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Dissolution Kinetics of MgO in Aqueous, Acidic Media**

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The method of the rotating disc was used to study the kinetics of MgO dissolution. Single crystals of MgO with the orientation {100}, {101}, and {111} were dissolved in N_2-saturated $HClO_4$—$NaClO_4$ solutions of constant ionic strength ($I = 1.0\,\mathrm{mol\,kg^{-1}}$). Chemical, mixed and diffusional control of the reaction leading to dissolution has been found between 25 to 90 °C and $0.5 < pH < 3$. The dissolution at 90 °C and $pH \geqslant 3$ occurred diffusionally controlled with respect to H^+ ions. Independent measurements of the limiting current densities for the cathodic reduction of H^+ ions were carried out in solutions of the same composition and confirmed this kind of control. In the chemical control region the dissolution rates were proportional to the Mg^{2+} ion densities of the single crystal surfaces investigated. The dissolution rates relative to {111}, at 40 °C and $pH = 1$, were found to be: 1.0 ± 0.1 (1.0) {111}; 1.3 ± 0.2 (1.2) {101} and 1.7 ± 0.2 (1.7) {100}. Figures in parentheses refer to the relative Mg^{2+} ion densities of the surface. Reproducible results of high quality can only be obtained when "fresh" dislocations are removed by chemical polishing.

In a limited *pH* range these results were formally consistent with the "complex formation" model of metal oxide dissolution. For substances with large surfaces this model applies frequently. However, for single crystals no methods are known which allow the independent determination of the amount of surface OH-groups and the surface complex formation constants. Although the overall dissolution behaviour of MgO, which is relevant for industrial applications, is now rather well known, not enough information for unambiguous mechanistic conclusions is available.

(Keywords: Dissolution kinetics; Magnesium oxide; Rotating disc)

Die Kinetik der Auflösung von MgO *in wäßrigen, sauren Medien*

Die Kinetik der Auflösung von MgO wurde mit der Methode der rotierenden Scheibe untersucht. Einkristalle mit der Orientierung {100}, {101} und {111} wurden in stickstoffgesättigten $HClO_4$—$NaClO_4$-Lösungen konstanter Ionenstärke ($I = 1.0\,\mathrm{mol\,kg^{-1}}$) gelöst. Die zur Auflösung führende Reaktion war zwischen 25 und 90 °C und $0.5 < pH < 3$ chemisch-, gemischt- oder diffusions-kontrolliert.

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Die Auflösung bei 90 °C und $pH \geqslant 3$ verlief diffusions-kontrolliert in bezug auf die H^+-Ionen. Unabhängige Messungen der Grenzstromdichte für die kathodische Reduktion von H^+-Ionen, die in Lösungen gleicher Zusammensetzung durchgeführt wurden, bestätigten diesen Befund. Im chemisch kontrollierten Bereich waren die Auflösungsgeschwindigkeiten proportional zu den Dichten der Mg^{2+}-Ionen an den Oberflächen der untersuchten MgO-Einkristalle. Folgende zu {111} relative Auflösungsraten bei 40 °C und $pH = 1$ wurden gefunden: 1.0 ± 0.1 (1.0) {111}; 1.3 ± 0.2 (1.2) {101} und 1.7 ± 0.2 (1.7) {100}. Die Werte in den runden Klammern beziehen sich auf die relativen Oberflächen-Dichten der Mg^{2+}-Ionen. Reproduzierbare Ergebnisse hoher Qualität können nur erhalten werden, wenn „frische" Versetzungen durch chemisches Polieren entfernt werden.

In einem begrenzten *pH*-Bereich sind die erhaltenen Resultate mit dem „komplexchemischen" Modell der Metalloxidauflösung konsistent. Für Substanzen mit großer Oberfläche wurde dieses Modell vielfach mit Erfolg angewendet. Derzeit ist jedoch keine Methode bekannt, die es gestattet, bei Einkristallen die Menge der oberflächenständigen OH-Gruppen und die Bildungskonstanten von Oberflächenkomplexen direkt zu bestimmen. Obwohl man nun das Auflösungsverhalten von MgO, soweit es von industrieller Bedeutung ist, recht gut kennt, liegen noch nicht genügend Informationen vor, um eindeutige mechanistische Zuordnungen zu treffen.

Introduction

The kinetics of the acid dissolution of MgO and $Mg(OH)_2$ has been investigated by several authors [1–12] and has recently been reviewed [13]. Depending on the range of *pH* and temperature chemical as well as diffusional control of the overall reaction (1) has been found* [1–3].

$$MgO_{(s)} + 2\,H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_2O_{(l)} \qquad (1)$$

However, the surface properties (e.g., dislocations) of the MgO and $Mg(OH)_2$ samples used were not taken into account in previous studies.

In view of the industrial importance of reaction (1) it seemed to be interesting to carry out conclusive experiments which allow a detailed analysis of the kinetic behaviour of MgO in acidic solutions. The rotating disc method was chosen for this work since it is best suited to study transport phenomena. Peliminary experiments with discs consisting of polycrystalline MgO showed visible differences of the dissolution rates when different crystal faces were exposed to acidic media. Therefore MgO single crystals of the orientation {100}, {101} and {111}, were used in the present investigation. It turned out that reliable results were only obtained when "fresh" dislocations, imposed by mechanical polishing, were removed by chemical polishing before kinetic runs were started, therefore rates measured without this precaution are slightly in error [14].

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* In this paper regions of chemical, diffusional and mixed control are distinguished. Chemical control can be brought about by chemical reaction, adsorption and desorption.

The rates of MgO dissolution were determined at constant ionic strength (1.0 mol kg^{-1} $NaClO_4$) in order to minimize activity coefficient variations. Throughout each run the *pH* was kept constant. The limiting diffusional currents of H^+ ions were determined by independent measurements and compared with the dissolution rates of MgO in the region of diffusional control.

Experimental

Magnesium oxide discs with the orientation {100}, {101} and {111} sliced from one single crystal (99.9% MgO) were obtained from W. & C. Spicer Ltd., (England). Thus the concentration of "grown-in" dislocations and the chemical composition were identical in all samples used in this study. The cylindrically shaped crystals had a useful surface area of $3.63 \cdot 10^{-4}\,m^2$ and were sintered with teflon into a teflon holder and fitted to the shaft of the rotating system. Details of the set-up were taken from *Pleskov* and *Filinovskii* [15]. For the measurements $HClO_4$—$NaClO_4$ solutions were used, the ionic strength $I = 1.0$ mol kg^{-1} kept constant and the range of $4 > pH > 0$ maintained. Solutions were made up with water three-times distilled from an all quartz-apparatus. Two hours before the start of the experiment and during each run N_2 (99.999%) was bubbled through the solution. The temperature was kept constant within ± 0.2 K by means of a water-jacketed glass vessel. The cover of this vessel contained glass joints for the rotating disc, *Wilhelm*'s salt bridge [16], glass electrode, condenser, inlet for N_2 and inlet for the solutions used to keep the *pH* constant during the dissolution of MgO. The *pH* of the solutions was controlled potentiometrically with a "Beckmann" *pH*-meter and a glass-Ag/AgCl-electrode system, and maintained within ± 0.02 *pH* units or better by adding standard acid using a weight burette. The amount of Mg^{2+} dissolved was determined by a standard method (AAS).

Before each measurement the disc surface was polished mechanically with emery paper and chemically with boiling H_3PO_4 for up to 10 min. The discs were washed with water and quickly dried. Immediately after this treatment runs were started. Measurements were performed at 5, 15, 25, 40, and 90 °C. The rotational speed of the disc was measured with a stroboscope. The measurements of the cathodic reduction of H^+ ions as described by *Sivier* and *Kabanov* [17] and *Zembura* et al. [18] were conducted with a rotating amalgamated copper disc of surface area $3.14 \cdot 10^{-4}\,m^2$. In addition the electrical circuit consisted of a constant direct current power supply, a decade rheostat, an ammeter and a Pt-anode. The cathodic region was protected against the products of the anode reaction. The potential of the cathode was measured using a Ag/AgCl reference electrode and *Luggin*'s capillary.

Results

The rates of the MgO dissolution, j_{Mg}, were obtained from the slopes of plots: amount of Mg^{2+} dissolved, n_{Mg}, vs. time. During preliminary experiments with mechanically but not chemically polished MgO discs a much higher initial dissolution rate was obtained. Fig. 1 shows different rates of mechanically and chemically polished discs. It can be seen that the rates slow down considerably when the mechanically imposed dislocations are removed. Consequently, dissolution rates were calculated

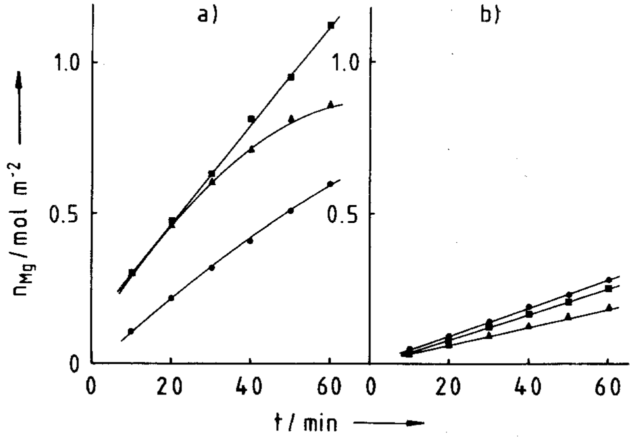

Fig. 1. Plots of amounts of Mg^{2+} dissolved vs. time at 40 °C and $pH = 1.0$. a) Mechanically polished; b) Chemically polished MgO single crystals: {100} ●; {101} ■; {111} ▲

only from experiments with chemically polished discs, i.e., when n_{Mg} was a linear function of time. A microscopic analysis of the surface demonstrated that "fresh" dislocations penetrate the MgO crystals only to a very small depth which has also been observed previously [19]. The dissolution rates were studied as a function of the frequency, f/s^{-1}, of disc revolutions, thus it was possible to distinguish chemically, mixed and diffusionally controlled regions of the reaction leading to dissolution [15, 20].

Dissolution Rates of MgO {100}

Fig. 2 summarizes the results obtained with MgO {100} between 25–90 °C. At 40 °C and $0.5 < pH < 2$ the rates of dissolution were independent of the frequency of revolutions of the disc, this indicates chemical control of the dissolution reaction. From the linear dependence of $\log j_{Mg}$ on pH the rate equation for dissolution in the region of chemical control was derived to be

$$j_{Mg} = k\,(c^{o}_{H^+})^{p} \tag{2}$$

where $c^{o}_{H^+}$/mol m^{-3} is the concentration of H^+ ion in the bulk of solution, k is the rate constant and $p = 0.26 \pm 0.02$.

These experiments established zero order of reaction (1) with respect to $[Mg^{2+}]$ in agreement with previous results [1].

At $pH = 3$, j_{Mg} became a characteristic function of $f^{1/2}$ indicative for mixed kinetics, as shown in Fig. 3. Since mixed kinetics can easily be

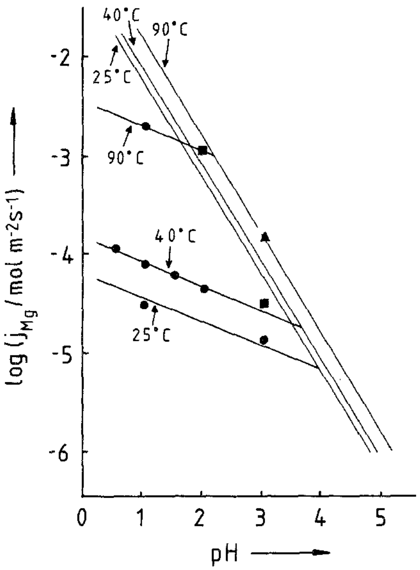

Fig. 2. Plots of log (dissolution rate) vs. *pH* for MgO {100}. Thin lines: $1/2\, j_{H^+}$ ($f = 10\,s^{-1}$). Chemical control ●; chemical component of mixed kinetics ■; diffusional control ($f = 10\,s^{-1}$) ▲

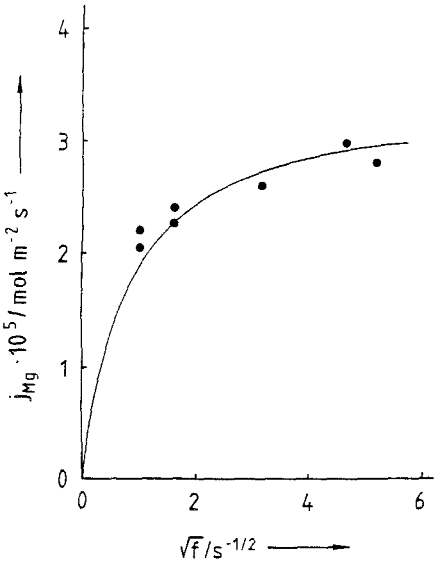

Fig. 3. Plot of dissolution rates of MgO {100} vs. square root of the frequencies of the disc revolutions at 40 °C and *pH* = 3.0; the data indicate mixed kinetics

confused with diffusionally controlled processes where the disc is partially covered by an "inactive" species [21, 22], the data were linearized as described by *Pleskov* and *Filinovskii* [15]. If mixed kinetics applies, equation (3) is valid

$$j_{\mathrm{Mg}}^{1/p} = c^{\mathrm{o}}_{\mathrm{H}^+} \cdot k^{1/p} - \frac{k^{1/p}}{0.62 \cdot (2\,\pi)^{1/2} \cdot D_{\mathrm{H}^+}^{2/3}\, \nu^{-1/6}} \cdot \frac{j_{\mathrm{Mg}}}{f^{1/2}} \qquad (3)$$

where D_{H^+} is the diffusion coefficient of H^+ ions, and ν is the kinematic viscosity of the solution investigated, moreover a dimensionless number appears in eq. (3), whose value equals 0.62 provided a consistent system of units is used. At constant temperature and H^+ ion concentration $j^{1/p}$ becomes a linear function of $j_{\mathrm{Mg}} f^{-1/2}$, and indeed the data replotted in this way fall on a straight line (Fig. 4). When f approaches infinity the chemical component of the dissolution rate can be derived from equation (3). The rate thus obtained agrees reasonably well with that extrapolated from the plot $\log j_{\mathrm{Mg}}$ vs. pH in Fig. 2. This agreement provides strong evidence for mixed kinetics. When "inactive" species cover the disc surface the chemical component of the dissolution rate obtained from "pseudo" mixed kinetics would be considerably smaller [15, 22]. As shown in Fig. 2 at 90 °C and $pH = 1$–2 the dissolution reaction of MgO occurs in the range of chemical and mixed control respectively. At 90 °C and $pH = 3$, j_{Mg} was a linear function of $f^{1/2}$ and the respective straight lines passed through the origin of coordinates, as shown in Fig. 5. This behaviour is predicted by the *Levich* equation (4) for diffusionally controlled reactions occurring at a rotating disc:

$$j_{\mathrm{Mg}} = 0.62\,(2\,\pi)^{1/2}\, D_{\mathrm{H}^+}^{2/3}\, \nu^{-1/6}\, c^{\mathrm{o}}_{\mathrm{H}^+} f^{1/2} \qquad (4)$$

In order to verify diffusional kinetics of MgO dissolution with respect to H^+ at 90 °C and $pH = 3$ the limiting current densities of cathodic reduction of H^+ ions at a rotating amalgamated Cu disc were measured. Similar experiments in different solutions and at different temperatures were carried out earlier [17, 18]. Current density and rate of the H^+ ion reduction are related by the equation:

$$j_{\mathrm{H}^+} = i_{\mathrm{H}^+} \cdot F \qquad (5)$$

where F is the *Faraday* constant.

At 90 °C in the diffusional range the following results were obtained: $j_{\mathrm{Mg}}/\mathrm{mol\,m^{-2}\,s^{-1}} = (4.4 \pm 0.5) \cdot 10^{-5} \cdot f^{1/2}$, $1/2\, j_{\mathrm{H}^+}/\mathrm{mol\,m^{-2}\,s^{-1}} = (4.4 \pm 0.4) \cdot 10^{-5} \cdot f^{1/2}$, thus within the experimental uncertainty j_{Mg} and $1/2\, j_{\mathrm{H}^+}$ agreed with each other. This should be so when the dissolution occurs according to the overall reaction (1).

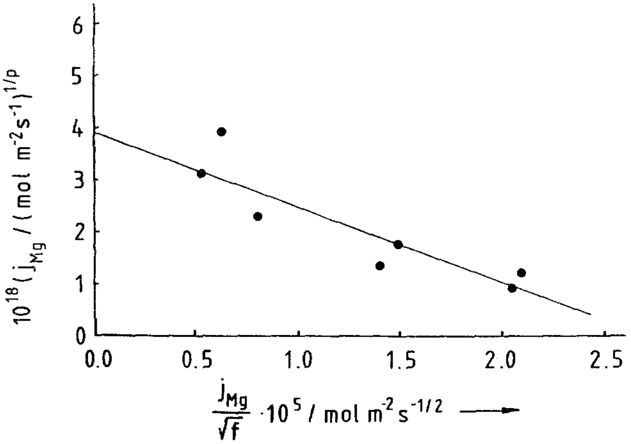

Fig. 4. Verification of mixed kinetics for the dissolution of MgO {100} at 40 °C and $pH = 3.0$ by plotting $j_{Mg}^{1/p}$ vs. $j_{Mg}/f^{1/2}$

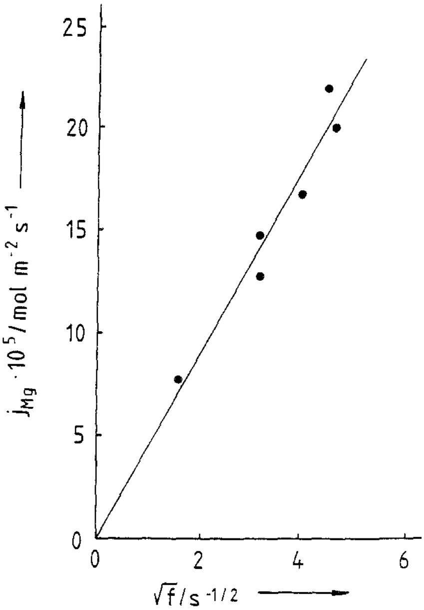

Fig. 5. Plot of dissolution rates vs. square root of the frequencies of disc revolutions for the diffusionally controlled dissolution of MgO {100} at 90 °C and $pH = 3.0$

The activation energy $E_a = 57.3 \pm 4.2\,\mathrm{kJ\,mol^{-1}}$ was determined in the chemically controlled range at $pH = 1$ between 5–90 °C. The activation energy for the diffusionally controlled range was assumed to be $13\,\mathrm{kJ\,mol^{-1}}$, and corresponding straight lines were drawn in Fig. 2.

Influence of the Crystallographic Orientation on the Dissolution Rates of MgO

When single crystals of MgO with the orientation {101} and {111} were investigated by the method described, it turned out that at 90 °C and $pH > 3$ the dissolution reaction occurred also in the diffusionally controlled range, and the rates were therefore completely independent of the MgO surface exposed to the acid.

Table 1. *Dissolution rates of* MgO *single crystals at 40 °C and* $pH = 1.0$

Plane	$j \cdot 10^{-5}/\mathrm{mol\,m^{-2}\,s^{-1}}$	Mg-atoms $d \cdot 10^{-19}/\mathrm{m^{-2}}$	$d/d_{\{111\}}$	$j/j_{\{111\}}$
{100}	7.6 ± 0.8	1.1263	1.732	1.7 ± 0.2
{101}	6.0 ± 0.8	0.7964	1.225	1.3 ± 0.2
{111}	4.6 ± 0.4	0.6503	1.000	1.0 ± 0.1

The dissolution rates in the chemically controlled region, however, were proportional to the surface density of Mg^{2+} ions. In the table dissolution rates relative to the {111} surface are compared with relative Mg^{2+} densities. It should be emphasized that highly precise results can only be expected when "fresh" dislocations are removed from the surface by chemical polishing with boiling H_3PO_4. In addition the concentration of "grown-in" dislocations were the same for all samples, since they were all sliced from one single crystal.

Discussion

In principle two models have been proposed to explain the dissolution kinetics of metal oxides and hydroxides.

In the "electrochemical" model [23–25] the dissolution can be described in terms of rate control by ion transfer across the double layer (*Butler-Volmer* approach). When the rate of anodic reactions (removal of O^{2-} or OH^- ions) is assumed to be proportional to the H^+ concentration, and the rate of cathodic reactions (removal of metal ions) is rate determining then the dependence of the dissolution rate on the H^+ concentration can be derived. Reaction orders of $[H^+]$ calculated in this way are criteria for the reaction mechanism operative. The $[H^+]$ dependence (p value, see Fig. 2) observed in this work agrees with neither of those predicted by the "electrochemical" model.

In the "adsorption" or "complex formation" model [26–30] it is assumed that reactive surface complexes are formed. The dissolution rate then depends upon the amount of surface complexes. Provided that in the present case the amount of surface OH-groups and the equilibrium constants of their protolysis reactions are known, a *Langmuir* isotherm for dissolution rates can be calculated and compared with the experimental data. For many suspensions of finely divided oxide samples the "complex formation" model agrees quite well with available data [29, 30]. However, for the tiny surface of single crystals there is so far no other way to determine the amount of surface complexes than to use crystallographic arguments. As shown in Fig. 6 our data fall in a limited *pH* range indeed on a *Langmuir* isotherm (6)

$$j_{Mg} = \frac{k \cdot A \cdot [H^+]}{K_s + [H^+]} \tag{6}$$

where $A = \{=MgOH_2^+\} + \{=MgOH\}$, the amount of surface OH-groups and $K_s = \{=MgOH\} \cdot [H^+]/\{=MgOH_2^+\}$, the surface protonation constant. It is, however, so far not possible to compare this curve with one constructed by means of independently measured equilibrium constants and amounts of surface OH-groups.

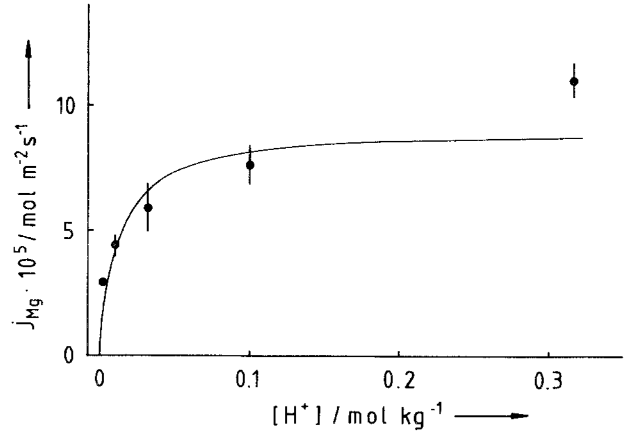

Fig. 6. Plot of dissolution rate of MgO {100} vs. H^+ concentration at 40 °C. The solid line has been fitted to the *Langmuir* isotherm. The error bars refer to the individual standard deviations

While the overall dissolution behaviour of MgO is now definitely known, there is still not enough information available so as to discuss mechanistic details.

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References

[1] *Vermilyea DA* (1969) J Electrochem Soc 116: 1179
[2] *Macdonald DD, Owen D* (1971) J Chem 49: 3375
[3] *Fruhwirth O, Herzog GW, Hollerer I, Rachetti A* (1985) Surf Techn 24: 301
[4] *Sangwal K, Arora SK* (1978) J Mater Sci 13: 1977
[5] *Sangwal K, Patel TC* (1978) Kristall u. Technik 13: 281
[6] *Sangwal K, Patel TC* (1978) Kristall u. Technik 13: 1407
[7] *Sangwal K, Patel TC, Kotak MO* (1979) J Mater Sci 14: 1869
[8] *Sangwal K, Patel TC, Kotak MO* (1979) Kristall u. Technik 14: 949
[9] *Segall RL, Smart RStC, Turner PS* (1978) JCS Faraday I 74: 29
[10] *Segall RL, Smart RStC, Turner PC* (1982) Chem Austr 49: 241
[11] *Jones CF, Segall RL, Smart RStC, Turner PS* (1982) Radiat Eff 60: 167
[12] *Jones CF, Segall RL, Smart RStC, Turner PS* (1981) Proc Roy Soc (London) A374: 141
[13] *Terry B* (1983) Hydrometallurgy 11: 315
[14] *Bugajski J, Gamsjäger H* (1983) Österr Chemie-Zeitschrift 84: 214
[15] *Pleskov YuV, Filinovskii VYu* (1976) The rotating disc electrode. Consultants Bureau, New York
[16] *Forsling W, Hietanen S, Sillén LG* (1952) Acta Chem Scand 6: 901
[17] *Sivier YuG, Kabanov BN* (1949) Zurn Fiz Chim 23: 428
[18] *Zembura Z, Ziolkowska W, Kolny H* (1965) Bull Acad pol Sci Chim 13: 487
[19] *Stockes RJ* (1962) Trans Met Soc AIME 224: 1227
[20] *Levich VG* (1962) Physicochemical hydrodynamics. Prentice Hall, New Jersey
[21] *Scheller F, Müller S, Landsberg R, Spitzer H* (1968) Electroanal Chem 19: 187
[22] *Zembura Z* (1977) Arch Hutnictwa 22: 38
[23] *Jaenicke W* (1952) Z Electrochem 56: 473
[24] *Engel HJ* (1956) Z Phys Chem NF 2: 158
[25] *Vermilyea DA* (1966) J Electrochem Soc 113: 1067
[26] *MacKay TL, Wadsworth ME* (1958) Trans AIME 212: 597
[27] *Surana VS, Warren IH* (1969) Trans Inst. Min Metall (Sec. C: Mineral Process Extr. Metall.) 78: C133
[28] *Warren IH, Devuyst EA* (1973) Leaching of metal oxides. In: *Evans DJ, Shoemaker RS* (eds) International Symposium on Hydrometallurgy, AIME, Chicago
[29] *Grauer R, Stumm W* (1982) Colloid and Polymer Sci 260: 959
[30] *Schindler PW* (1985) Österr Chemie-Zeitschrift 86: 141