} - \frac{K_{sp}[H^+]^x}{(K_w)^x c_M}, \quad (5)$$

which allows calculation of the relative fraction of metal ($\alpha = m/c_M V M$) present in the hydroxide precipitate.

It is quite simple to obtain the equation determining the total concentration of metal ions and its hydroxycomplex (c, mol/L) over the hydroxide precipitate from equation (5):

$$c = \frac{K_{sp}(K_w)^{y-x}}{[H^+]^{y-x} K} + \frac{K_{sp}[H^+]^x}{(K_w)^x} \quad (6)$$

Taking into account that $[H^+] = 10^{-pH}$ the last two equations can be rewritten as follows:

$$\alpha = 1 - \frac{K_{sp}(K_w)^{y-x}}{10^{-pH(y-x)} K C_M} - \frac{K_{sp} 10^{-pHx}}{(K_w)^x c_M} \quad (7)$$

$$c = \frac{K_{sp}(K_w)^{y-x}}{10^{-pH(y-x)} K} + \frac{K_{sp} 10^{-pHx}}{(K_w)^x} \quad (8)$$

Equations (7) and (8) describe, respectively, the dependence of the relative fraction of the metal hydroxide or total metal ion concentration over the deposit (free ions and hydroxycomplexes) on the pH of solution, that previously [11, 12] was described by two equations. These equations are valid only under the condition that $m/M \leq c_M V$.

As follows from equation (7), the relative fraction of the metal ion, present in a hydroxide precipitate is dependent on the type of metal ion, the initial concentration and the pH of the solution, which was noted in [13].

The first term of equation (8) allows to calculate the concentration of the metal ion, and the second term the concentration of its hydroxycomplex depending on the pH of the solution.

3. EXAMPLE 1: A SOLUTION CONTAINING ALUMINUM IONS

For the solution containing aluminum ion, which forms one complex compound $[Al(OH)_4]^-$ only the relative fraction of aluminum hydroxide containing in the precipitate will be given by the following equation

$$\alpha = 1 - \frac{K_{sp}}{c_M 10^{3pH} (K_w)^3} - \frac{K_{sp} K_w 10^{pH}}{K C_M} \quad (9)$$

From this expression it follows that the relative fraction of aluminum hydroxide at a constant pH increases as the initial concentration of the aluminum salt in solution increases, and depends strongly on pH.

The validity of this equation is confirmed by the fact that the calculated values of pH at the start of aluminum hydroxide precipitation and at the complete dissolution of the precipitate practically coincide with the values determined experimentally. Thus, when the initial aluminum salt concentration was 0.01 mol/L the pH of start of precipitation onset and complete dissolution of the aluminum hydroxide respectively determined experimentally are equal to 4.0 and 10.8 [13], and the last equation gives the values of 3.52 and 10.78.

Figure 1 shows the dependence of the relative fraction of aluminum hydroxide on the pH of the solution at the concentration of aluminum sulfate $3 \cdot 10^{-4}$ mol/L (100 mg/L).

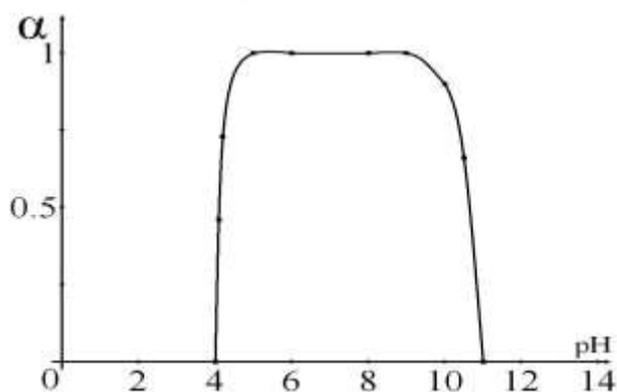


Figure 1 - The relative fraction of the aluminum hydroxide (α) depending on the pH of the solution.

The figure shows that almost all aluminum in the solution is present in the form of a poorly soluble hydroxide in the pH range from 5 to 10, what practically coincides with the pH values recommended in [14-16]. The optimum pH value for each water source is usually established experimentally, but these calculations reduce the time of necessary measurements.

The data of solubility product of the aluminum hydroxide and instability constant of its hydroxyl-

complexes were taken from [13], and, the pH value at which 10% of initial amount of metal ions was precipitated [12] was defined as the beginning of precipitation.

The differences in the data of solubility product given in the literature may cause the differences in the results. For example, the use of the value of K_{sp} equal to $3.2 \cdot 10^{-32}$ [17], leads to the pH of precipitate beginning equal to 4.27.

4. EXAMPLE 2: A SOLUTION CONTAINING ZINC AND CHROMIUM IONS

Considering that zinc and chromium ions form hydroxides $Zn(OH)_2$ and $Cr(OH)_3$, as well as the hydroxycomplexes $[Zn(OH)_4^{2-}]$ and $[Cr(OH)_4^{-3}]$ respectively, the last two equations for solutions containing these metals, can be written as follows:

$$\alpha_{Zn} = 1 - \frac{K_{sp,Zn} (K_w)^2 10^{2pH}}{K_{Zn} c_{Zn}} - \frac{K_{sp,Zn}}{10^{2pH} (K_w)^2 c_{Zn}} \quad (10)$$

$$\alpha_{Cr} = 1 - \frac{K_{sp,Cr} (K_w) 10^{pH}}{K_{Cr} c_{Cr}} - \frac{K_{sp,Cr}}{10^{3pH} (K_w)^3 c_{Cr}} \quad (11)$$

$$c_1 = \frac{K_{sp,Zn} (K_w)^2 10^{2pH}}{K_{Zn}} + \frac{K_{sp,Zn}}{10^{2pH} (K_w)^2} \quad (12)$$

$$c_2 = \frac{K_{sp,Cr} (K_w) 10^{pH}}{K_{Cr}} + \frac{K_{sp,Cr}}{10^{3pH} (K_w)^3} \quad (13)$$

where: c_1 is the total concentration of zinc ions and its hydroxycomplex above the precipitate of zinc hydroxide, c_2 the total concentration of chromium ion and hydroxycomplexes above the precipitate chromium hydroxide, K_{Cr} and K_{Zn} , $K_{sp,Cr}$ and $K_{sp,Zn}$ – the instability constants of hydroxycomplexes of chromium and zinc, and the solubility products of chromium and zinc hydroxide, respectively, which values were taken from [13, 17].

For practical purposes, it is the most important to know the pH value at which the total metal ion concentration present in the form of an ion and a soluble hydroxycomplex reaches the maximum allowable concentration in the wastewater (MAC mg/L), i.e. $[M(OH)_y^{-(y+x)}] = [MAC] / Ax1000$ (where A – atomic mass of metal). In this case, the last two equations take the form

$$\frac{[MAC_{Zn}]}{65,4 \cdot 1000} = \frac{K_{sp,Zn} (K_w)^2 10^{2pH}}{K_{Zn}} + \frac{K_{sp,Zn}}{10^{2pH} (K_w)^2} \quad (14)$$

$$\frac{[MAC_{Cr}]}{52 \cdot 1000} = \frac{K_{sp,Cr} (K_w) 10^{pH}}{K_{Cr}} + \frac{K_{sp,Cr}}{10^{3pH} (K_w)^3} \quad (15)$$

The solution of these equations for zinc is a range of pH values from 9.15 to 10.3 (the MAC value for zinc is 0.01 mg/L), i.e., the precipitation of zinc hydroxide down to the value of MAC occurs in a very narrow pH range.

Precipitation of the chromium down to the MAC value (MAC for chromium (III) is 0.03 mg/L) occurs in a wider range of pH, and namely 6-9.5. As it is shown by calculations performed according to the equations (10) and (11), in these pH range most complete precipitation of the hydroxides of these metals occurs. The calculated pH intervals coincide almost exactly with the values given in the literature [3, 13, 19-20].

When the above mentioned two ions are simultaneously present in the solution, the range of pH, wherein their concentration does not exceed the assigned limits of MAC's becomes more narrow, and is equal to 9.15-9.5.

It should be emphasized that the simultaneous presence of aluminum ions and other metal ions in the solution can lead to the co-precipitation with aluminum hydroxide [14-16], thereby reducing their concentration in water.

5. CONCLUSIONS

Equation (7) allows calculation of the pH range in which the maximum formation of sludge of metal hydroxides occurs, i.e. prevent the ingress of metal ions on urban wastewater treatment plants.

The equation (8) allows determination of the pH range in which the ion concentrations of metals forming the hydroxycomplexes in the industrial wastewater would be under the value of maximum allowable concentration.

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IZVOD

ODREĐIVANJE RAVNOTEŽE U RASTVORU IZNAD TALOGA METAL HIDROKSIDA PRI FORMIRANJU KOMPLEKSA HIDROKSIDA

U ovom radu prikazane su jednostavne jednačine za određivanje oblasti pH u kojima će se formirati maksimalna količina taloga metal hidroksida pri minimalnoj koncentraciji metalnih jona u rastvoru.

Ključne reči: talog metal hidroksida, metalni hidro kompleksi, ravnoteža, tretman otpadnih voda.

Naučni rad

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