# Light Metals 2024

Edited by SAMUEL WAGSTAFF





Samuel Wagstaff Editor

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# **Preface**

It is with great pleasure and honor that I present to you the *Light Metals 2024 proceedings*. This collection of manuscripts serves as a time capsule for later researchers to not only see how we approach technical problems but also what we value and esteem as an industry. The challenges the industry faces today around energy efficiency and sustainability represent difficult obstacles not unlike those faced by our forefathers previously. By contributing to these proceedings, authors have committed themselves to advancing the collective whole of the industry over any individual gain. The problems we face today are more than any one of us can handle individually. The key does not lie in a single technological breakthrough, derivation, or calculation. Instead, as we look at the exciting breakthroughs happening around us today, we can see that it is through cross-industry collaboration that the greatest strides are made. This is largely the magic of TMS. Each year we gather as an industry to discuss contributions we have all made to making things better than they were the year before.

The *Light Metals 2024* proceedings embody countless hours of work supplied by the volunteer Symposium Organizers, Session Chairs, Reviewers, and TMS staff who labor tirelessly to bring this tome into fruition each year. Of course, this collection of articles would be empty without the contribution of the individual authors, whose work brings us together this year. Special thanks and acknowledgment also go out to the symposium chairs of the five technical symposia assembled for 2024. I would like to offer my personal thanks to Michael Coley, Nabeel Aljallabi, Julien Lauzon-Gauthier, Anne Kvithyld, Tao Wang, Christopher Hutchinson, Sazol Das, and Timothy Langan. Without their invaluable help, none of this would have happened. The consistent guiding efforts of TMS staff have been integral as always this year. Patricia Warren and Trudi Dunlap were there every step of the way making sure that neither deadlines nor quality were allowed to slip.

There are exciting times ahead. With unprecedented expansion projects, bold sustainability targets, and expanding markets, I cannot wait to see the new developments about to touch off. I invite you all to read these proceedings with a spirit of growth and collaboration in your heart. As you seek to create partnerships and discuss these proceedings with colleagues, I hope we will continue to see great leaps in science and innovation.

Samuel Wagstaff

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# **About the Editor**



Samuel Wagstaff is currently a partner at Oculatus Consulting, specializing in aluminum processing and product development. He holds degrees in Mechanical Engineering from Cornell University (B.S.) and Materials Science from MIT (M.S., Sc.D.). Previously as the Lead Scientist at Novelis, he led new product and process development for the entire R&D ecosystem across three continents. Currently, Dr. Wagstaff focuses on increasing profitability and productivities of nonferrous products by process improvement and fundamental research. He has helped to design over 1 million tons of recycle capacity in the aluminum sector and is the author of over 35 patents. Dr. Wagstaff is currently serving as the principal investigator on a \$1M ReMADE grant to develop technology to improve the recyclability of organic laden aluminum scrap and is involved in much of the industrial expansion of the aluminum sector in North America. In his private life Sam enjoys being with his wife, hunting, fishing, and scuba diving.

# **Program Organizers**

### Alumina & Bauxite



**Michael Coley** is a Lecturer and Section Head of the Applied Chemistry Division, Department of Chemistry, The University of the West Indies, Mona, Jamaica. He has a Ph.D. in Chemistry and teaches Industrial, Analytical and Environmental Chemistry. Dr. Coley's research interests include Air Quality and Renewable Energy however he is especially involved in Bayer Process Technology research. His areas of focus include alumina precipitation, the management of process impurities, and the development of strategies for processing marginal bauxites. Over the last 20 years, he has worked on several major projects that involve study of Jamaican bauxites and has reported on his work at major conferences and in academic journals. Dr. Coley enjoys mentoring and is the senior Undergraduate Coordinator for his Department. He is married and has two daughters.

### Aluminum Alloys: Development and Manufacturing



**Christopher Hutchinson** is a Professor in the Department of Materials Science and Engineering at Monash University in Melbourne, Australia, and co-Chair of the Woodside Energy FutureLab at Monash University. He received his Ph.D. from the University of Virginia in the USA, and after several post-doc years at Grenoble Institute of Technology in France, joined the faculty at Monash. His work covers both the relationship between processing and structure, and structure and properties of engineering alloys with a large fraction of his activities on steels, stainless steels, aluminum, and copper and brasses. The coupling of modelling and experiment, wherever possible, is a priority for his approach to problems. Approximately half of his research is funded in association with industry and half from fundamental agencies such as the Australian Research Council. He is an Editor of Acta Materialia and Scripta Materialia.

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**Sazol Das** is an R&D Leader at Novelis Global Research and Technology Center, Kennesaw, GA, USA. He has over 16 years of experience in Product & Process Development, Diffusion Kinetics, Thermodynamic Modeling, Electronic Materials Packaging, and Thin Film Coating. Dr. Das graduated from McGill University, Montreal, QC, Canada with a Doctoral Degree in Materials Engineering. He is a certified agile Scrum Master and Product Owner who enjoys mentoring, empowering, and inspiring young professionals in their career advancement.

### **Aluminum Reduction Technology**



Nabeel Al Jallabi has been a Sr. Manager in Process Control and Development for 30 years with Alba. He has worked in different disciplines including Reduction Lines, Process Control and Development, and Operation Support Services. Al Jallabi has played instrumental roles in many projects including Reduction Lines 1–3 conversion from side break to point feed system, Reduction Lines 3 expansion, Reduction Line 5 commissioning, KA increase across Reduction Lines, lean manufacturing along with the McKinsey team, SPL detoxification and recycling project, Reduction Line 6 commissioning, and Reduction Line 5 restart. Al Jallabi has participated in many conferences as an author and delegate including TMS, ICSOBA, and Australasian. Al Jallabi's educational background includes a BSc in Mechanical Engineering, MCs in Aluminum Smelting Technology, and an MBA.

### **Electrode Technology for Aluminum Production**



Julien Lauzon-Gauthier is a Sr. research engineer at Alcoa, within the Operational Excellence smelting technology development group. He is responsible for the development and deployment of new technology and process optimization linked to anode manufacturing for Alcoa's carbon plants. He is a chemical engineer and holds an M.Sc. and Ph.D. from Université Laval in Canada. His postgraduate work focused on multivariate statistics and machine vision applied to the anode manufacturing process. Dr. Lauzon-Gauthier also held different process engineer roles at Alcoa smelters in Canada before joining the technology development team. He has published his work in scientific journals and at the TMS annual meeting and received the TMS Light Metals Division Young Leaders Professional Development Award in 2020 as well as the Electrode Technology best paper award in 2021.

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### Melt Processing, Casting and Recycling



Anne Kvithyld is a senior research scientist at SINTEF, Norway, where she has been since 2007. Her research interests are centered around refining and recycling of metals. She earned her Ph.D. entitled "Thermal Decoating of Aluminium Scrap" in 2003. She has been a Visiting Post.Doc at the Colorado School of Mines, USA, and was the winner of the 2011 Vittorio de Nora Award for Environmental Improvements in Metallurgical Industries. She is the co-author and co-editor of the book *Principles of Metal Refining and Recycling* published in 2021 and an active member of The Minerals, Metals & Materials Society (TMS).



**Tao Wang** currently holds the position of Technical Marketing Manager-Atlantic at Rio Tinto focusing on aluminum product development and customer technical support. Before joining Rio Tinto, he served as a chief metallurgist in the steel industry. He has over 10 years of experience in product/market development and has published more than 20 journal papers and 8 patents related to metal casting, rolling, and heat treatment. Tao holds a Ph.D. degree in metallurgical engineering from The University of Alabama, and a bachelor's degree in materials science and engineering from Jiao Tong University in China.

Scandium Extraction and Use in Aluminum Alloys



**Timothy Langan** began his career at Martin Marietta developing advanced aluminum alloys for space and Marine applications. He received his Ph.D. in Materials Science from Johns Hopkins University. Dr. Langan is currently working with Sunrise Energy Metals to develop applications for scandium that will be produced from its Sunrise Project in New South Wales, Australia. In this role, Dr. Langan is working with industrial partners to guide, develop, and focus research efforts on aluminum-scandium alloys at universities including Deakin University, Michigan Technological University, Monash University, and Chongqing University.

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Frank Palm is a Senior Expert (1990-present) in metallic materials and processes focusing on welding and additive manufacturing for Airbus Central Research & Technology (CR&T). He is a dedicated and passionate specialist in the aerospace technology field, including failure analyzes with a strong current focus on metallic additive manufacturing (laser powder bed fusion material and process fundamentals), elaborating the prospects of Sc in Al-alloy applications for more than 25 years. Over the past 30 years, he has initiated, written, contributed, and published nearly 100 presentations and scientific papers. His background includes mentoring, teaching, and accompanying 12 Airbus in-house Ph.D. theses and about 50 diplomas, masters, and bachelor's theses. He caused more than 30 invention filings and Airbus-related patent applications and, together with Airbus, currently holds more than 15 patents in the field of additive manufacturing, metallic materials technology, and integral aircraft fuselage constructions (e.g., Scalmalloy®—AlMgSc alloy concept for Additive Manufacturing (brand and patent)).

He is a member of the German Engineering Community (VDI), the American Society of Materials (ASM), and of the German Welding Society (DVS). In the frame of the publicly hosted German Research Community (IGF) he has served for more than 10 years voluntarily as an appointed project consultant and assessor.



**Thomas Dorin** is a Senior Research Fellow at Deakin University and the leader of the aluminum research group. Dr. Dorin has a distinct specialization in the incorporation of scandium in aluminum alloys.

After gaining his Ph.D. from the University of Grenoble in 2013, Dr. Dorin has been instrumental in the development of innovative aluminum alloys, with his work leading to multiple patents and influential research papers. Among his many accolades, he was awarded the esteemed ICAA16 Early Career Researcher award in 2018. Additionally, he was recognized with the Discovery Early Career Researcher Award by the Australian Research Council in 2019. Dr. Dorin was an organizer and co-chair of the TMS symposium titled "Scandium Extraction and Use in Aluminum Alloys" in both TMS2023 and TMS2024. Dr. Dorin has co-authored 47 journal papers, 21 conference papers, 3 book chapters, and holds 4 patents. Furthermore, his work has been cited over 1800 times, with an h-factor of 22.

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Paul Rometsch obtained his Ph.D. in Materials Engineering at the University of Queensland, Australia, and has published widely in the field of aluminum metallurgy. He has held various academic and industrial positions focused on R&D within the global aluminum industry, including appointments at Comalco Aluminium (Australia); the University of Southampton and the Luxfer Group (UK); Hydro Aluminium Precision Tubing (Europe and China); and Monash University (Australia). Since 2018, Paul is has been a Principal Research Scientist with Rio Tinto Aluminium, where he currently works on aluminum product metallurgy at the Arvida Research and Development Centre in Saguenay, Québec (Canada).



**Henk van der Laan** is a senior consultant and owner of Van der Laan International Consultancy BV (V.I.C.). Henk was born in 1954 in Rotterdam, The Netherlands. Henk has worked 44 years in the aluminum industry of which 34 years at KBM Affilips BV as an international sales manager for specialty alloys and master alloys in the non-ferro industry. The last 15 years he has been active as specialist for critical metals like magnesium, titanium, and scandium. Henk studied Metallurgy in Utrecht and Business Economics in Rotterdam and Industrial Marketing in Arnhem, all in The Netherlands. As a metallurgist he specializes in the grain refining mechanism of aluminum titanium boron, which is the main product of KBM. Besides his passion for aerospace, astronomy, aluminum, and scandium, Henk is an active mountain biker, golfer, and a fan of all kinds of sports like soccer, cycling, and formula 1.



Efthymios Balomenos studied Mining and Metallurgical engineering at National Technical University of Athens and received his Ph.D. degree in Thermodynamics in the same school in 2006. Since 2008 he has been working in the Laboratory of Metallurgy as a postdoc researcher focusing on sustainable process development, CO<sub>2</sub> mitigation strategies, exergy analysis, and resource utilization efficiency. He is involved in the research management and coordination of several collaborative large scale research projects (ENEXAL, EURARE, SCALE, ENSUREAL, RemovAl, BIORECOVER, AlSiCaL, SISAL PILOT, HARARE, and ReActiv) most of which focus on Bauxite Residue valorization or alumina production. He has more than 80 research publications in journals and conference proceedings with more than 1,000 citations and an h-index of 19. Since 2015, he has cooperated with MYTILINEOS-Metals as a senior consultant on R&D projects. He was a recipient of the TMS Light Metals Subject Award – Alumina & Bauxite in 2017 and since 2022 he has been on ICSOBA's board of directors.

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Muhammad Akbar Rhamdhani is currently the Director of Fluid and Process Dynamics (FPD) Group; and Program Leader of Net Zero Carbon Materials and Processes (Manufacturing Future Research Platform) at Swinburne University of Technology, Australia. Dr. Rhamdhani is a Professor in Extractive Metallurgy and Metals Recycling and obtained his Ph.D. from McMaster University, Canada, in Materials Science and Engineering. He was a teaching-research academic at the Institute of Technology Bandung (ITB) and the University of Queensland, before joining Swinburne. Dr. Rhamdhani was a Visiting Professor at Katholieke Universiteit Leuven Belgium and a Visiting Scientist at CSIRO. He is also currently an Adjunct Professor at the Faculty of Engineering, Universitas Indonesia.

Dr. Rhamdhani's research expertise is on advanced metal/material refining and impurities removal (e.g., in steel, aluminium, magnesium, silicon, nickel, and minerals); development of new processes for metal production; thermodynamics and kinetics of high temperature metal and chemical processes; and physical chemistry of interface. Dr. Rhamdhani's current research directions include: (1) recycling and recovery of metals from urban resources (e-waste, end-of-life alkaline and lithium ion batteries, solar panel, permanent magnet; (2) decarbonization and hydrogenation of metallurgical processes; (3) pyrometallurgical processes of rare earth elements (REE) minerals; (4) solar metallurgy (the use of concentrated solar thermal energy for minerals and metals processing); and (5) astro metallurgy (extra-terrestrial minerals and metals processing; e.g., metals extraction on Mars and Lunar).

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Part I Alumina & Bauxite



# **Chemical Thermodynamics and Reaction Kinetics of Bayer Process Desilication**

Hong Peng, James Vaughan, Sicheng Wang, John Vogrin, and Dilini Seneviratne

### **Abstract**

With increasing amount of high silica bauxites used as Bayer refinery feed, the re-precipitation of dissolved silicates results in greater volumes of desilication product (commonly known as DSP) which corresponds to elevated caustic consumption and issues with bauxite residue neutralisation and storage. Furthermore, incomplete desilication of pregnant Bayer liquor also results in silicate reactor and piping scaling as well as the possibility of contamination of the alumina product. Optimization of silicate management in the Bayer process is therefore a high priority. Understanding the chemistry of silicate leaching and precipitation of silicate in Bayer process underpins potential process improvements. This literature review summarises the chemistry of DSPs, with a focus on chemical-thermodynamics and reaction kinetics.

### Keywords

Desilication products • Bayer process • Sodalite • Solubility • Bauxite

### Introduction

Since the Bayer process was patented in 1888 by Australian chemist Karl Bayer, this technology has been the major industrial process for the producing of alumina from bauxite ores [1, 2]. Even after 135 years, this process remains unchanged for four major key sections: digestion of aluminarich minerals (gibbsite, boehmite, and diaspore) into hot caustic solution, clarification of the insoluble phases (bauxite

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residue/red mud), and precipitation of gibbsite and calcination of the gibbsite to alumina.

Bauxite is also comprised of iron phases such as goethite and hematite, titanium oxides, clay minerals comprised of quartz (SiO<sub>2</sub>), and kaolinite (Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O) as well as other impurities such as organics [1, 3, 4]. During bauxite digestion, in addition to extraction of aluminium from bauxite ores (Eqs. 1 and 2), there is also the desilication products (DSP) from clay minerals in solution as shown by Eqs. 3 and 4.

### **Alumina-Bearing Minerals Digestion**

$$\frac{Al(OH)_3(s)}{gibbsite} + NaOH(a) \Leftrightarrow NaAl(OH)_4(a)$$
 (1)

$$\begin{array}{l} \frac{AlOOH(s)}{diaspore/Boehmite} \ + \ NaOH(a) + \ H_2O(a) \\ \Leftrightarrow \ NaAl(OH)_4(a) \end{array} \eqno(2)$$

The reactive silica in the bauxite, mainly kaolinite, reacts with the sodium hydroxide to form the sodium metasilicate solution. Once sufficiently supersaturated, the silicates then re-precipitate as insoluble sodium aluminosilicate DSP. Based on the different types of X anions and solution temperature, DSP could be hydroxysodalite, Cl-sodalite and cancrinite [1, 5, 6]. While DSP is costly, it plays a beneficial role in the Bayer process in terms of purifying the liquor of impurities such as sulphate, carbonate, and chloride, and therefore a certain amount of DSP is helpful to ensure a high degree of recyclability of the Bayer liquor.

### **Reactive Silica Dissolution**

$$\frac{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O}{kaolinite} + 6NaOH \\ \Leftrightarrow 2Na_2SiO_3 + 2NaAlO_2 + 5H_2O$$
 (3)

### **Dissolved Silica Precipitation**

$$\begin{aligned} 6\text{Na}_2\text{SiO}_3 \ + \ 6\text{NaAlO}_2 \ + \ \text{Na}_2\text{X} \ + \ 12\text{H}_2\text{O} \\ & \Leftrightarrow \frac{\Delta T}{3(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O})\text{Na}_2\text{X}}{\text{Bayer} - \text{sodalite}} \ + \ 12\text{NaOH} \end{aligned}$$

$$X = OH^{-}, Cl^{-}, SO_4^{2-}$$
 and  $CO_3^{2-}$ .

The principles of Bayer desilication have been described in many studies [7, 8]. Impurities in bauxite dissolve and accumulate in the Bayer circuit, contributing to an array of process issues thus making it difficult to operate and control [9] with silicate phases being a primary contributor. Silicates such as kaolinite, halloysite, chamosite, and quartz exhibit different solubilities and reaction kinetics [1, 10]. Quartz typically does not significantly dissolve during the extraction of alumina from bauxite, unless the grain structure is fine and the digestion temperature and residence time are high. However, if quartz does dissolve it is especially costly as it leads to additional loss of dissolved aluminium. Halloysite is reactive but tends to be a minor component if present at all. Kaolinite is the most commonly found reactive silica and dissolves readily in caustic soda [5, 11, 12]. In the absence of crystallization seed, most of the reactive silica forms soluble sodium silicate which then precipitates as DSP during the predesilication and digestion stages of the Bayer process [13].

This review summarises the factors that influence thermodynamics solubility and kinetic DSP crystallisation, and mineral phase transformation during Bayer processes. The objective is to bring together the relevant fundamental information about reaction equilibrium and kinetics to enable the optimisation or improvement of predesilication and digestion in terms of economic and environmental outcomes

# Thermodynamic Research of Desilication Products

Despite several empirical solubility correlations proposed for silicates [14, 15], there is a lack of reliable chemical-thermodynamic data relevant to the Bayer process. This data is essential for predictive solubility modelling of DSPs. Only a single report has been found on the measurement of thermodynamic data for anhydrous sodalite (Na<sub>6</sub>(Al-SiO<sub>4</sub>)<sub>6</sub>\*NaCl<sub>2</sub>) by Komada et al. [16]. Using the group contribution method for calculating properties such as enthalpies, free energies of formation, and heat capacities proposed by Mostafa et al. [17, 18], Park and Englezos [19] estimated the equilibrium constant for sodalite solubility as it was not available in the literature. The results showed that the equilibrium constant ln(*K*) was 88.7 with large

uncertainty  $\pm 10.4$  with 95% confidence level. The major contribution in the uncertainties was due to the uncertainty in the Gibbs energy of formation of the DSP phase. Later, Moloy et al. [20] reported the formation and hydration enthalpies of the hydroxysodalite family by hydrothermally synthesising the material from a zeolite phase. More recently, Zeng and Li [21] determined the solubility of sodalite in NaOH-NaAl(OH)<sub>4</sub> solutions at temperatures between 30 and 75 °C by dissolving synthetic sodalite into solution. By data regression, they reported sodalite enthalpies and Gibbs energies of formation at standard conditions. For cancrinite, Kurdakova et al. [22] estimated the thermodynamic properties of synthetic sodium carbonate cancrinite at 27 °C using the reported thermodynamic data for calcium cancrinite by Liu et al. [23] and Ogorodova et al. [24]. In this section, the solid (synthesised under hydrothermal conditions) is different from the phases that would be formed during the Bayer process. No reports have been identified that include the enthalpies and Gibbs energies of formation for sodalite and cancrinite at Bayer process conditions. Furthermore, there is no reliable report of the heat capacity temperature relationship for the high-alumina, semicrystalline DSPs forming in the Bayer process.

### **Empirical Solubility Models**

The equilibrium concentration of sodium aluminosilicate in sodium aluminate solutions has been the subject of a number of studies. There is a considerable amount of evidence in literature to suggest that the desilication kinetics are directly proportional to the liquor SiO<sub>2</sub> supersaturation ratio. Therefore, in order to optimise desilication it is important to accurately predict equilibrium SiO<sub>2</sub> values. The supersaturation ratio is defined in Eq. 5 [25]:

$$\sigma = \frac{\left[\text{SiO}_2\right]_t - \left[\text{SiO}_2\right]_{\text{eq}}}{\left[\text{SiO}_2\right]_{\text{eq}}} \tag{5}$$

where  $[SiO_2]_t$  is the silicate concentration (expressed as  $SiO_2$  equivalent) at time t and  $[SiO_2]_{eq}$  is the equilibrium silicate concentration. Previous research has led to development of models predicting equilibrium silicate concentration. However, most of these models are empirical in nature and not based on any experimentally determined thermodynamic parameters, which strictly limits their application to a set range of factors such as temperature, solution ionic strength, caustic concentration, and liquor impurities [26]. Models used in industry (which are confidential and therefore not published) are also limited to their specific refinery due to the empirically determined nature [27]. When conditions fall outside their parameterisation, the model predictions become almost meaningless [28]. Fundamental understanding of

silicate precipitation behaviour and accurate prediction of the products could enable novel, efficient methods of desilication to be realised. Table 1 outlines the correlations for  $SiO_2$  solubility in open literature and their range of applicability. As these are empirical models, they have expressed the equilibrium concentration of silicate as  $[SiO_2]_{eq}$ .

### **Thermodynamics Solubility Models**

Outside of empirical correlations, only a few studies have attempted to construct a silica solubility model from a thermodynamics perspective. The earliest thermodynamic-based model found in literature was created by Jamialahmadi and Müller-Steinhagen [10]. They used the equilibrium constant for the precipitation reaction in Eq. 6 to provide a fit to experimental data.

$$K_c(T) = \frac{[\text{NaOH}]^2}{[\text{Na}_2 \text{SiO}_3][\text{NaAlO}_2][\text{H}_2 \text{O}]}$$
(6)

A later study by Park and Englezos modelled silicate solubility from a chemical-thermodynamics perspective at conditions applicable to Kraft pulp mills. In their model, a slightly different precipitation reaction was used to give the corresponding equilibrium constant in Eq. 7 [19]:

$$K_c(T) = \frac{\alpha_{\text{H}_2\text{O}}^4(m_{\text{OH}^-}^{12}\gamma_{\text{OH}^-}^{12})}{(m_{\text{N}a^+}^8\gamma_{\text{N}a^+}^8)(m_{\text{Al}(\text{OH})_4}^6\gamma_{\text{Al}(\text{OH})_4}^6)(m_{\text{SiO}_3^{-2}}^6\gamma_{\text{SiO}_3^{-2}}^6)}$$
(7)

Although both models were reported to have good predictions, they consistently predicted higher values than the measured data, especially at higher temperatures. When considering solubility from thermodynamic first principles, the equilibrium product  $K_p$  is dependent exactly on the nature of the chemical species. Given newly understood speciation, the equilibrium constant  $K_c$  can be written as Eq. 8 which considers silicate species in terms of  $\mathrm{H_2SiO_4}^{2^-}$  molality—the predominant silicon ion in Bayer process conditions [36]:

**Table 1** Correlations for silicate equilibrium solubility

Author	Correlation	Range of applicability
Adamson et al. [29]	$SiO_2 = 2.6 \times 10^{-5} [Na_2O][Al_2O_3]$	Not stated
Smirnov [30]	$SiO_2 = 2 + 6.6 \times 10^{-4} [Al_2O_3]^2 - 3.3 \times 10^{-2} [Al_2O_3]$	T = 298-368  K [NaOH] = 12-378 g/L [Al(OH) <sub>3</sub> ] = 13- 431 $g/L$
Leiteizen [31]	$SiO_2 = 1.28 \times 10^{-5} [Na_2CO_3][Al_2O_3]$	Not stated
Cresswell [32]	$SiO_2 = 0.1587 - 6.058 \times 10^{-4} T(^{\circ}C) - 2.078 \times 10^{-3} [Na_2CO_3] + 9.156 \times 10^{-6} [Na_2CO_3]^2 + 9.509 \times 10^{-6} [Na_2CO_3]T(^{\circ}C)$	T = 373-513  K [NaOH] = 136 g/L [Al (OH) <sub>3</sub> ] = unknown
Hewett et al. [33]	$SiO_2 = 1.44 \times 10^{-5} [Al_2O_3]^2 + 1.85 \times 10^{-4} T(^{\circ}C) + 2.97 \times 10^{-4} [NaOH]$	T = 328-460  K [NaOH] = 50-190 g/L [Al(OH) <sub>3</sub> ] = 69- 275 g/L
Smith et al. [34]	Below 180 °C: $SiO_2 = 2.67 \times 10^{-3} [Al_2O_3] + 1.18 \times 10^{-4} [Na_2CO_3]$ Above 180 °C: $SiO_2 = 2.67 \times 10^{-3} [Al_2O_3] + 1.18 \times 10^{-4} [Na_2CO_3] + 2.5 \times 10^{-3} (T - 100)$	T = 373-523  K [NaOH] = 113-226 g/L [Al(OH) <sub>3</sub> ] = 69- 321 g/L
Sizgek and Aguila [35]	$SiO_2 = 1.82 \times 10^{-6} [Na_2CO_3]^2 + 3.37 \times 10^{-13} [Na_2CO_3]^2 T^3 (^{\circ}C) + 2.08 \times 10^{-5} [Na_2CO_3]^2 (A/C)^3$	T = 373-523  K [NaOH] = 121-196 g/L [Al(OH) <sub>3</sub> ] = 97- 302 g/L
Barnes et al. [14]	$SiO_2 = -2.26 \times 10^{-3} [Al(OH)_3]^{0.5} + 2.42 \times 10^{-4} [NaOH] + 6.66 \times 10^{-4} [Al(OH)_3] [NaOH] + 1.47 \times 10^{-5} T(^{\circ}C) - 1.77 \times 10^{-3}$ (All concentrations in mol/L)	T = 363-493  K [NaOH] = 155-217 g/L [Al(OH) <sub>3</sub> ] = 108-174 g/L

Where all the concentrations are in g/L of that compound unless otherwise stated