Hydrometallurgy 140 (2013) 95–101

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

# Kinetic study of gallium electrochemical reduction in alkaline solution

S. Gladyshev [a], A. Akcil [b,*], R. Abdulvaliev [a], Y. Tastanov [a], K. Beisembekova [a], S. Temirova [a]

[a] *Centre of Earth Sciences, Metallurgy and Ore Beneficiation, Shevchenko St. 29/133, 050010 Almaty, Kazakhstan*
[b] *Department of Mining Engineering, Mineral Processing Division (Mineral–Metal Recovery and Recycling Research Group), Suleyman Demirel University, TR32260 Isparta, Turkey*

A R T I C L E I N F O

*Article history:*
Received 13 March 2013
Received in revised form 19 August 2013
Accepted 27 August 2013
Available online 21 September 2013

*Keywords:*
Gallium anions
Electrochemical reduction
Alkaline solution
Background electrolytes
Reduction mechanism

A B S T R A C T

The article reviews the cathodic process of gallium ion reduction in alkaline solutions. The solution composition influence on the gallium anion reduction kinetics was analyzed by measuring the polarization curves on a dropping mercury electrode. It was found that the cathodic process rate is proportional to the specific adsorption of background cations in the sequence $Na^+ < K^+ < Li^+ < Cs^+ < La^{3+}$. A higher rate of reduction of gallium anion present in alkaline solution of lithium cation is a result of participation of the water molecules from the hydration shell of $Li^+$ as a proton donor. In the presence of polyvalent lanthanum cations in alkaline solution, the gallium anion reduction rate increases sharply. This is related to a shift in the $\psi_1$-potential and participation of hydrated cations $La(H_2O)^{3+n}$. The presence of surface-active agents, which have no proton–donor properties, in the solution, complicates the reduction reaction. Certain patterns of the mechanism of the gallium ion discharge reaction in alkaline solutions allow qualifying it as the second group of anions, and the slow stage of the reduction reaction comes down to simultaneous transfer of an electron and proton to the discharging anion. The estimated charge of the discharging gallium anion, which is equal to $-0.24$ in the transition state of the reaction, is indicative of formation of associates with background electrolyte cations $[Me^+ \ldots GaO_2^-]$, $[Me^+ \ldots GaO(OH)_2^-]$ by gallate anions in alkaline solutions (pH 12).

## 1. Introduction

The analysis of the world market tendencies of nonferrous and rare metals indicates a rapid growth in demand for gallium, up until 2020. For this reason there is a need for substantial increase of its output (Naumov and Plekhanov, 2011). Currently, the main source of gallium is aluminum raw materials processed by the aluminum oxide plants, which simultaneously extract gallium (Chou et al., 2008; Dovbysh et al., 1981; Gupta et al., 2007; Ibragimov and Budon, 2010; Ivanova, 1973; Kekesi, 2007; Korovin et al., 2003; Ma et al., 2011; Moskalyk, 2003; Puvvada et al., 1996; Wu et al., 2007; Xu et al., 2007; Zelikman et al., 1980; Zhao et al., 2012). Metal gallium is extracted from alkaline solutions in alumina production using electrochemical methods of recovery of its ions. Studies of kinetics and reduction process mechanisms expand the knowledge on gallium chemistry and electrochemistry and are of considerable interest for the practical application of these methods in the gallium production technology (Abdollahy and Koleini, 2008; Jang and Numata, 1989; Jayachandran and Dhadke, 1998; Krissar, 1985; Mecevic and Lourece, 1983; Sato et al., 1996; Varadharaj et al., 1988).

Reduction of gallium ions from alkaline solutions is one of the complex reactions, in which the metal is in the form of hydrated tetrahydroxy gallate anions $Ga(OH)_4^- \ldots n(H_2O)$, which, depending on the solution composition (free alkali and gallium concentration), can form dimers, polymer complexes and associates (Fedorovich, 1979). The mechanism of cathodic deposition of gallium in the alkaline solutions is considered from three different points of view (Naumov and Plekhanov, 2011). According to the first one, despite extremely small concentration of free gallium ions in alkaline solutions $-1.2 \cdot 10^{-41}$ mol/dm$^3$, simple cations are reduced on the cathode. By contrast to this view an assumption is developed that complex ions are discharged on the cathode. According to the third point of view, metal gallium is extracted on the cathode as a result of the secondary processes and disproportionation reactions.

This paper provides analyses of the mechanism of gallium ion discharge in the alkaline solution from the point of view of the anion reduction theory. According to this theory, the process of electrochemical reduction of anions, like any electrochemical reaction, has a number of successive steps, and the total reaction rate is determined by the rate of the most hindered step (Berezina and Fedorovich, 1967a,b).

According to the mechanism of reduction reactions anions are divided into two groups. In the first group are the anions; the reduction rate of which is determined by the slowness of electron transfer to the discharging anion:

$$A + \bar{e} \rightarrow R. \quad (1)$$

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[*] Corresponding author. Tel.: +90 246 2111321; fax: +90 246 2370859.
*E-mail address:* ataakcil@sdu.edu.tr (A. Akcil).

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http://dx.doi.org/10.1016/j.hydromet.2013.08.012

Kinetic equations are provided for the discharge reaction rate of the first group anions:

$$i = n\ F\frac{\gamma_A}{\gamma_R}Ks \cdot C_A \exp\left[-\frac{\alpha F(E-\psi_1)}{RT}\right] \exp\left[\frac{(1-\alpha)g_A+\alpha g_R}{RT}\right] \exp\left[-\frac{Z_A F\psi_1}{RT}\right] \tag{2}$$

$$Ks = \chi\frac{KT}{h}\exp\left(-\frac{\Delta G^{-}{}_{o}}{RT}\right) \tag{3}$$

where, i is the reaction rate; n is the number of electrons participating in the reaction; F is the Faraday number; $\gamma_A$ and $\gamma_R$ are the rep article activity ratio; Ks is the universal heterogeneous constant of the reaction rate determined by the ratio (2); T is the absolute temperature; $C_A$ and $Z_A$ are the concentration and charge of reactants in bulk solution, respectively; $\alpha$ is the transfer coefficient ($0 < \alpha < 1$); $\psi_1$ is the mean value of the potential in the plane, where reactant charge centers are concentrated in the transition state of the reaction; E is the measured electrode potential read off the standard equilibrium potential of the analyzed reaction; $g_A$ and $g_R$ are non-Coulombic (specific) components of the free energy of reactants and reaction products; $\chi$ is the transmission ratio; K and h are the Boltzmann's and Planck's constants, respectively; $\Delta G^{-}{}_{o}$ is the component of free energy of reaction activation depending on the nature of reactants and nature of the solvent.

Due to the fact that standard equilibrium potential of the analyzed reaction is generally not realized, the measured potential is read off the reference electrode. The measured value differs from the equilibrium standard potential of the analyzed reaction for the constant value $E^0$.

It has been established that for a large number of anions with different structures and compositions ($S_2O_8{}^{2-}$, $S_2O_4^{2-}$, $Fe(CN)_6^{3-}$, Co $(C_2H_4)^{3-}$, $PtCl_4^{2-}$, $PtCl_6^{2-}$, $Pt(CNS)_4^{2-}$, Pd $(CNS)_4^{2-}$ and others) dependence of the reduction reaction rate on the electrode potential, background electrolyte concentration and nature of the solvent can be explained on the basis of the theory of reduction of the first group anions.

In the slow stage of anion reduction in the second group ($NO^{3-}$, $BrO^{3-}$, $IO^{3-}$, $CrO_4^{2-}$ and others) a proton donor is involved, and the elementary discharge process is replaced by a simultaneous electron and proton transfer to the discharging anion:

$$A^{ZA} + HB^{ZPD} + \bar{e} \rightarrow HA^{ZA+1} + B^{ZPD-1} \tag{4}$$

where, $A^{ZA}$ is a reducing anion with $z_A$ charge; $HB^{ZPD}$ is a proton donor (PD) with $Z_{PD}$ charge; $HA^{ZA+1}$ is a result of a proton and an electron attachment to the original anion, charge $Z_{A+1}$; $B^{ZPD-1}$ is a base associated with proton donor with a charge of $Z_{PD-1}$.

For the second group anion reduction rate following equations were established (Berezina and Fedorovich, 1967a,b):

$$i = nF\overline{K}C_AC_{PD}\exp\left[\frac{Z_A+Z_{PD}}{RT}\psi\right]\exp\left[-\frac{\alpha F}{RT}(E-\psi_1)\right]\exp\left(\frac{\widetilde{g}}{RT}\right) \tag{5}$$

$$\overline{K} = \chi\cdot\frac{kT}{h}\left(\frac{\gamma_A\cdot\gamma_{PD}}{\gamma_{HA}\cdot\gamma_B}\right)^{\alpha}\exp\left(-\frac{G_o^{-}}{RT}\right)\exp\left(\frac{\alpha F}{RT}E^0\right) \tag{6}$$

$$\widetilde{g} = (1-\alpha)g_A + (1-\alpha)g_{PD} + \alpha g_{HA} + \alpha g_B + (\alpha - Z_{PD})F(\psi_2 - \psi_1) \tag{7}$$

where, $\overline{K}$ is the reaction rate constant; $C_A$ and $C_{PD}$ are the anion and proton donor concentration in bulk solution; $Z_A$ and $Z_{PD}$ are the values of their charge in bulk solution; $\psi_1$ and $\psi_2$ are mean potential values in the planes, where charge centers of reactants (anion and proton donor, respectively) are concentrated in the transition state of the reaction; E and $E^0$ are the electrode potential and standard equilibrium electrode potential of the reaction under review read off the reference electrode; $\widetilde{g}$ is the amount of nonelectric (specific) adsorption energies; $\gamma_A$, $\gamma_{PD}$, $\gamma_{HA}$, and $\gamma_B$ are the activity ratios of respective particles.

Kinetics of electrical reduction of the second group anions significantly depends on the nature of proton donor. If any neutral solvent particles, such as water, adsorbed on the electrode participate in the reaction as PD, then the equation will look as under:

$$i = \overline{K}C_A\exp\left[-\frac{Z_AF}{RT}\psi_1\right]\exp\left[-\frac{\alpha F(E-\psi_1)}{RT}\right]\exp\left[\frac{(1-\alpha)g_{H_2O}}{RT}\right] \tag{8}$$

where, $g_{H_2O}$ is the nonelectric (specific) water adsorption energy.

It follows from Eq. (8) that value $\widetilde{g}$ determined from relation 7 depends only on $g_{H_2O}$, since with the negative charge $g_A = g_{HA} = g_B = 0$.

If ammonium cations act as proton donor, then the equation will look as follows:

$$i = \overline{K}C_AC_{NH_4{}^+}\exp\left[-\frac{\alpha F\ (E-\psi_1)}{RT}\right]. \tag{9}$$

The Eqs. (2), (3), (5) to (7) provided explain the fact that taking into account the dependence of $\psi_1$ on E in diluted solutions of indifferent background electrolyte the reaction rate (lgi) of anion reduction from the electrode potential is expressed by a compound curve (Fedorovich, 1979) with the maximum current under positive surface charges and minimum under negative ones. Such dependence is due to the fact that the reaction rate in the event of anion charge is determined by two opposite factors — change of the discharging anion concentration surface and change of activation energy. With the potential close to the zero charge potential the first factor has dominant influence over the reaction rate, since abrupt change of the value and sign of $\psi_1$-potential at the transition from positive to negative surface charges results in rapid dilution of discharging anion in double electric layer. Change of $\psi_1$-potential at high-charge surfaces is relatively small and the reaction rate is determined, first of all, by the activation energy decrease with the growing cathodic potential of the electrode. The increase of the background electrolyte concentration results in reduction of the absolute value of $\psi_1$-potential, increase in the reaction rate under negative surface charges and decrease under positive ones. In the presence of high background concentrations, when $\psi_1$-potential value may be disregarded, dependence of lgi on E is linear and corresponds to the Tafel equation. Such dependence is only observed for the anions, which reduction begins under positive charges of the electrode surface. For the anions reduced under high negative values of the electrode charge, polarization curves will correspond to the exponential dependence.

Strong influence of the double electric layer on the anion discharge rate is due to the fact that influence of $\psi_1$-potential on anion concentration on the electrode surface and activation energy is combined, and at the cation discharge they have opposite direction and compensate each other. Therefore, influence of the structure of the double electric layer on the anion reduction reaction is much more pronounced than on the cation reduction reaction.

Deviation from the linear dependence of lgi on E is also connected with the influence of $\psi_1$-potential on concentration of the reactant and reaction activation energy. Equation expressing dependence of lgi on E:

$$lgi + \frac{Z_AF}{2.3RT}\psi_1 = lgKC_A - \frac{\alpha F}{2.3RT}\ (E-\psi_1). \tag{10}$$

It follows from Eq. (10) that dependence of the reaction rate on the potential expressed in the coordinates $\left(lgi + \frac{Z_AF}{RT} - \psi_1\right), -(E-\psi_1)$ is linear like the Tafel dependence of the reaction rate on the potential (Fedorovich, 1979).

The curves of these coordinates were called the adjusted Tafel dependencies (ATD-1). ATD-1 for different background concentrations on one electrode must correspond to the whole range of application of the Eqs. (2), (3), (5) to (7). Based on the slope of the dependence of