


University of Belgrade
Technical Faculty in Bor and
Mining and Metallurgy Institute Bor



48th International October Conference on Mining and Metallurgy

www.ioe.tf.bor.ac.rs

PROCEEDINGS



Anode casting at Copper Smelter and Refinery Bor, Serbia

www.tf.bor.ac.rs

Editors:
Nada Štrbac
Dragana Živković

IOOC 2016
International October
Conference

Bor, Serbia
September 28 to October 01, 2016

**PROCEEDINGS,
48th INTERNATIONAL OCTOBER CONFERENCE
on Mining and Metallurgy**

Editors:

Prof. dr Nada Štrbac

University of Belgrade - Technical Faculty in Bor

Prof. dr Dragana Živković

University of Belgrade - Technical Faculty in Bor

Technical Editors:

Doc. dr Ljubiša Balanović

University of Belgrade - Technical Faculty in Bor

Msc. Uroš Stamenković

University of Belgrade - Technical Faculty in Bor

Publisher: University of Belgrade - **Technical Faculty in Bor**

For the publisher: Acting Dean Prof. dr Nada Štrbac

Circulation: 200 copies

Printed in Serbia by „Happy trend DOO“ Zaječar

ISBN 978-86-6305-047-1

CIP - Каталогизacija у публикацији - Народна библиотека Србије, Београд

622(082)

669(082)

INTERNATIONAL October Conference on Mining and Metallurgy (48 ; 2016 ; Bor)
Proceedings / 48th International October Conference on Mining and
Metallurgy - IOC 2016, Bor, Serbia, September 28 - October 01, 2016 ;
[organized by] University of Belgrade, Technical Faculty Bor and Mining and
Metallurgy Institute Bor ; editors Nada Štrbac, Dragana Živković. - Bor :
University of Belgrade, Technical Faculty, 2016 (Zaječar : Happy trend). -
XIX, 517 str. : ilustr. ; 25 cm

Tiraž 200. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-6305-047-1

1. Štrbac, Nada, 1964- [urednik]

a) Рударство - Зборници b) Металургија - Зборници

COBISS.SR-ID 226011916

Bor, Serbia, September 28 - October 01, 2016

SCIENTIFIC COMMITTEE

48th INTERNATIONAL OCTOBER CONFERENCE on Mining and Metallurgy

Prof. dr Dragana Živković (Serbia) – president,
Prof. dr Radoje Pantović (Serbia) – v. president,
Prof. dr Nada Štrbac (Serbia) – v. president,

Prof. dr Svetlana Nestorović (Serbia) †.

Dr Walter Valery (Australia),
Prof. dr Boyan Boyanov (Bulgaria),
Prof. dr Stoyan Groudev (Bulgaria),
Prof. dr Jelena Penavin Škundrić (B&H),
Prof. dr Sulejman Muhamedagić (B&H),
Prof. dr Mirsada Oruc (B&H),
Prof. dr Fathi Habashi (Canada),
Prof. dr Vladimir Krstić (Canada),
Prof. dr Yong Du (China),
Prof. dr Faruk Unkić (Croatia),
Prof. dr Mirko Gojić (Croatia),
Prof. dr Heikki Jalkanen (Finland),
Dr Jacques Yvon (France),
Prof. dr Aleksandar Dimitrov (FYR Macedonia),
Prof. dr Carl Heinz Spitzer (Germany),
Dr Srećko Stopić (Germany),
Prof. dr Costas Matis (Greece),
Prof. dr Dimitris Panias (Greece),
Prof. dr György Kaptay (Hungary),
Prof. dr Iwao Katayama (Japan),
Prof. dr Kemal Delijić (Montenegro),
Prof. dr Žarko Radović (Montenegro),
Prof. dr Krzysztof Fitzner (Poland),
Prof. dr Luis Filipe Malheiros (Portugal),
Prof. dr Sanda Krausz (Romania),
Dr Andrei Rotaru (Romania),
Prof. dr Dimitriu Sorin (Romania),
Prof. dr Petr M. Solozhenkin (Russia),
Dr Slavomir Hredzak (Slovakia),
Prof. dr Jakob Lamut (Slovenia),
Prof. dr Jožef Medved (Slovenia),
Dr Mirjam Jan-Blažič (Slovenia),

Prof. dr Seshadri Seetharaman (Sweden),
Dr Magnus Ericsson (Sweden),
Prof. dr Guven Onal (Turkey),
Prof. dr Onuralp Yucel (Turkey),
Prof. dr Batrić Pešić (USA),
Prof. dr Velimir Radmilović (USA),
Prof. dr Vladislav Kecojević (USA),
Dr Ana Kostov (Serbia),
Prof. dr Andjelka Mihajlov (Serbia),
Prof. dr Branka Jordović (Serbia),
Prof. dr Desimir Marković (Serbia),
Prof. dr Dragoslav Gusković (Serbia),
Prof. dr Duško Minić (Serbia),
Prof. dr Endre Romhanji (Serbia),
Prof. dr Karlo Raić (Serbia),
Dr Mile Bugarin (Serbia),
Prof. dr Milan Antonijević (Serbia),
Prof. dr Mile Dimitrijević (Serbia),
Dr Milenko Ljubojev (Serbia),
Prof. dr Mirjana Rajčić Vujasinović (Serbia),
Prof. dr Dragan Manasijević (Serbia),
Dr Miroslav Sokić (Serbia),
Dr Nadežda Talijan (Serbia),
Prof. dr Nenad Vušović (Serbia),
Prof. dr Nenad Radović (Serbia),
Prof. dr Nedeljko Magdalinović (Serbia),
Prof. dr Rodoljub Stanojlović (Serbia),
Prof. dr Svetlana Ivanov (Serbia),
Prof. dr Tatjana Volkov-Husović (Serbia),
Prof. dr Zoran Marković (Serbia),
Dr Zvonko Gulišija (Serbia),
Prof. dr Vitomir Milić (Serbia),
Prof. dr Vlastimir Trujić (Serbia),
Dr Vladan Čosović (Serbia),
Prof. dr Željko Kamberović (Serbia),
Prof. dr Živan Živković (Serbia)

ORGANIZING COMMITTEE

48th INTERNATIONAL OCTOBER CONFERENCE on Mining and Metallurgy

Prof. dr Nada Štrbac -president
Doc. dr Ljubiša Balanović
Doc. dr Ivana Marković
Prof. dr Svetlana Ivanov
Prof. dr Dragoslav Gusković
Prof. dr Dragan Manasijević
Prof. dr Snežana Urošević

Dr Ana Kostov
Doc. dr Vesna Grekulović
Doc. dr Srba Mladenović
Doc. dr Saša Stojadinović
Doc. dr Aleksandra Mitovski
Doc. dr Dejan Petrović
Doc. dr Milan Gorgievski

Doc. dr Milan Radovanović
M.Sc. Uroš Stamenković
M.Sc. Žaklina Tasić
Sandra Vasković, prof. eng.
Oliver Marković, dipl. ing. el.

Ivana Jovanović, Miomir Mikić, Srđana Magdalinović (Serbia) <i>Modeling of froth flotation processes by population balance approach – A short review</i>	297
Vesna Cvetković, Nataša Vukićević, Jasmina Stevanović, Jovan Jovićević (Serbia) <i>Magnesium oxide nanowhiskers electrochemically synthesized from nitrate melts</i>	301
Nataša Vukićević, Vesna Cvetković, Jasmina Stevanović, Jovan Jovićević (Serbia) <i>Alloy formation by Al and Nb electrodeposition from chloroaluminate low temperature melt</i>	305
Zoran Janjušević, Zoran Karastojković, Nikola Bajić, Mihailo Mrdak, Mileša Srećković (Serbia) <i>Characteristics of plasma and laser cladding on stainless steel for exhaust motor valves</i>	309
Zoran Slović, Tomislav Bradarić, Nataša Slović (Serbia) <i>The effect of (%Fetot. + %MnO) on final sulfur steel content at the end of Vd ladle treatment</i>	313
Anja Terzić, Marko Pavlović (Serbia) <i>Kinetics of gibbsite leaching in sodium hydroxide aqueous solution</i>	319
Stefan Đordiević, Marija Milivojević, Jelena Đorđević, Jelena Petrović, Radojka Jonović, Ljiljana Avramović, Radmila Marković (Serbia) <i>Heavy metals and arsenic in soil, corn and wheat from municipality of Bor, Serbia</i>	323
Uroš Stamenković, Svetlana Ivanov, Ivana Marković (Serbia) <i>Effect of ageing temperature on properties of EN-AW 6060 aluminium alloy</i>	327
Tamara Urošević, Zorica Sovrlić, Nevenka Petrović, Ivan Svrkota, Radmila Marković, Marija Milivojević, Jelena Petrović (Serbia) <i>Citrus fruits peels as biosorbent for sorption heavy metals, copper and zinc</i>	331
Predrag Stolić, Borislav Đorđević (Serbia) <i>Some considerations about development of future big data oriented file systems</i>	335
Stoja Rešković, Ivan Jandrlić, Tin Brlić (Croatia) <i>Stress distribution in deformation zone</i>	339
Sima Razmjooei, Mahmoud Abdollahy, Mohammad Reza-Khalesi, (Iran) <i>The effect of gas dispersion parameters on entrainment in mechanical flotation cells</i>	343
Zorica Sovrlić, Tamara Urošević, Radmila Marković, Tatjana Apostolovski-Trujić, Renata Kovačević, Kazutoshi Haga, Nobuyuki Masuda (Serbia) <i>Concentrations of anions and cations in the waste water in Bor municipality in different weather conditions</i>	347
Dragan Radulović, Ljubiša Andrić, Slavica Mihajlović, Vladimir Jovanović, Milan Petrov (Serbia) <i>Obtaining fillers based on limestone from deposit Možura" – Ulcinj, for applications in various industries</i>	351
Branka Kaluderović, Mileša Srećković, Milovan Janičijević, Dragana Vručinić, Aleksander Kovačević, Slobodan Bojanić, Dragan Druzijanić (Serbia) <i>Interaction of laser beams with carbon-based materials</i>	355
Branka Kaluderović, Vesna Mandušić, Đuro Čokeša, Vladimir Dodevski, Sanja Krstić, Dragana Vručinić (Serbia) <i>Carbonaceous material obtained by hydrothermal carbonization process – antimicrobial effects</i>	359

KINETICS OF GIBBSITE LEACHING IN SODIUM HYDROXIDE AQUEOUS SOLUTION

Marko Pavlović¹, Anja Terzić²

¹Faculty of Technology and Metallurgy, University of Belgrade, Karnegy st. 4, 11000 Belgrade, Serbia

²Institute for Testing of Materials IMS, Vojvode Mišića Bl. 43, 11000 Belgrade, Serbia

Abstract

In order to study the kinetics and mechanism of the reaction, laboratory leaching was carried out on industrially produced gibbsite γ -Al(OH)₃ in aqueous solutions containing an excess of sodium hydroxide. The results obtained reaction temperature, duration and base concentration varied. The basic parameters were determined from: the reaction rate constant $k=8.72 \cdot 10^7 \exp(-74990/RT)$ and the activation energy in the range $E_a=72.5-96.81 \text{ kJ/mol}$.

Keywords: leaching; mass transfer; kinetics; activation energy.

1. INTRODUCTION

Gibbsite leaching in an aqueous solution of NaOH is a heterogeneous process consisting of a chemical reaction and mass transfer to the boundary reaction area. Both processes may comprise a whole series of individual stages: it is generally known that the stage with the slowest rate determines the total reaction rate [1, 2]. In heterogeneous reactions where mass transfer plays an important role, the variables are numerous and complex [3, 4]. The reaction rate is influenced to a large extent by the positions of the phase boundary areas, which are determined by the structure of the solid, the dispersion level, porosity and geometrical characteristics of the reacting particles [5, 6]. Determinations of the reaction rate in a heterogeneous process, besides being of practical importance, provides the possibility of theoretical explanation of the rate constants and process development mechanism, which was the aim of this study in which the leaching process in industrial gibbsite was examined.

2. EXPERIMENTAL

Gibbsite γ -Al(OH)₃, produced industrially according to the Bayer process, was rinsed with distilled water until a negative reaction to phenolphthalein was attained, and then dried in a stream at 80°C. Grain size analysis was carried out with standard sieves for particles up to 100 µm. The composition of the gibbsite sample was determined by chemical analysis: 63.78% Al₂O₃; 34.26% H₂O; 0.55 SiO₂; 0.97% Na₂O and other impurities (TiO₂; ZnO; P₂O₅; MnO₂); total 100%. Na₂O may be due to the excess of rinse base, sodium aluminium silicate (because of the presence of O₂) or to the base built the gibbsite crystal itself.

Identification of gibbsite from DTA curves was carried out on the basis of endothermic peaks at 275°C, 375°C and 560°C. Total mass loss of 34.31wt% was observed in the temperature interval from 25-1000°C by thermogravimetry. Pure gibbsite phase was identified on the basis of the d values and the corresponding intensities in the X-ray patterns. The infrared spectrum of the sample indicated gibbsite on the basis of two absorption bands: $\nu(\text{OH})$ at 3500 and 3000 cm⁻¹ and $\delta(\text{OH})$ at 975 and 1025 cm⁻¹. In order to study the leaching kinetics in industrial gibbsite according to the reaction:



fluence of temperature, reaction duration and base concentration upon reaction rate was studied. The variable parameters were: leaching temperature, $T=323-363\text{K}$; sodium hydroxide concentration, $\rho=145.7-307.75\text{ g/cm}^3$; leaching duration, $\tau=300-900\text{s}$. The following parameters kept constant: grain-size composition, volume of NaOH solution (0.250dm^3), gibbsite mass fraction in the reaction mixture volume (80g/dm^3), stirring rate (1 s^{-1}). The experiment was carried out in a beaker flask (0.5dm^3) immersed in an oil bath to reach the operating temperature, the flask equipped with a thermometer and stirrer. The experimental method enabled the course of reaction to be followed under isothermal conditions from the beginning by determining the change in Al_2O_3 concentration in the liquid phase. The volumetric method according to [1] was used for analysis.

RESULTS AND DISCUSSION

Figure 1 shows the changes in Al_2O_3 concentration with time. The curves show that the reaction rate increases with increasing temperature. At lower temperatures, lower concentrations and longer leaching duration, the curves tend to increase slowly. At higher temperatures, the concentration increases more abruptly, while at the highest temperature (363K) the reaction reached equilibrium in very short time.

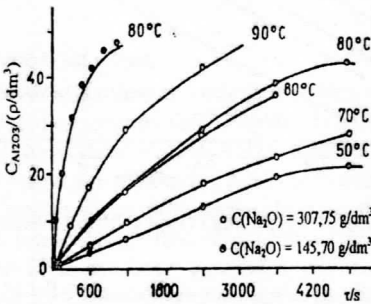


Figure 1 - ρ - τ curve of gibbsite leaching in NaOH solution

The logarithmic representation of the dependence of the logarithmic change in Al_2O_3 concentration on time yields straight lines as it is illustrated in Fig.2.

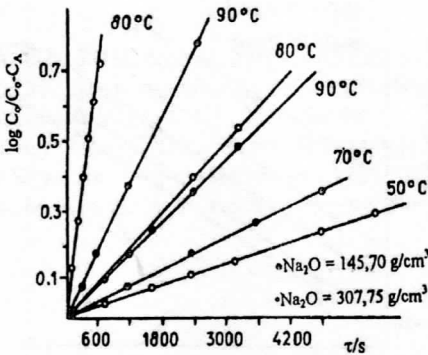


Figure 2 - Logarithmic changes of Al_2O_3 concentration for gibbsite leaching reaction in NaOH solution

The highest dispersion of the results was noticed for the highest NaOH concentration (307.75g/dm^3). This result may deviate due to a relatively high reaction rate at high NaOH

concentrations. It takes a certain time to initiate and to stop a chemical reaction, so the sampling error is greater if the reaction mechanism could change at higher concentrations, so that the assumed kinetic equation would no longer correspond to the actual mechanism.

Fitting of the Kazaev equation: $\alpha = 1 - \exp(-K \cdot \tau^n)$ to the data by means of the least square method (Fig.5 and Fig.6) yielded the parameter n , the values of which ranged from 0.89 to 1.0 (mean value 0.98 ± 0.08). According to Kazaev, the parameter n is determined by the mechanism of process development. For values greater than or equal to 1 the process takes place in the kinetic area and for smaller than 1 ($n=0.5$) in the diffusion area. As the mean value $n=0.98$ is very close to 1, it may be assumed that the gibbsite digestion process takes place in the kinetic area, i.e. the chemical reaction rate determines the total process rate [3,4].

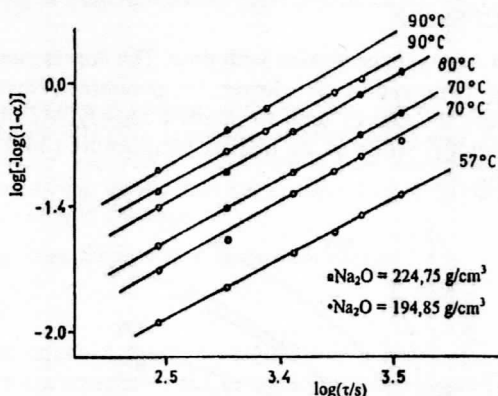


Figure 3 - The dependence of $\log[-\log(1-\alpha)]$ vs. $\log(\tau)$ for gibbsite leaching reaction in NaOH solution

The gibbsite leaching reaction rate at Na_2O concentrations of 145.70 g/dm^3 and 224.75 g/dm^3 doubles if the temperature increases 10 K. At 307.75 g/dm^3 of Na_2O the rate increases 3 times. This agrees with the known empirical fact indicated by Van't Hoff for reactions the rate of which are determined by the reaction stage. The Arrhenius plot of the temperature dependence of the rate constants is shown in Fig 3. The results of the least square computations are presented in Table 1.

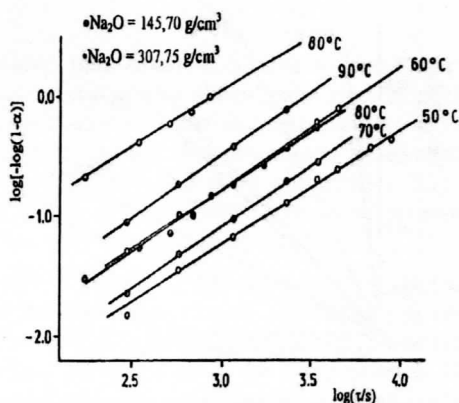


Figure 3 - Dependence of $\log k$ vs. $1/T$ for gibbsite leaching in NaOH solution of varying concentration

Table 1 - Process activation energy for gibbsite leaching

ρ (Na ₂ O) (g/dm ³)	Ea (kJ/mol)
145.70	72.57
194.85	75.97
224.75	76.45
307.75	96.81

activation energy gradually increases with increasing NaOH concentration up to the concentration of 224.75 g/dm³ Na₂O and at concentration of 307.75 g/dm³ Na₂O the activation energy is much higher. This could also be due to errors in determination of the concentration. The variation in the activation energy due to base concentration changes, which is small in the concentration interval from 145.70 to 224.75 g/dm³ Na₂O, allow calculation of the average activation energy for this concentration range $E_a = 74.99 \pm 3.7$ kJ/mol. The effect of the NaOH concentration upon the leaching reaction rate was not quantitatively studied, because the concentration of NaOH was not determined, which would be necessary for exact measurements, as stated by Schorford and Glastonbury [3].

CONCLUSION

Gibbsite leaching process takes place according to a first order kinetic equation, which was determined at the highest base concentration (307.75 g/dm³ Na₂O). This fact might be due to the experimental errors in determination of the concentration or to changes in the reaction mechanism. The calculated value for parameter n of the Kazaev equation is 0.98 ± 0.08 , which indicates that the gibbsite leaching reaction takes place in the kinetic area, i.e. the chemical reaction rate determines the total process rate. The gibbsite leaching reaction rate doubles if the temperature increases by 10 K in the base concentration range from 145.70 to 224.75 g/dm³ Na₂O, which is in accordance with the well-known empirical fact reactions the rates of which are determined by the chemical reaction rate. The average activation energy value for the gibbsite leaching process, calculated using the Arrhenius equation, has the following form: $74.99 \cdot 10^3 \exp(-74990/RT)$.

REFERENCES

- S. Ruan, L. Shi, J. Li, A. Gerson, Hydrometallurgy, 163 (2016) 1-8.
- A.V. Bekker, T.S. Li, I. Livk, Hydrometallurgy, doi:10.1016/j.hydromet.2016.06.002
- L. Bao, A. Nguyen, Hydrometallurgy, 104:1 (2010) 86-98.
- A. Zhao, Y. Liu, T. Zhang, G. Lu, Z. Dou, T. Nonferr. Metals Soc., 23:1 (2013) 266-270.
- B. Xu, P. Smith, L. De Silva, Int. J. Mineral Process., 122 (2013) 22-28.
- M. El Hazek, F. Ahmed, M. El Kasaby, R. Attia, Hydrometallurgy, 90:1 (2008) 34-39