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**PRECIPITATION OF METALS BY METALS (CEMENTATION) EQUILIBRIA IN ABSCENCE OR IN PRESENCE OF COMPLEXES IN THE SOLUTION****WYTRĄCANIE METALI METALAMI (CEMENTACJA) RÓWNOWAGI W ROZTWORACH SOLI PROSTYCH LUB KOMPLEKSOWYCH**

Cementation equilibria, in presence of the complexing ligands of the  $L^-$  or  $L^0$  type, have been discussed. Equations expressing dependence of the equilibrium concentration  $c_A^*$  on the process parameters are presented. They indicate that in the cyanide or ammonia complexes solutions, dependently on the reacting metal pair,  $c_A^*$  may rise, decline or remain unchanged — when the concentration of the complexing compound increases.

Equilibria concentrations  $c_A^*$  are several ranges of value higher than those  $c_A^{**}$ , reached in absence of complexes. Solely in the case of the  $Ag^+/Cu$  system a reverse dependence may be expected.

Omówiono równowagi cementacyjne w roztworach soli kompleksowych (ligandy typu  $L^-$  lub  $L^0$ ). Wprowadzono równanie wyrażające zależność równowagi stężenia  $c_A^*$  od parametrów procesu. Równanie to wskazuje że  $c_A^*$ , ze wzrostem stężenia czynnika kompleksującego, może rosnać, zmniejszać się lub pozostać bez zmiany. Zależy to od reagujących metali oraz rodzaju czynnika kompleksotwórczego (cjanki, amoniak).

Stężenia równowagowe  $c_A^*$ , odpowiadające cementacji z roztworów kompleksów cjanowych lub amoniakalnych, są szereg rzędów wielkości większe od równowagowych stężeń  $c_A^{**}$  odpowiadających wytrąceniu z roztworów nie zawierających kompleksów. Jedyne w przypadku układu  $Ag^+/Cu$  wyprowadzone równania wskazują na istnienie odwrotnej zależności.

## LIST OF SYMBOLS

$A$  and  $B$  — respectively the more noble metal, being precipitated and the less noble precipitating,  
—  $a$  and  $b$  number of their mols in the stoichiometric equations,

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- $a_{A,B}$  activities of the metal ions,
- $m$  and  $n$  valencies of the metal ions,
- $\varepsilon_{A,B}^{\circ}$  standard potentials,
- $c$  — analytically determined concentrations,
- $c_A^{\circ}$  — initial concentration of the being precipitated metal,
- $c_A^{*}$  — equilibrium concentration attained for processes in the complex salts solutions,
- $c_A^{**}$  — equilibrium concentration for processes taking place in absence of the complexing ligands,
- $c_L$  — concentration of the complexing ligand,
- $r$  and  $s$  — numbers of ligands in the complexes,
- $K_{A,B}$  — stability constants of the complexes,
- $\alpha$  and  $\beta$  — valencies of the complex ions,
- $||$  — concentration of ions.

### 1. Cementation equilibria in absence of complexes

Equation (1) presents the stoichiometry of such a process



where  $am = bn$ . Equilibrium is attained when, as a result of that reaction, concentration of the more noble metal ions  $A^{m+}$  declines and that of the less noble  $B^{n+}$  rises to such an extent that the equilibrium potentials of both metals become equal.

$$\varepsilon_A^{\circ} + \frac{2.3 RT}{mF} \lg a_{A^{m+}} = \varepsilon_B^{\circ} + \frac{2.3 RT}{nF} \lg a_{B^{n+}}. \quad (2)$$

Equation (2) enables one to calculate the ratio of the activities of metal ions which correspond to the cementations equilibrium. Influence of the hydrogen ions concentration, on the cementation equilibria, and influence of different factors on the kinetics of the process, have been discussed in another text [1].

When discussing hydrometallurgical processes, performed in absence of complexes in the solution, a simplifying assumption is usually made that activities of ions are equal to their concentrations. Eq. (2) may be then transformed, for processes performed at 298°K, to the eq. (3 a)

$$\frac{(a_{A^{m+}})^n}{(a_{B^{n+}})^m} = \frac{c_A^{**n}}{c_B^{**m}} = 10^{\frac{mn(\varepsilon_B^{\circ} - \varepsilon_A^{\circ})}{0.059}} = E^{mn}, \quad (3 a)$$

where  $c_{A,B}^{**}$  represent analytical concentrations of the metal ions corresponding to the cementation equilibrium. It follows from the stoichiometry of the process that

$$c_B^{**} = \frac{b}{a}(c_A^{\circ} - c_A^{**}).$$

Subsequently eq. (3 a) may be transformed in (3 b).

$$\frac{c_A^{**n}}{\left| \frac{b}{a}(c_A^o - c_A^{**}) \right|^m} = E^{mn}. \quad (3b)$$

In the typical industrial cementations processes ( $\text{Cu}^{2+}/\text{Fe}$ ,  $\text{Zn}$  or  $\text{Al}$ ;  $\text{Au}^+$  or  $\text{Ag}^+/\text{Zn}$ ,  $\text{Cu}$ ) equilibria concentrations of the precipitated metals are usually several ranges of value less than their initial ones ( $c_A^{**} \ll c_A^o$ ). Often  $c_A^{**}$  is even below the limits of the classical analytical methods. In such cases, assuming that  $c_A^o - c_A^{**} \cong c_A^o$  a simplified version (3c) may be applied.

$$c_A^{**} = \left( \frac{b}{c} c_A^o \right)^{m/n} E^m. \quad (3c)$$

## 2. Cementation equilibria in presence of the complexes in the solution

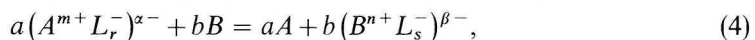
Equation (2) expresses equilibrium condition both in absence and in the presence of complexes. Also the simplifying assumption, that the ratio of the reacting metals ions activities is equal to that of their concentrations, does not influence markedly the results of the calculations.

However, in contrast to the plain salts solutions, concentration of ions differs significantly from the analytical concentration of the metal. The latter is equal to the sum of the metal present in the form of a complex (main part) and of the metal ions released in the process of its dissociation.

Eq. (3a), which presents cementation equilibrium condition, includes concentrations of the ions of the metals participating in the process. These concentrations are difficult to determine experimentally in the complex salts solutions. Therefore an attempt has been made to transform the eq. (3a) in such a way as to express the cementation equilibria condition, in the complex salts solutions, applying the analytically determined concentrations and stability constants of the reacting metal complexes. It is obvious that in such system, equilibrium will also depend on the concentration of additionally introduced complex forming compounds (for instance cyanides, ammonia etc.).

### 2.1. Cementation equilibria in presence of the complex forming ligands of the type $L^-$

When the complexing ligand is of the type  $L^-$  (for instance  $\text{CN}^-$ ,  $\text{Cl}^-$ ) then the stoichiometry of the cementation process presents eq. (4).



where:  $a\alpha = b\beta$ ;  $\alpha = r - m$ ;  $\beta = s - n$ ;  $am = bn$ .

When no extra addition of the complex forming ligands is added to the solution, for instance in form of the Na or K salts, then  $ar = bs$ .

Stability constants of the complexes, participating in the reaction, may be presented in form of the eqs. (5 a, b). Symbols  $c_{A,B}$  express there the analytically determined concentrations.

$$K_A = \frac{|A^{m+}L_r^-|^{\alpha-}}{|A^{m+}||L^-|^r} = \frac{c_A - |A^{m+}|}{|A^{m+}||L^-|^r} \quad (5 a)$$

$$K_B = \frac{|B^{n+}L_s^-|^{\beta-}}{|B^{n+}||L^-|^s} = \frac{c_B - |B^{n+}|}{|B^{n+}||L^-|^s}. \quad (5 b)$$

It follows from the eq. (4) that  $c_B = \frac{b}{a}(c_A^o - c_A)$ . When introduced in eq. (5 b) it leads to (5 c).

$$K_B = \frac{b(c_A^o - c_A) - a|B^{n+}|}{a|B^{n+}||L^-|^s}. \quad (5 c)$$

Eqs. (5 a) and (5 c) can be subsequently transformed to (6 a) and (6 b), which express concentrations of the  $A^{m+}$  and  $B^{n+}$  ions, in the system in which cementation equilibrium has been reached ( $c_A = c_A^*$ ).

$$|A^{m+}| = \frac{c_A^*}{K_A |L^-|^{r+1}} \quad (6 a)$$

$$|B^{n+}| = \frac{b}{a} \frac{c_A^o - c_A^*}{K_B |L^-|^{s+1}}. \quad (6 b)$$

Assuming that activities of the metal ions are equal to their concentrations, and taking into consideration equilibrium condition expressed by the eq. (2), one gets eq. (7). In absence of complexes (i.e. for  $|L^-| = 0$ ) eq. (7) transforms in (3 c).

$$\frac{|A^{m+}|^n}{|B^{n+}|^m} = \left( \frac{c_A^*}{K_A |L^-|^{r+1}} \right)^n \left( \frac{a K_B |L^-|^{s+1}}{b (c_A^o - c_A^*)} \right)^m = E^{mn} \quad (7)$$

In the following text eq. (7) is applied to discuss cementation equilibria in the cyanide complexes solutions. In the industrial processes, like cementation of gold by copper or zinc, solutions with a significant stoichiometric excess of the, well dissociating, cyanides (NaCN, KCN) are applied. Concentration of the ligand  $|L^-|$  is then practically equal to the concentration of these salts  $c_L$ .

The Table 1 presents dependencies, established on the basis of the eq. (7), for different pairs of the cemented metal  $A$  and the less noble  $B$ . These dependencies were applied to calculate the runs of the curves in the Figs. 1 and 2. — Calculations were performed for the systems with a high stoichiometric excess of the cyanide to the cemented metal ( $c_A^o = 0.005$  to  $0.04$ ;  $c_L = 0.5$  to  $2.0$  mol/l). Therefore complexes with the highest number of ligands were considered.

TABLE 1

Cementation equilibria in the cyanide complexes solutions, in presence of the stoichiometric excess of the cyanide (Na, K);  $c_L$  concentration of the cyanide; T 298°K;  $E = 10^{\frac{e_B^0 - e_A^0}{0.059}}$ . Stability constants of the cyanide complexes:  $K_{Au} 2.0 \times 10^{38}$ ;  $K_{Ag} 5.01 \times 10^{20}$ ;  $K_{Cu} 2.0 \times 10^{30}$ ;  $K_{Zn} 5.25 \times 10^{16}$  [2]

No.	$a(A^{m+}L_r^-)^{2-} + bB = aA + b(B^{n+}L_s^-)^{\beta-}$	$\left(\frac{c_A^*}{K_A c_L^r + 1}\right)^n \left(\frac{a K_B c_L^s + 1}{b c_A^0 - c_A^*}\right)^m = E^{mn}$ (1)	$(c_A^{**})^n \left[\frac{a}{b(c_A^0 - c_A^{**})}\right]^m = E^{mn}$ (2)
1	$(Au^+L_2^-)^- + Ag + 2L^- = Au + (Ag^+L_4^-)^{3-}$	$\frac{c_A^*}{c_A^0 - c_A^*} \left(\frac{K_B c_L^4 + 1}{K_A c_L^2 + 1}\right) = E = 5.36 \times 10^{-16}$	$\frac{c_A^{**}}{c_A^0 - c_A^{**}} = E$
2	$(Au^+L_2^-)^- + Cu + 2L^- = Au + (Cu^+L_4^-)^{3-}$	$\frac{c_A^*}{c_A^0 - c_A^*} \left(\frac{K_B c_L^4 + 1}{K_A c_L^2 + 1}\right) = E = 1.00 \times 10^{-20}$	
3	$(Ag^+L_4^-)^{3-} + Cu = Ag + (Cu^+L_4^-)^{3-}$	$\frac{c_A^*}{c_A^0 - c_A^*} \left(\frac{K_B c_L^4 + 1}{K_A c_L^4 + 1}\right) = E = 1.87 \times 10^{-5}$	
4	$2(Au^+L_2^-)^- + Zn = 2Au + (Zn^{2+}L_4^-)^{2-}$	$\frac{c_A^*}{\sqrt{c_A^0 - c_A^*}} \frac{\sqrt{2(K_B c_L^4 + 1)}}{(K_A c_L^2 + 1)} = E = 1.80 \times 10^{-42}$	
5	$2(Ag^+L_4^-)^{3-} + Zn = 2Ag + (Zn^{2+}L_4^-)^{2-} + 4L^-$	$\frac{c_A^*}{\sqrt{c_A^0 - c_A^*}} \frac{\sqrt{2(K_B c_L^4 + 1)}}{(K_A c_L^4 + 1)} = E = 3.55 \times 10^{-27}$	
6	$2(Cu^+L_4^-)^{3-} + Zn = 2Cu + (Zn^{2+}L_4^-)^{2-} + 4L^-$	$\frac{c_A^*}{\sqrt{c_A^0 - c_A^*}} \frac{\sqrt{2(K_B c_L^4 + 1)}}{(K_A c_L^4 + 1)} = E = 1.80 \times 10^{-22}$	

(1)  $c_A^*$  equilibrium concentration of the cemented metal "A" when concentration of the cyanide is equal  $c_L$ ; presented equations follow from the eq. (7).  
 (2) when concentration of the cyanide ligand  $c_L = 0$  then  $c_A^* = c_A^{**}$ . For the discussed range of concentrations  $c_A^0$  (0.005 to 0.04 mol/l) the equilibrium concentrations  $c_A^{**}$  are respectively equal:  $Au^+/Ag$  (0.3 to 2.1)  $\times 10^{-17}$ ;  $Au^+/Cu$  (0.5 to 4.0)  $\times 10^{-22}$ ;  $Ag^+/Cu$  (0.9 to 7.5)  $\times 10^{-7}$ ;  $Au^+/Zn$  (0.9 to 2.5)  $\times 10^{-43}$ ;  $Ag^+/Zn$  (1.7 to 4.7)  $\times 10^{-28}$ ;  $Cu^+/Zn$  (0.9 to 2.5)  $\times 10^{-23}$

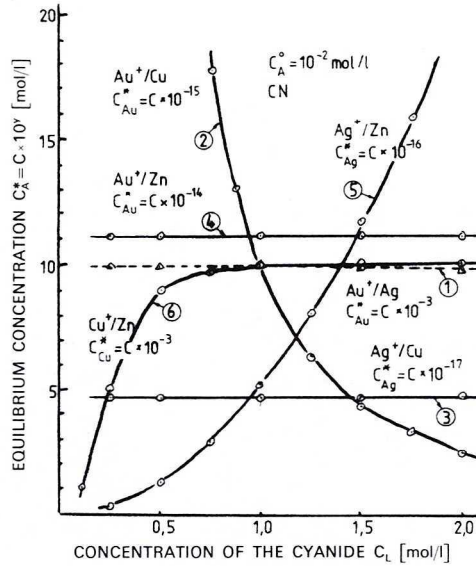


Fig. 1. Cementation from the cyanide complexes solutions. Dependence of the equilibrium concentration  $c_A^*$  on the concentration of the cyanide  $c_L$ . Numbers of curves correspond to those in the Table 1. The ratios  $c_A^*/c_A^{**}$ , calculated on the basis of the equations and data presented in the Table 1 (for  $c_A^0 = 10^{-2}$  mol/l and  $c_L = 0.5$  to  $2.0$  mol/l) are respectively equal:  $\text{Au}^+/\text{Ag}$   $2 \times 10^{15}$ ;  $\text{Au}^+/\text{Cu}$   $(4.0 \text{ to } 0.3) \times 10^7$ ;  $\text{Ag}^+/\text{Cu}$   $2.5 \times 10^{-10}$ ;  $\text{Au}^+/\text{Zn}$   $8.0 \times 10^{28}$ ;  $\text{Ag}^+/\text{Zn}$   $(0.6 \text{ to } 9.0) \times 10^{12}$ ;  $\text{Cu}^+/\text{Zn}$   $(0.7 \text{ to } 8.0) \times 10^{19}$ .

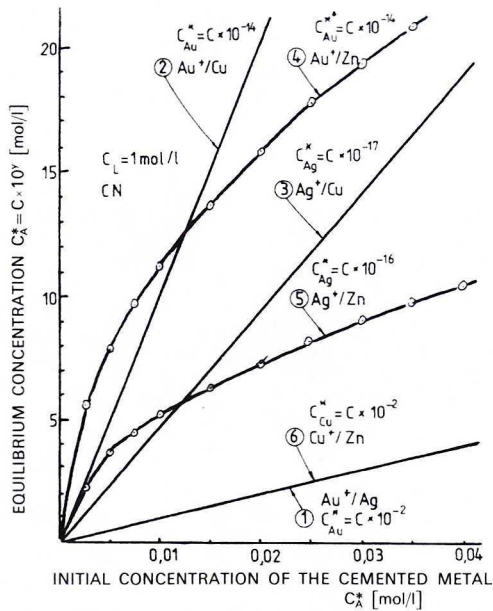


Fig. 2. Cementation from the cyanide complexes solutions. Dependence of the equilibrium concentration  $c_A^*$  of the precipitated metal, on its initial concentration  $c_A^0$ . Numbers of curves correspond to those in the Table 1.

The data in the Table 1, and the representing them curves in the diagrams, indicate that cyanide concentration may influence cementation process in different ways. It depends on the reacting metals, their standard potentials and also on the number of ligands and stability constants of the complexes.

In the case of  $\text{Cu}^+/\text{Zn}$  system equilibrium concentration rises (see Fig. 1) with the increase of that of the cyanide. In solutions containing more than one mol of cyanide per litre,  $c_{\text{Cu}}^*$  attains  $c_{\text{Cu}}^o$  value, i.e. cementation does not occur. — With the increase of the cyanide content in the solution equilibrium concentration of Au, cemented by Cu, declines and that of Ag cemented by Zn rises. — Cyanide concentration has not any influence on the cementation equilibria in the  $\text{Au}^+/\text{Zn}$  and  $\text{Ag}^+/\text{Cu}$  systems. — Silver practically does not precipitate gold from the discussed complexes solutions. Solely at high cyanide concentrations a slight decrease of the gold equilibrium concentration  $c_{\text{Au}}^*$ , from its initial value  $c_{\text{Au}}^o$ , can be seen.

The diagram 2 shows that with the increase of the initial concentration  $c_A^o$  equilibria concentrations  $c_A^*$  rise linearly ( $\text{Au}^+/\text{Cu}$ ;  $\text{Ag}^+/\text{Cu}$ ) or parabolically ( $\text{Au}^+/\text{Zn}$ ;  $\text{Ag}^+/\text{Zn}$ ). It has been already mentioned that, in the discussed solutions, Ag does precipitate Au. Neither Zn precipitates Cu when  $c_L > 1$  mol/l.

The values of the ratios  $c_A^*/c_A^{**}$ , calculated for different metal pairs (caption of the Fig. 1), indicate that cementation equilibria concentrations attained in presence of cyanides are usually ranges of value higher than in the processes performed in absence of complexes. However a reverse dependence has been also observed. In the case of the  $\text{Ag}^+/\text{Cu}$  system  $c_{\text{Ag}}^*/c_{\text{Ag}}^{**} < 1$ .

## 2.2. Cementation equilibria in presence of the complex forming ligands of the type $L^o$

Stoichiometry of the cementation is expressed by the eq. (8), symmetrical to the eq. (4).

$$a(AL_r)^{m+} + bB = aA + b(BL_s)^{n+}, \quad (8)$$

where, when no additional complex forming compound is present in the solution,  $ar = bs$ .

Discussion, parallel to that presented in the case of the cyanide solutions, leads to the eq. (9), symmetrical to the eq. (7).

$$\frac{|A^{m+}|^n}{|B^{n+}|^m} = \left( \frac{c_A^*}{K_A |L|^r + 1} \right)^n \left( \frac{a K_B |L|^s + 1}{b (c_A^o - c_A^*)} \right)^m = E^{mn}. \quad (9)$$

An example of the  $L^o$  type ligand is ammonia. In solutions where ammonia is present in a large excess to the complex forming metal ions,  $|L|$  is practically equal to the concentration of the added ammonia  $c_L$ .

TABLE 2

Cementation equilibria in the ammonia complexes solutions, in presence of the stoichiometric excess of the ammonia.  $c_L$  concentration of ammonia; T 298°K;  $E = 10^{\frac{\epsilon_B^0 - \epsilon_A^0}{0.059}}$ . Stability constants of the ammonia complexes:  $K_{Au} 1.00 \times 10^{27}$ ;  $K_{Ag} 2.50 \times 10^7$ ;  $K_{Cu^+} 6.30 \times 10^{10}$ ;  $K_{Cu^{2+}} 3.89 \times 10^{12}$ ;  $K_{Zn} 1.15 \times 10^9$  [2]

No.	$a(A^{m+}L_r)^{m+} + bB = aA + b(B^{n+}L_s)^{n+}$	$\left(\frac{c_A^*}{K_A c_L^r + 1}\right)^n \left(\frac{a K_B c_L^s + 1}{b c_A^o - c_A^*}\right)^m = E^{mn}$ (1)	$(c_A^{**})^n \left[\frac{a}{b(c_A^o - c_A^{**})}\right] = E^{mn}$ (2)
1	$(Au^+L_2)^+ + Ag = Au + (Ag^+L_2)^+$	$= 5.36 \times 10^{-16}$	
2	$(Au^+L_2)^+ + Cu = Au + (Cu^+L_2)^+$	$\frac{c_A^*}{c_A^o - c_A^*} \left(\frac{K_B c_L^2 + 1}{K_A c_L^2 + 1}\right) = E = 1.00 \times 10^{-20}$	$\frac{c_A^{**}}{c_A^o - c_A^{**}} = E$
3	$(Ag^+L_2)^+ + Cu = Ag + (Cu^+L_2)^+$	$= 1.87 \times 10^{-5}$	
4	$2(Au^+L_2)^+ + Cu = 2Au + (Cu^{2+}L_4)^{2+}$ (3)	$= 7.91 \times 10^{-24}$	
5	$2(Ag^+L_2)^+ + Cu = 2Ag + (Cu^{2+}L_4)^{2+}$ (3)	$= 1.48 \times 10^{-8}$	
6	$2(Au^+L_2)^+ + Zn = 2Au + (Zn^{2+}L_4)^{2+}$	$\frac{c_A^*}{\sqrt{c_A^o - c_A^*}} \sqrt{\frac{2(K_B c_L^4 + 1)}{K_A c_L^2 + 1}} = E = 1.80 \times 10^{-42}$	$c_A^{**} \sqrt{\frac{2}{c_A^o - c_A^{**}}} = E$
7	$2(Ag^+L_2)^+ + Zn = 2Ag + (Zn^{2+}L_4)^{2+}$	$= 3.35 \times 10^{-27}$	
8	$2(Cu^+L_2)^+ + Zn = 2Cu + (Zn^{2+}L_4)^{2+}$	$= 1.80 \times 10^{-22}$	
9	$(Cu^{2+}L_4)^{2+} + Zn = Cu + (Zn^{2+}L_4)^{2+}$ (3)	$\sqrt{\frac{c_A^*}{c_A^o - c_A^*} \left(\frac{K_B c_L^4 + 1}{K_A c_L^4 + 1}\right)} = E = 2.27 \times 10^{-19}$	$\sqrt{\frac{c_A^{**}}{c_A^o - c_A^{**}}} = E$

(1)  $c_A^*$  equilibrium concentration of the cemented metal "A" when concentration of ammonia is equal  $c_L$ .

(2) when concentration of the ammonia ligand  $c_L = 0$  then  $c_A^* = c_A^{**}$ . For the discussed range of concentrations  $c_A^o$  (0.005 to 0.4 mol/l) the equilibrium concentrations  $c_A^{**}$  are presented in the Table 1.

(3) cementation in the aerated solutions.



The Table 2 presents dependencies, established on the basis of the eq. (9), for different reacting metal pairs  $A$  and  $B$ . It follows from the presented there equations that cementation equilibria, in the discussed ammonia complexes solutions, do not depend, in contrast to those in the cyanide solutions, on the concentration of the complexing agent. It follows also from the data presented in the Table 2 that the equilibrium concentration  $c_A^*$  rises with the increase of  $c_A^o$ . It can be seen in the Fig. 3 that the shape of curves depends on the valencies of the metals ions participating in the reactions.

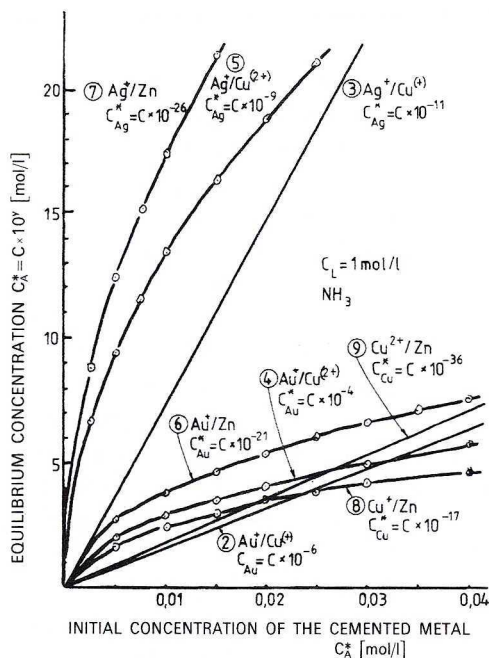


Fig. 3. Cementation from the ammonia complexes solutions. Dependence of the equilibrium concentration  $c_A^*$ , of the precipitated metal, on its initial concentration  $c_A^o$ . Numbers of curves correspond to those in the Table 2. The ratios  $c_A^*/c_A^{**}$ , calculated on the basis of the equations and data presented in the Table 2 (for  $c_A^o = 0.01$  to  $0.04$  mol/l) are respectively equal:  $\text{Au}^+/\text{Ag}$   $1.9 \times 10^{15}$ ;  $\text{Au}^+/\text{Cu}(+)$   $1.6 \times 10^{16}$ ;  $\text{Ag}^+/\text{Cu}(+)$   $3.9 \times 10^{-4}$ ;  $\text{Au}^+/\text{Cu}(2+)$   $(5.0 \text{ to } 5.2) \times 10^{20}$ ;  $\text{Ag}^+/\text{Cu}(2+)$   $(13.3 \text{ to } 12.5) \times 10^9$ ;  $\text{Au}^+/\text{Zn}$   $(2.9 \text{ to } 1.8) \times 10^{22}$ ;  $\text{Ag}^+/\text{Zn}$   $(7.3 \text{ to } 7.4) \times 10^2$ ;  $\text{Cu}^+/\text{Zn}$   $1.8 \times 10^6$ ;  $\text{Cu}^{2+}/\text{Zn}$   $3.3 \times 10^3$ .

The values of the ratio  $c_A^*/c_A^{**}$  (caption of the Fig. 3) depend neither on the concentration of ammonia nor on the initial concentration  $c_A^o$  (in the cyanide solutions that ratio does not depend on  $c_A^o$  but depends on the concentration of the complexing cyanide). The values of these ratios indicate also that equilibria concentrations in the ammonia solutions are usually several ranges of value higher than those in absence of ammonia. However, like in the cyanide solutions, a reverse dependence exists in the case of the  $\text{Ag}^+/\text{Cu}$  system.

### 3. Summary and conclusions

a. Cementation equilibria, in absence or in presence of the complex forming ligands (of the  $L^-$  or  $L^o$  type), have been discussed. An equation has been presented expressing dependence of the equilibrium concentration  $c_A^*$ , in the complex solutions, on the equilibria determining factors, i.e. — on the initial concentration  $c_A^o$ , standard potentials  $\varepsilon_{A,B}^o$  of the reacting metals, on  $c_L$  concentration of the complex forming compounds and on the stability constants of  $K_{A,B}$  of the complexes participating in the process.

b. Equilibria concentrations have been calculated for, performed in the cyanide solutions, cementation processes of the metal pairs:  $Au^+/Ag$ ,  $Cu$  or  $Zn$ ;  $Ag^+/Cu$  or  $Zn$ ;  $Cu^+/Zn$ . — It has been found that, with the increase of the cyanide concentration,  $c_A^*$  may rise, decline or remain unchanged (depending on the valencies of the metal ions, on the number of ligands and on the stability constants of the complexes).

The calculated equilibria concentrations  $c_A^*$  in the cyanide complexes solutions, are several ranges of value higher than those  $c_A^{**}$  in absence of cyanide. Solely in the system  $Ag^*/Cu$  a reverse dependence has been found.

c. In the case of cementation from ammonia complexes solutions ( $Au^+/Ag$ ,  $Cu$  or  $Zn$ ;  $Ag^+/Cu$  or  $Zn$ ;  $Cu^+/Zn$ ;  $Cu^{2+}/Zn$ ) equilibrium concentration  $c_A^*$  depends, like in the cyanide solutions, on  $c_A^o$ . However, in contrast to the cyanide solutions, it does not depend on the concentration of the complex forming ammonia.

In ammonia complexes solutions, like in the cyanide ones, equilibrium concentrations  $c_A^*$  are several ranges of value higher than those  $c_A^{**}$  in absence of the complex forming ligands. Again a reverse dependence has been found in the case of the  $Ag^+/Cu(+)$  system. When silver is cemented by copper from the aerated solution ( $Ag^+/Cu(2+)$ ) then, like in the case of other discussed metal pairs  $c_A^* \gg c_A^{**}$ .

d. A particular case of the cementation in the system with two complexing compounds, one forming complexes with the being precipitated metal  $A$  and another with the precipitating metal  $B$ , has been discussed by the author in another paper [3].

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