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## PRECIPITATION OF METAL BY METAL (CEMENTATION) FROM COMPLEX SALT SOLUTION

### WYTRĄCANIE METALU METALEM (CEMENTACJA) Z ROZTWORU SOLI KOMPLEKSOWYCH

Generally accepted eq. (2), describing kinetics of the cementation, does not take into consideration that the system reaches the state of equilibrium when concentration  $c_e > 0$ . This fact is expressed by the suggested eq. (3). When cementation is performed in the simple salt solution, then  $c_e$ , calculated from the condition of potentials equality, is negligible in comparison with the concentrations being determined experimentally ( $c_e \ll c$ ). For such a cases eq. (3) converts practically in (2).

The situation changes when cementation takes places in the complex salt solution. Analytically determined equilibrium concentrations  $e_e$  of the precipitated metal, is then much greater than concentration of its ions, which decides this equilibrium state. In such a case the eq. (3) should describe cementation kinetics better than the classic eq. (2).

Experimental results presented by Guerra and Dreisinger [4], who investigated precipitation of gold by copper from the thiosulphate-ammonia solutions, have been applied to verify that hypothesis. These data have been subsequently introduced into eqs (2), (3) as well as into an empirical eq. (4) suggested by these authors. Each time the correlation coefficient has been calculated. Its highest value was stated for eq. (3).

The equilibrium concentration  $c_{eAu}$  has been also calculated from the condition of equality of the Au and Cu potentials at the state of equilibrium. The stability constants values of complexes of these metals have also been used in these calculations.

The  $c_{eAu}$  values obtained in these two ways are close to each other. It speaks for the equilibrium hypothesis, represented by the eq. (3), and against the Guerra's and Dreisinger's hypothesis of "passivation" of copper by the precipitated gold.

Powszechnie stosowane równanie (2), opisujące kinetykę cementacji, nie uwzględnia ustalania się równowagi po osiągnięciu stężenia  $c_e > 0$ . Zaproponowano równanie (3) uwzględniające ten fakt. W przypadku cementacji prowadzonej z roztworów soli prostych  $c_e$ , wyliczane z warunku istnienia w stanie równowagi równości potencjałów metali wytrącającego i wytrącanego, są zaniedbywalnie małe w stosunku do stężeń oznaczanych

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w trakcie doświadczeń ( $c_e \ll c$ ). Równanie (3) przekształca się wówczas praktycznie w równanie (2).

Odmierna jest sytuacja w przypadku cementacji z roztworów soli kompleksowych. Analitycznie oznaczane równowagowe stężenie wytrącanego metalu  $c_e$  jest wówczas znacznie większe od, decydującego o tej równowadze, stężenia jego jonów. W takim przypadku równanie (3) powinno lepiej opisywać kinetykę cementacji niż klasyczne równanie (2). Celem weryfikacji tego przypuszczenia posłużono się, opublikowanymi przez *Guerrę i Dreisingera* [4], wynikami wytrącania złota miedzią z roztworów tiosiarczanowo-amoniakalnych. Wprowadzając te dane do równań (2) i (3), jak również do podanego przez *G i D* równania empirycznego (4), liczone każdorazowo współczynniki korelacji. Najwyższą wartość uzyskano w przypadku równania (3). Opierając się na tym równaniu, oraz na danych doświadczalnych, wyliczono  $c_{eAu}$ .

Niezależnie wyliczono wartość  $c_{eAu}$  z warunku równości potencjałów Au i Cu w stanie równowagi, wykorzystując w tych obliczeniach również stałe trwałości kompleksów tych metali.

Dobra zgodność wartości  $c_{eAu}$  wyliczanych tymi dwoma drogami przemawia za prawdziwością, reprezentowanej przez równanie (3) hipotezy przerwania cementacji w wyniku osiągnięcia równowagi, jak również przeciw, sugerowanej przez *G i D*, hipotezie „pasywacji” miedzi przez wytrącone złoto.

#### LIST OF SYMBOLS

- $c$  — analytically determined concentration,  
 $c_0$  — initial concentration,  
 $c_e$  — equilibrium concentration of the precipitated (cemented) metal,  
 $||$  — potential determining concentrations of ions and also concentrations of the dissociation products of complexes,  
 $\delta$  — diffusion layer thickness,  
 $D$  — diffusion coefficient,  
 $k$  — rate constant of the chemical reaction,  
 $k^*$  — constants of the empirical equations,  
 $K$  — stability constants of the complexes,  
 $M_A$  — more noble metal precipitated (cemented) by the less noble  $M_B$ ,  
 $S$  — reaction surface area (usually assumed as equal to the surface area of the precipitating metal  $M_B$ ),  
 $t$  — time,  
 $V$  — volume of the solution.

### 1. Kinetics of the process

The stoichiometry of the process is described by the equation (1).

$$a M_A^{m+} + b M_B = a M_a + b M_B^{n+}; \quad n = \frac{a}{b} m. \quad (1)$$

Assumption that the rate of the process is proportional to the concentration of the precipitated metal ions leads to the generally accepted eq. (2) [1, 2, 3].

$$\ln \frac{c}{c_0} = - \frac{S}{V} k^* t. \quad (2)$$

Consecutive stages of the process are: transfer of the  $M_A^{n+}$  ions to the reaction surface (i.e. to the  $M_B$  metal surface), reaction itself and finally transport of the  $M_B^{n+}$  ions into the bulk of the solution.

When the reaction is of the first order equation (2) describes kinetics of the process regardless of the rate determining stage the only difference is that  $k^*$  has then different meanings. For the diffusion control  $k^* = \frac{D}{\delta}$ , while for activation control  $k^* = k$  and in the case of a mixed control (i.e., when the rate of the  $M_A^{n+}$  ions transfer and the rate of the reaction are of the same order of magnitude)  $k^* = \frac{kD}{k\delta + D}$ .

Equation (2) seems to indicate that with the progress of time concentration aims asymptotically at zero. It is obvious that in reality an equilibrium state will be reached. Therefore equation (3) has been suggested, which takes into consideration the existence of the equilibrium concentration  $c_e > 0$ .

$$\frac{dc}{dt} = -\frac{S}{V}k^*(c - c_e) \quad (3a)$$

$$\ln \frac{c - c_e}{c_0 - c_e} = -\frac{S}{V}k^*t. \quad (3b)$$

In the typical industrial processes, for instance in the case of cementation of copper by iron from sulphate solutions,  $c_e$  is several ranges of order smaller than  $c$  ( $c \gg c_e$ ). Consequently eq. (3) converts into well known eq. (2).

The situation differs when the cemented metal is precipitated from the solution of its complex salt. Equilibrium concentration  $c_e$  of the metal, present in the solution mainly in the form of a complex, is then much greater than concentration of its ions which decides on equilibrium. In such case eq. (3) should express the dependence  $c = f(t)$  better than eq. (2). To verify this hypothesis experimental results published by Guerra and Dreisinger [4] have been applied.

When investigating cementation of gold by copper, from the thiosulphate-ammonia complexes solutions, these authors have established empirical equation (4).

$$\ln \frac{c}{c_0} = -k_1^*t + k_2^*t^2. \quad (4)$$

The second component on the right side of this eq. indicates on existence of a factor which inhibits the process. Guerra and Dreisinger assumed that it is a result of „passivation” i.e. the screening of the precipitating metal (Cu) surface by the cementation product (Au).

The form of the suggested equation as well as its interpretation rise some doubts. Analysis of the eq. (4) leads to the obviously erroneous conclusion that the concentration of the cemented metal, which initially decreases, reaches a minimum at

$t = \frac{k_1}{2k_2^*}$  and then rises again.



In the process of cementation both metals contact with each other and with the electrolyte, forming a short circuited cell. Consequently they have practically the same potential determined usually by the less noble participant ( $M_B$ ). As a result, reduction of  $M_A^{m+}$  ions may equally well proceed either on the surface of the metal  $M_B$  or on the surface of the already deposited  $M_A$ . Therefore, the cementation product rarely diminishes the rate of the process. On the contrary sometimes, when the cemented metal deposits in the dendritic or spongy form, the reaction surface area increases and consequently the reaction runs faster [5].

Cementation process may come to the end, at higher than equilibrium concentrations, in two cases: a) when  $M_A$ , deposited on the  $M_B$  surface, hinder transport of  $M_B^{n+}$  ions into bulk of the electrolyte, to such extent that the rate of their removal (by diffusion) becomes smaller than the rate of their formation. In effect concentration of these ions rises in the vicinity of the reaction surface and finally a passivating salt layer precipitates there; b) when the layer of the precipitated metal is as compact that it entirely isolates  $M_B$  from the solution.

Experimental data, gathered in the Table, were used to judge which of the presented equations describes better the kinetics of the cementation of Au by Cu from the thiosulphate-ammonia complexes solution. The results of these calculations are presented in the diagram 1. Comparison of the correlation coefficients, and of the shapes of curves leads to the conclusion that eq. (3 b)\* describes the kinetics of the discussed process better than eqs (2) or (4).

TABLE

Cementation of gold, from thiosulphate-ammonia solution, by copper powder\*

Initial concentration of Au 13.33 ppm (i.e. $6.8 \times 10^{-5}$ mol/l). NH <sub>3</sub> 0.73 mol/l, S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> and SO <sub>3</sub> <sup>2-</sup> 0.1 mol/l each, Cu 1 g/l (i.e. 0.016 mol/l). Copper powder (100 to 200 mesh) 5 g/3.75 l of electrolyte; t° 50°C.									
t [min]	0	5	10	15	20	30	45	60	90
$-\ln \frac{c}{c_0}$	0	0.246	0.448	0.629	0.798	1.080	1.538	1.888	2.530
c [ppm]	13.33	10.42	8.52	7.11	6.00	4.53	2.86	2.02	1.06

\* the  $-\ln \frac{c}{c_0}$  values have been read out from the diagram 4 in the paper by Guerra and Dreisinger [4]. According to these authors each point in that diagram presents an average value of 5 experiments.

\* the equilibrium concentration  $c_e$  used to verify the eq. (3 b) has been determined by substituting different assumed values of  $c_e$  into that equation. Each time the correlation coefficients have been calculated, using the Table data. The diagram 2, which shows results of these calculations, proves existence of a distinct maximum of the correl. coeff. for  $c_{eAu} = 0.65$  ppm.

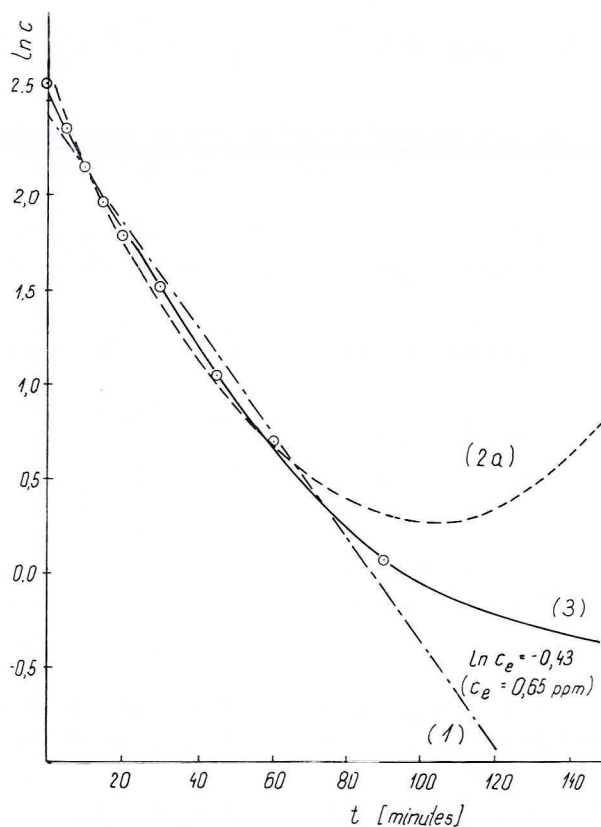


Fig. 1. Cementation of gold, from thiosulphate-ammonia solution, by copper powder. Coefficients of the eqs (2), (3 b) and (4 a) have been calculated, using the least square method, applying experimental results presented in the Table

$$\ln \frac{c}{c_0} = -(0.160 \pm 0.036) - (0.0278 \pm 0.0009) t; \text{ correl. } 0.9925 \quad (2)$$

$$\ln \frac{c-c_e}{c_0-c_e} = -(0.0712 \pm 0.0127) - (0.0370 \pm 0.0003) t; \text{ correl. } 0.9992 \quad (3 \text{ b})$$

$$\left( \ln \frac{c}{c_0} \right) / t = -(0.046 \pm 0.001) + (2.275 \pm 0.310) \times 10^{-4} t; \text{ correl. } 0.9367 \quad (4 \text{ a})$$

$$t_{\min} = 101 \pm 1 \text{ [min]}; c_{\min} = 1.43 \pm 0.23 \text{ ppm}$$

$$\ln \frac{c}{c_0} = -(0.043 \pm 0.003) t + (1.832 \pm 0.266) \times 10^{-4} t^2; \text{ correl. ?} \quad (4 \text{ b})$$

$$t_{\min} = 117 \pm 7 \text{ [min]}; c_{\min} = 1.07 \pm 0.10 \text{ ppm}$$

Equation (4 b) includes mean values of the coefficients  $k_1^*$  and  $k_2^*$  of five experiments [4]

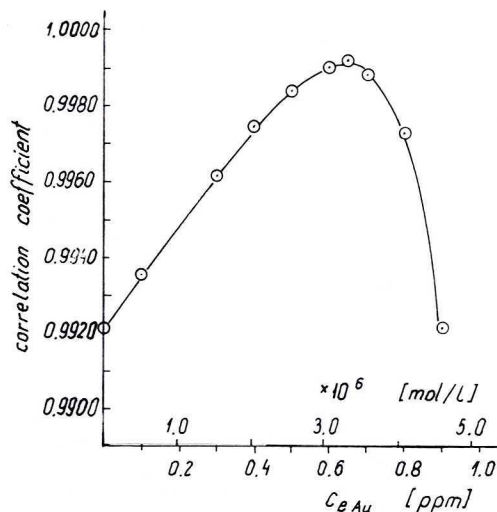


Fig. 2. Dependence of the correlation coefficient of the eq. (3 b) on the assumed value of the equilibrium concentration  $c_e$ . Experimental data presented in the Table have been used in these calculations

## 2. Equilibrium concentration $c_{eAu}$ of gold, in the discussed cementation process, calculated from the standard potentials and stability constants of Au and Cu complexes

Cementation comes to the end when equilibrium potentials of both metals, participating in the process, became equal to each other.

$$\varepsilon_{Au^+/Au}^0 + \frac{RT}{F} \ln |Au^+| = \varepsilon_{Cu^+/Cu}^0 + \frac{RT}{F} \ln |Cu^+| \quad (5a)$$

$$|Au^+| = |Cu^+| \exp \left| \frac{F}{RT} (\varepsilon_{Cu^+/Cu}^0 + \varepsilon_{Au^+/Au}^0) \right|$$

$$\varepsilon_{Au^+/Au}^0 = 1.68 \text{ V}; \quad \varepsilon_{Cu^+/Cu}^0 = 0.52 \text{ V}; \quad T = 298^\circ \text{K}$$

$$|Au^+| = 2.18 \times 10^{-20} \times |Cu^+|. \quad (5b)$$

In the discussed solutions gold and copper were present mainly in a form of complexes:  $Au(S_2O_3)_2^{3-}$  and  $Cu(NH_3)_2^+$ . — Concentrations of the undissociated complex ions are respectively equal:

$|Au(S_2O_3)_2^{3-}| = c_{Au} - |Au^+|$  and similarly  $|Cu(NH_3)_2^+| = c_{Cu} - |Cu^+|$ . As a result the stability constants [6, 7] may be presented in form of eqs (6) and (7).

$$K_{\text{Au/S}_2\text{O}_3^-} = \frac{|\text{Au}(\text{S}_2\text{O}_3)_2^{3-}|}{|\text{Au}^+||\text{S}_2\text{O}_3^{2-}|^2} = \frac{c_{\text{Au}} - |\text{Au}^+|}{|\text{Au}^+||\text{S}_2\text{O}_3^{2-}|^2} = 5 \times 10^{28} \quad (6)$$

$$K_{\text{Cu/NH}_3} = \frac{|\text{Cu}(\text{NH}_3)_2^+|}{|\text{Cu}^+||\text{NH}_3|^2} = \frac{c_{\text{Cu}} - |\text{Cu}^+|}{|\text{Cu}^+||\text{NH}_3|^2} = 7.24 \times 10^{10}. \quad (7)$$

When the cementation equilibrium is reached, in these complexes solution, then  $c_{\text{Au}} = c_{e\text{Au}}$ . Therefore substitution of the concentrations  $|\text{Au}^+|$  and  $|\text{Cu}^+|$ , from (6) and (7) into eq. (5b) leads to the eq. (8).

$$\begin{aligned} c_{e\text{Au}} &= 2.18 \times 10^{-20} \times \frac{1 + K_{\text{Au}^+/\text{S}_2\text{O}_3^-}}{1 + K_{\text{Cu}^+/\text{NH}_3}} \times \left( \frac{|\text{S}_2\text{O}_3^{2-}|}{|\text{NH}_3|} \right)^2 \times c_{\text{Cu}} = \\ &= 1.50 \times 10^{-2} \times \left( \frac{|\text{S}_2\text{O}_3^{2-}|}{|\text{NH}_3|} \right)^2 \times c_{\text{Cu}} \quad \text{mol/l.} \quad (8) \end{aligned}$$

In the discussed Guerra and Dreisinger experiments:  $c_{\text{Cu}} = 1$  g/l i.e. 0.016 mol/l (would all Au be precipitated Cu concentration would change less than 0.5%); concentrations of thiosulphate and ammonia were respectively equal 0.1 and 0.73 mol/l.

A simplifying assumption has been made that  $|\text{S}_2\text{O}_3|$  and  $|\text{NH}_3|$  are equal to their analytical concentrations. Substitution of all these data into eq. (8) gives:  $c_{e\text{Au}} = 4.4 \times 10^{-6}$  mol/l (i.e. 0.88 ppm).

Guerra and Dreisinger experiments were performed at 50°C. The values of the standard potentials and of the stability constants of the complexes refer to 25°C. All these data are burdened with some unevitable experimental errors. These facts lead to the conclusion that the equilibrium concentrations:

$c_{e\text{Au}} = 0.65$  ppm ( $3.3 \times 10^{-6}$  g/l) calculated from the eq. (3b), using presented in the Table experimental results of *G* and *D*, and as well  $c_{e\text{Au}} = 0.88$  ppm ( $4.5 \times 10^{-6}$  g/l) calculated from the standard potentials and the stability constants of complexes, — agree satisfactorily with each other. It speaks for the “equilibrium” and against the “passivation” hypothesis as a cause of the deflection of the  $\ln c = f(t)$  dependence from linearity observed in the discussed cementation process.

Increase of the  $c_{e\text{Au}}$  means rise of the Au losses (i.e. decrease of the % of Au recovered from the solution). — Eq. (8) has been used to draw the diagram 3. It indicates that  $c_{e\text{Au}}$  diminishes with the increase of ammonia concentration and with the decrease of the concentrations of copper and thiosulphate. If the influence of solution components on  $c_{e\text{Au}}$  is simply additive then — as follows from the eq. (8) — 50% increase of  $c_{\text{NH}_3}$  ad simultaneous 50% decrease of the  $c_{\text{Cu}}$  and  $c_{\text{S}_2\text{O}_3}$ , would diminish the  $c_{e\text{Au}}$  to 0.03 ppm.

Unfortunately neither of the presented equations, describing kinetics of the cementation, makes it possible to calculate the time required to reach the state of equilibrium.

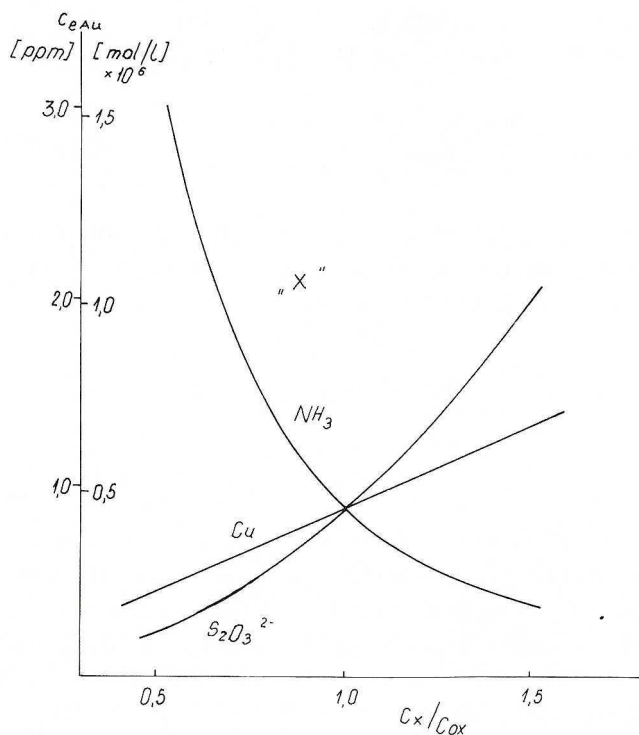


Fig. 3. The graphical presentation of the eq. (8):  $c_{\text{Cu}} = 0.016 \text{ mol/l}$ ,  $c_{\text{S}_2\text{O}_3} = 0.1 \text{ mol/l}$ ,  $c_{\text{NH}_3} = 0.73 \text{ mol/l}$ . Each line represents the dependence of the  $c_{\text{eAu}}$  on the concentration of one component, while the two other ones remain constant

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## THE EFFECT OF THE GASEOUS PHASE COMPOSITION ON THE REDUCTION RATE OF CADMIUM OXIDE

### WPLYW SKŁADU FAZY GAZOWEJ NA SZYBKOŚĆ REDUKCJI TLENKU KADMU

The aim of the study was to determine the possibility of a selective reduction process of the oxide compounds of cadmium in the presence of zinc compounds. The performed investigation of reduction in the mixture of gases ( $\text{CO} + \text{CO}_2$ ), of various composition and at different temperatures allowed to determine the conditions in which cadmium or cadmium oxide with a small content of zinc can be obtained.

Celem prezentowanej pracy było określenie możliwości selektywnego przeprowadzenia procesu redukcji tlenkowych związków kadmu w obecności związków cynku. Przeprowadzone badania redukcji w mieszaninie gazów ( $\text{CO} + \text{CO}_2$ ), o różnym składzie oraz w różnych temperaturach, pozwoliły określić warunki, które umożliwią otrzymanie kadmu lub tlenku kadmu o małej zawartości cynku.

### 1. Introduction

Cadmium is the typical dispersed metal, which does not form isolated deposits, but accompanies the zinc ores. The mean ratio of zinc to cadmium in zinc concentrates varies within the limit 200—300. The metallurgy of cadmium is thus based mainly on the processing of various kinds of waste material and intermediate products of the zinc industry, in which cadmium compounds concentrate.

In obtaining cadmium two basic methods are used: the hydrometallurgical and the combined process. The hydrometallurgical method consists in obtaining a solution of cadmium sulfate, from which cadmium is obtained by way of electrolysis. In the combined method the so-called cadmium sponge is obtained through cementa-

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tion from a sulfate solution, which is next subjected to distillation in a reduction atmosphere.

In the hydrometallurgical process of zinc preparation the cadmium, present in the roasted ore and in the dust obtained in the course of roasting in the fluid state, passes to the solution during their leaching in a solution of sulfuric acid. Cadmium is precipitated from this solution by means of zinc in the form of the so-called cadmium sponge.

When the pyrometallurgical method of zinc preparation is applied, considerable amounts of cadmium pass to the dust during roasting on D-L machines. To recover cadmium from the dust, it is subjected to leaching, and next cadmium sponge or zinc-cadmium carbonate, containing 10—15% of Zn and about 40—45% of Cd, are precipitated from the solution. Preliminary information on the processing of this material directly into metallic cadmium can be found in the studies [1—2]. Cadmium sponge can be also melted into metallic cadmium under a layer of salt, however this process causes great loss of the material, and the obtained cadmium is contaminated with a marked content of zinc.

The aim of the present work is the determination of the effect of the composition of the gaseous phase ( $\text{CO} + \text{CO}_2$ ) and the temperature on the reduction rate of cadmium oxide and on the zinc content in the products in the case of the reduction of the mixtures of cadmium and zinc oxides.

## 2. Determination of the conditions of a selective process of CdO reduction

Cadmium, as well as zinc, belong to those metals which, after reduction of their oxides, are obtained in the gaseous phase. As the system in which these reactions take place, at constant pressure and temperature, has 1 degree of freedom, the equilibrium compositions of the gaseous phase are illustrated by respective curves in the system  $\text{Cd}-\text{CO}-\text{CO}_2$  and  $\text{Zn}-\text{CO}-\text{CO}_2$ . The composition of the gaseous phase in the equilibrium state thus depends on the starting composition. According to the opinion of Ptak and Sukiennik [3—4], the reactions, for which the sum of the stoichiometric coefficients occurring in the gaseous components of the reaction differs from zero, are characterized by the so-called characteristic point, and the compositions of the gaseous phase change as the reduction proceeds along the straight lines linking the starting state with the characteristic point. The composition of the gaseous phase in the state of equilibrium is defined by the point of intersection of the given straight line with the equilibrium curve of the respective reaction. Using the data [3—5], there have been calculated the equilibrium compositions of the gaseous phase for the reduction reactions of CdO and ZnO by means of CO, beginning with various starting compositions of the gaseous phase. In the calculations consideration has been given also to the course of the reduction reaction by means of carbon with simultaneous course of Boudouard's reaction. The

equilibrium composition of the gaseous phase, as depending on the starting composition, has been calculated using the parametric equations [6]:

$$x_{\text{CO}} = [\lambda(x_{\text{CO}}^{\circ} + 1) - 1]$$

$$x_{\text{CO}_2} = [\lambda(x_{\text{CO}_2}^{\circ} - 1) + 1]$$

$$x_{\text{Cd}} = [\lambda(x_{\text{Cd}}^{\circ} - 1) + 1],$$

where:

$x_{\text{CO}}, x_{\text{CO}_2}, x_{\text{Cd}}$  — equilibrium composition of the gaseous phase,  
 $x_{\text{CO}}^{\circ}, x_{\text{CO}_2}^{\circ}, x_{\text{Cd}}^{\circ}$  — starting composition of the gaseous phase,  
 $\lambda$  — parameter of the equation.

Making use of the dependence:

$$K = \frac{x_{\text{CO}_2} \cdot x_{\text{Cd}}}{x_{\text{CO}}} = \frac{[\lambda(x_{\text{CO}_2}^{\circ} - 1) + 1][\lambda(x_{\text{Cd}}^{\circ} - 1) + 1]}{[\lambda(x_{\text{CO}}^{\circ} + 1) - 1]},$$

the parameter  $\lambda$  was determined for the given composition of the starting phase, and next the equilibrium composition of the gaseous phase was calculated. The calculation results are listed in Table 1.

These results show that the composition of the gaseous phase in the state of equilibrium depends on the composition of the starting phase. With increasing CO concentration in the starting gaseous phase, there will increase the CO<sub>2</sub> and the cadmium concentration in the system. For a given starting composition of the gaseous phase the temperature has a minimal effect on the change of the equilibrium composition of the gaseous phase.

For the reduction reaction of zinc oxide  $\text{ZnO} + \text{CO} = \text{Zn}_1 + \text{CO}_2$  at temperatures below 1180 K, the equilibrium compositions of the gaseous phase are as follows:

$$T = 1048 \text{ K} \quad x_{\text{CO}} = 0.9966 \quad x_{\text{CO}_2} = 0.0034$$

$$T = 1073 \text{ K} \quad x_{\text{CO}} = 0.9958 \quad x_{\text{CO}_2} = 0.0042$$

These values show the possibility of the reduction of zinc oxide by means of CO. In the case of co-reduction with cadmium oxide, the composition of the gaseous phase will be shifted towards higher contents of CO<sub>2</sub> which will oxidize the probably reduced zinc passing to the gaseous phase as the pressure of zinc vapours above liquid zinc at the temperature 1048 K equals 170,88 mm Hg. If we assume that after ZnO reduction zinc appears in the gaseous phase, then the equilibrium composition of the gaseous phase at the temperature 1100 K will be:

$$x_{\text{CO}} = 0.868 \quad x_{\text{CO}_2} = 0.066 \quad x_{\text{Zn}} = 0.066$$



TABLE 1

Equilibrium composition of the gaseous phase for the reduction  $\text{CdO} + \text{CO} = \text{Cd}_g + \text{CO}_2$  depending on the starting composition of the gaseous phase (in molar fraction)

Temp. [K]	Starting phase composition		Equilibrium composition of the gaseous phase		
	$x_{\text{CO}}^{\circ}$	$x_{\text{CO}_2}^{\circ}$	$x_{\text{CO}}$	$x_{\text{CO}_2}$	$x_{\text{Cd}}$
1048	1/3	2/3	0.000270	0.74993	0.249800
	1/2	1/2	0.000350	0.66655	0.333100
	2/3	1/3	0.000375	0.59985	0.399775
	1	0	0.000400	0.49980	0.499800
1073	1/3	2/3	0.0002000	0.749950	0.249850
	1/2	1/2	0.0002750	0.666575	0.333150
	2/3	1/3	0.0002917	0.599883	0.399825
	1	0	0.0003000	0.499850	0.499850

The performed investigations show that it is highly probable to select such temperature of the process and the composition of the gaseous phase that they will secure the selective course of the reduction process of cadmium oxide from a material containing zinc oxide.

### 3. Experimental results and their discussion

Investigations of the reduction were carried out on pure cadmium oxide and on material containing 49.95% of Cd and 16.8% of Zn, obtained after roasting zinc-cadmium carbonate at the temperature 1073 K. The experiments were performed in an electric pipe furnace through which a gaseous phase with a definite content of CO and CO<sub>2</sub> was passed. The aim of the experiments conducted on pure cadmium oxide was the determination of the effect of temperature and CO concentration in the gaseous phase on the reduction rate of CdO. On the other hand, the experiments conducted on material containing zinc and cadmium oxides were expected to provide the answer to the question how the CO<sub>2</sub> concentration in the gaseous phase and temperature of the process affect the zinc content in the gaseous products of the reduction. The degree of cadmium oxide reduction, calculated on the basis of recorder losses of mass during the process, is shown in Fig. 1. Similar dependences were obtained for other temperatures.

For a mathematical description of the occurring process of reduction there has been adapted the equation in the form [7—8]:

$$\sqrt[3]{(1 - \alpha)^2} = A - k \cdot t,$$



where:

- $\alpha$  — degree of reduction,
- $t$  — time of the process [min],
- $k$  — constant proportional of the reaction rate [ $\text{min}^{-1}$ ],
- $A$  — starting co-ordinate, which for  $t = 0$  should be equal to 1.

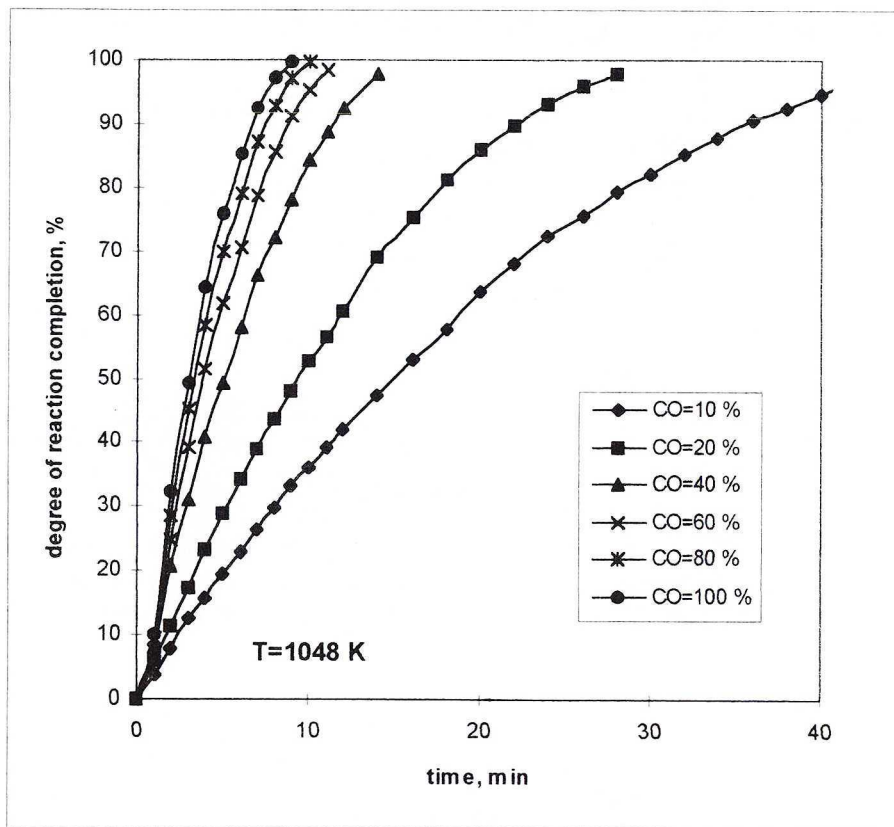


Fig. 1. Degree of CdO reduction depending on the duration of the process at the temperature 1048 K for various CO contents in the gaseous phase

The parameters of the kinetic reactions, calculated on the basis of experimental data, are listed in Table 2, while Fig. 2 illustrated the course of the calculated equations at the temperature 1073 K against the background of experimental points. In the final phase of the process the reduction rate becomes distinctly diminished in relation to the course resulting from the calculated equation. This follows from the gradual transformation of the cylindrical shape of the starting sample into a spherical shape, which means reduced surface of reaction for the same mass of a sample obtained as a result of incomplete reaction.

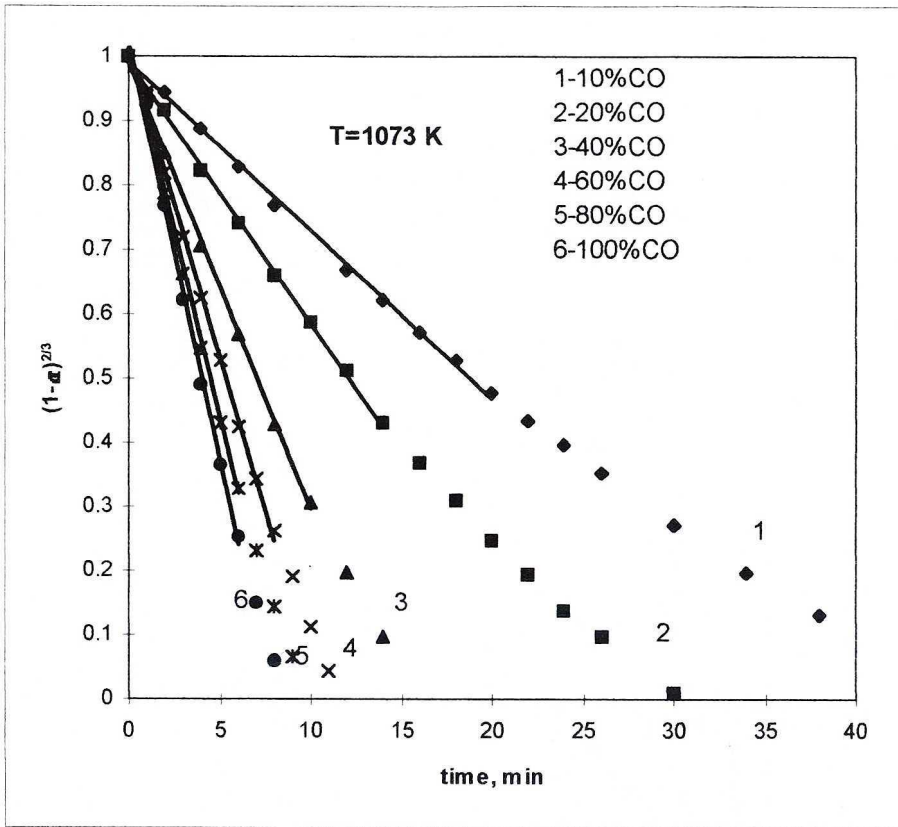


Fig. 2. The course of the calculated kinetic equations against the background of experimental points for the temperature 1073 K, at various CO content in the gaseous phase

TABLE 2

Calculated values of the kinetic equation

Temp. [K]	CO in the gaseous phase, [%]	A	k
1048	10	0.9877	0.0236
	20	0.9930	0.0380
	40	0.9994	0.0717
	60	1.0109	0.0941
	80	1.0192	0.1127
	100	1.0210	0.1255
1073	10	0.9902	0.0261
	20	0.9914	0.0404
	40	0.9911	0.0696
	60	1.0112	0.0955
	80	1.0211	0.1166
	100	1.0212	0.1300

When analyzing the changes in the value of the regression coefficient we find that the temperature of the reduction process affect in a minimal degree the rate of the process, whereas the CO content in the gaseous phase has a significant effect on it. If we assume that the rate of the reduction process at constant temperature is proportional to the distance from the equilibrium state by:

$$\Delta x_{\text{CO}} = x_{\text{CO}}^{\circ} - x_{\text{CO}}$$

where:

$x_{\text{CO}}^{\circ}$  — concentration of carbon oxide in the starting gaseous phase [%],  
 $x_{\text{CO}}$  — concentration of carbon oxide in the gaseous phase in the state of equilibrium [%],

and assuming, on the basis of the performed calculations, that  $x_{\text{CO}} = 0$  then the reaction rate is proportional to  $x_{\text{CO}}^{\circ}$ .

Having to our disposal the values of  $k$  for various  $x_{\text{CO}}^{\circ}$  contents at constant temperature, the mutual relation between these values was determined. It has been defined by the relation:

$$k = a \cdot (x_{\text{CO}}^{\circ})^n$$

where:

$a, n$  — equation constant.

The equation parameters calculated on the basis of linear regression analysis gave the following values:

$T = 1048 \text{ K}$	$a = 0.0042$	$n = 0.7494$
$T = 1073 \text{ K}$	$a = 0.0049$	$n = 0.7191$

In both cases the correlation coefficient was higher than 0.997.

In the further part of the study there have been carried out the investigations of CdO reduction from an oxide material containing zinc and cadmium oxides. The aim of these investigations was to test whether under conditions of intense reduction of cadmium oxide there takes place a simultaneous reduction of zinc oxide. As the conditions in which the reduction process was carried out did not allow the condensation of cadmium vapours, the conclusions concerning the selectivity of the reduction process will be drawn on the basis on analysis of the obtained dust for the content of zinc and the analysis of the remainder after reduction for the content of cadmium. The investigations were carried out at the temperatures 1048, 1073 and 1148 K, at various CO content in the starting gaseous phase.

Changes of the mass in the samples, registered during reduction have shown that the relative loss of the sample mass was the greater, the higher the CO content in the flowing gaseous phase. The total relative loss of the mass of the samples resulting only from CdO reduction should be equal to 52,5%. The experimental results indicated that especially at higher temperatures of the process and with higher CO contents in the gaseous phase this value was exceeded. This fact may be an indication

that in these conditions the zinc oxide was also reduced. This observation has been confirmed by the results of chemical analysis listed in Table 3.

TABLE 3  
Zinc and cadmium content in the reduction products

Temperature [K]	CO in the gaseous phase [%]	Relative loss of mass [%]	Cd content in the remainder [%]	Zn content in the dust [%]
1048	33	49.40	1.16	0.85
	50	51.19	1.03	1.64
	67	52.41	0.88	1.93
	100	54.16	0.75	1.80
1073	33	52.76	0.96	1.44
	50	52.40	0.84	1.65
	67	51.92	0.54	1.48
	100	54.97	0.55	1.84
1148	33	52.23	0.80	1.46
	50	53.21	0.76	1.64
	67	56.04	0.33	2.07
	100	62.08	0.19	4.47

The obtained results may be interpreted as indicating that it is not possible to obtain metallic cadmium of high purity from oxide material containing zinc and cadmium by way of reduction. When the composition of the gaseous phase and the conditions of the condensation of zinc and cadmium vapours are taken into consideration, it may be stated that in the gaseous phase when it passes from the reactor to the condenser there exist conditions favouring the reoxidation of zinc vapours which in the condenser may form the so-called melting loss, which enables to obtain metallic cadmium of high purity.

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