DEPOSITION OF SILICA IN HYDROMETALLURGICAL PROCESSES

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\textbf{Summary:}

Introduction/purpose: Dissolution of nonferrous metals from oxidic ores such as laterite, high silicon bauxite and eudialyte during acidic treatment was connected with silica gel formation.

Methods: Familiarity with behavior of silica in hydrometallurgical processes such as dissolution at atmospheric and high pressure, precipitation, neutralization and filtration is most important for the recovery of metals from water solution.

Results: Gel formation was avoided using dry digestion and a carbonation process of olivine under high pressure in an autoclave.

Conclusion: Fine silica was prepared from olivine in water solution at 175°C and 120 bar for 4 hours in an autoclave using some additives such as sodium bicarbonate and oxalic acid.

Key words: silicon, hydrometallurgy, gel, silica.

Introduction

Nanosilica has sparked strong interest in hydrometallurgy. Controlling silica deposition during hydrometallurgical processes has high significance for metal recovery.

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During acid pressure leaching of ores containing silicates, pregnant liquor becomes saturated with silica. Nanosilica has caused strong interest among researchers due to its interesting properties for biomedical and catalytic applications. Its synthesis can be realized by using geo-resources like olivin, nickeliferous laterites, bauxite or other high silica containing minerals. In all cases, common acidic leaching leads to gel formation which hinders an efficient synthesis process. This literature review aims at an alternative method avoiding this effect by disclosing the controlling mechanisms. The hypothesis presented is based on the preliminary experimental results accidentally obtained by the carbonation treatment of olivin minerals in the frame of a carbon capture sequestration (CCS) research results.

Silica gel formation

The treatment of silicate based ores with different acids under atmospheric pressure leads to the formation of silica gel and breaking of a leaching process. Silica gel represents an amorphous and porous form of silicon dioxide consisting of an irregular tridimensional framework of alternating silicon and oxygen atoms with nanometer-scale pores (Zulfiqar et al, 2016, pp.91-96). The dissolution of silicon from quartz or amorphous silica involves hydrolysis in the access of water to form monosilicic acid (as shown in Eq. 1). The supersaturation of Si(OH)\(_4\) is required for polymerization (Queneau et al, 1983). The formed precipitate represents polymerized silica in the form of a colloid, a precipitate or a gel, as shown in Figure 1.

\[
\text{SiO}_2 (s) + 2 \text{H}_2\text{O} = \text{Si(OH)}_4 (aq) \quad (1)
\]

![Formation of silica gel](image.png)

**Figure 1 – Formation of silica gel**

**Рис. 1 – Гелеобразование из диоксида кремния**

**Слика 1 – Формирање гела од силицијум-диоксида**
Similarly, high Si content in aluminium laterites makes these resources untreatable with acid leaching routes again due to the formation of silica gel. Alkan et al (2019, pp.266-272) studied the effects when such materials are exposed to sulfuric acid at room temperature. An empirical dry digestion-leaching model was proposed for each starting material in a comparative manner in order to prevent the formation of silica gel using sulfuric acid. As shown in Figure 2, avoiding gel formation is possible using hydrogen peroxide during acidic leaching. Nevertheless, despite this positive result, no nanosilica was formed.

![Figure 2 – Silica gel formation mechanism and precipitation (Alkan et al, 2019, pp.266-272)](image)

Eudialyte is a further example due to its good solubility in acid as it contains more than 50% of silica. The treatment of eudialyte leads again to strong silica gel formation during a treatment with some acids (Ma et al, 2019, pp.2-13). Ma et al (2018, p.267) studied neural network modeling for the optimization of the extraction process by dry digestion.
avoiding the formation of silica gel in the presence of hydrochloric acid, but again without nanosilica presence, as shown in Figure 3.

In a method by Olerud (1998) for manufacturing silica, the leaching of natural silicates (Olivin) is performed with hydrochloric acid or other mineral acids at 110°C, followed by draining, drying and possibly grinding up of the residue of the product obtained (US Patent 5,780,005), as shown in Fig. 4.

In order to obtain spherical silica with a controlled particle size and surface characteristics, a mineral (Mg₂SiO₄) was used with the highest possible degree of purity. The product is colloidal amorphous silica in the form of a gel. The silica gel is separated from the liquid by pressure filters, washed clean of acid remains, dried and ground. The extraction of silica gel and magnesium compounds from olivine is proposed by Hansen and Zander (2011) who used sulphuric acid in a thermal treatment at temperature between 150 and 400°C (European Patent EP 1373 139 B1) for 4 to 12 hours.
Current synthesis methods for nanosilica

Development of ceramic nanoparticles such as silica, alumina and titania with improved properties has been studied with much success in several areas such as synthesis and surface science (Hansen & Zander, 2011), (Stopic et al, 2013, pp.3633-3635). Advancement in nanotechnology has led to the production of nanosized silica which has been widely used as a filler in a catalysis and glass industry. Silica particles extracted from natural resources contain metal impurities and are not favorable for advanced scientific and industrial applications.

The sol-gel process is widely applied to produce silica, glass, and ceramic materials due to its ability to form pure and homogenous
products at mild conditions. The process involves hydrolysis and condensation of metal alkoxides (Si(OR)$_4$) such as tetraethylorthosilicate (TEOS, Si(OEt)$_4$) or inorganic salts such as sodium silicate (Na$_2$SiO$_3$) in the presence of a mineral acid (e.g., HCl) or a base (e.g., NH$_3$) as a catalyst (Rahman & Padavettan, 2012, pp.1-15). The synthesis of spherical hollow silica particles from the sodium silicate solution with boric acid or urea as an additive was carried out by the ultrasonic spray pyrolysis method. This work dealt with the effect of four parameters (concentration of boric acid and urea, feed rate of a reactant, reaction temperature, and time) on the particle size and the standard deviation. As a result, the mean particle size and the standard deviation decreased with increasing of all parameters except urea (Kim et al, 2005, pp.193-198). Ratanathavorn et al (2018, pp.1-5) studied the silica nanoparticles synthesis by the ultrasonic spray pyrolysis (USP) technique using tetraethylorthosilicate (TEOS) as a precursor in order to produce a fixative material for cream perfume formulation. The results showed that the synthesis temperature of 500 °C provided the smallest size of silica nanoparticles, about 106 nm. The particle size decreased from 347 nm to 106 nm when the synthesis temperature increased from 300 °C to 500 °C.

Ultra-small hollow silica nanoparticles were synthesized using the prepared amorphous calcium carbonate (ACC) particles as a template. The ACC particles were firstly prepared by the carbonation method, where the procedure was conducted in the methanol solvent to form Ca(OCH$_3$)$_2$ layers on ACC particles. The methanol concentration effect on the morphology of ACC particles was also investigated (Nakashima et al, 2018, pp.904-908). ACC particles were prepared by the carbonation method via bubbling CO$_2$ gas into calcium ions dispersing in the methanol solution. The effect of the methanol concentration on the CaCO$_3$ formation was investigated. The pH of the ACC preparation was studied in a range of 9.4 and 10. After that, ultra-small HSNPs were synthesized using the prepared ACC particles in the one-pot process. The results suggested that the synthesis of HSNPs using ultra-small ACC particles via the one-pot process is one of the most effective methods to produce ultra-small HSNPs regarding energy and cost savings.

Carbonation of silicate minerals in water solution

For such a mineral carbonation process, all common silicate minerals like forsterite (Mg$_2$SiO$_4$), antigorite (Mg$_3$Si$_2$O$_5$(OH)$_4$) and
Wollastonite (CaSiO$_3$) and their overall reaction rates are suitable for carbonation. The related reactions are given in Equations (2–4):

\[
\begin{align*}
\text{Mg}_2\text{SiO}_4(s) + 2 \text{CO}_2(g) + 2 \text{H}_2\text{O}(l) &= 2 \text{MgCO}_3(s) + \text{H}_4\text{SiO}_4(aq) + 89 \text{kJ/mol} \quad (2) \\
\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4(s) + 3 \text{CO}_2(g) + 2 \text{H}_2\text{O}(l) &= 3 \text{MgCO}_3(s) + 2 \text{H}_4\text{SiO}_4(aq) + 64 \text{kJ/mol} \quad (3) \\
\text{CaSiO}_3(s) + \text{CO}_2(g) + 2 \text{H}_2\text{O}(l) &= \text{CaCO}_3(s) + \text{H}_4\text{SiO}_4(aq) + 90 \text{kJ/mol} \quad (4)
\end{align*}
\]

Stopic et al (2018, p.993) have shown the reaction path of direct forsterite carbonation for a synthesis of magnesium carbonate in aqueous solution without any deeper consideration of the formed silica particles as shown in Equations (5–7), but in the presence of additives: sodium bicarbonate, oxalic acid, and ascorbic acid (as shown in Equations (7–8). Although olivine is a mixed crystalline material (Mg, Fe)$_2$SiO$_4$, for simplicity, olivine consists only of Mg$_2$SiO$_4$, namely forsterite. First, gaseous carbon dioxide dissolves in aqueous solution. Simultaneously, forsterite is dissolved in aqueous solution (Equation (5)) forming aqueous silicic acid, then it precipitates as amorphous silica (Equation (6)) which is a by-product, and lastly, magnesium ions and carbonate form magnesite as shown in Equation (7):

\[
\begin{align*}
\text{Mg}_2\text{SiO}_4(s) + 4 \text{H}^+(aq) &\overset{r_{\text{Mg}_2\text{SiO}_4}}{\rightarrow} 2 \text{Mg}^{2+}(aq) + \text{H}_4\text{SiO}_4(aq) \quad (5) \\
\text{H}_4\text{SiO}_4(aq) &\overset{r_{\text{SiO}_4}}{\rightarrow} \text{SiO}_2(s) + 2 \text{H}_2\text{O} (l) \quad (6) \\
\text{Mg}^{2+}(aq) + \text{CO}_3^{2-}(aq) &\overset{r_{\text{MgCO}_3}}{\rightarrow} \text{MgCO}_3(s) \quad (7)
\end{align*}
\]

This positive effect of additives may be due to "reaction-driven cracking" in the presence of NaHCO$_3$, formation of etch pits, and/or other processes that continually renew the reactive surface area of Mg$_2$SiO$_4$.

\[
\text{NaHCO}_3(aq) \rightarrow \text{Na}^+ + \text{H}^+ + \text{CO}_3^{2-} \quad (8)
\]

The addition of oxalic acid leads to the formation of Mg-ions in the solution, which react with carbonate ions forming magnesium carbonate.
$$\text{Mg}_2\text{SiO}_4 + 2 \text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{Mg}^{2+} + \text{C}_2\text{O}_4^{2-} + \text{H}_4\text{SiO}_4$$  (9)

The determination of the process parameters such as temperature, pressure and pH for maximum overall conversion rates is elementary. Direct CO₂ sequestration at high pressure with olivine as a feedstock has already been performed in numerous studies at different temperatures and pressures with or without the use of additives such as carboxylic acid and sodium hydroxide. It is reported that optimal reaction conditions are in the temperature range of 150–185 °C and in the pressure range of 135–150 bar (Rahmani et al, 2014, pp.5953-5958). Additives are reported to have a positive influence on the carbonation rate, but without a study in detail. Optimal addition of additives is reported by (Béarat et al, 2006, pp.4802-4808) in studies about the mechanism that limits aqueous olivine carbonation reactivity under the optimum sequestration reaction conditions observed as follows: 1 M NaCl + 0.64 M NaHCO₃, at 185 °C and P (CO₂) about 135 bar. A reaction limiting silica-rich passivating layer forms on the feedstock grains, slowing down carbonate formation and raising process costs.

Eikeland et al (2015, pp.5258-5264) reported that NaCl does not have significant influence on the carbonation rate, but, in the absence of NaCl, the conversion rate amounted to more than 90% using a NaHCO₃ concentration of 0.5 M. Ideally, the solid phases exist as pure phases without growing together. In reality, different observations are made on the behavior of solid phases. Daval et al (2011, pp.193-209) reported about a high influence of amorphous silica layer formation on the dissolution rate of olivine at 90 °C and at elevated pressure of carbon dioxide. This passivating layer, as shown in Fig. 5, may be either built up from non-stoichiometric dissolution, precipitation of amorphous silica on forsterite particles or from a combination of both.

These results suggest that the formation of amorphous silica layers plays an important role in controlling the rate of olivine dissolution by passivating the surface of olivine, an effect that has yet to be quantified and incorporated into standard reactive-transport codes. Queneau et al (1983) reported that the solubility of silica is sensitive to the pH level in alkaline solution, but relatively insensitive to pH in acid solution. Certain inorganic metallic impurities, particularly aluminium, can sharply reduce the rate of dissolution of silica. Unfortunately, these silica collectors are not effective in the pH range bellow 3 of concern to leaching of laterites with sulfuric acid. Therefore, a carbonation process of olivine in water solution at 175°C offers a possibility to avoid gel formation.
Stopic et al (2019, p.708) used Steinsvik olivine from Norway with a chemical analysis in (wt %): 48.7 SiO$_2$, 41.7 MgO, 7.8 Fe$_2$O$_3$, 1.2 NiO, 0.5 Al$_2$O$_3$, 0.4 Cr$_2$O$_3$, 0.2 CaO, 0.1 ZnO) for the absorption of gaseous carbon dioxide. The treatment of olivine was performed using the operations such as milling, sieving, carbonation in an autoclave, filtration, and a chemical analysis of solid and liquid samples shown in Figure 6.

The carbonation tests were carried out in the 1500 mL autoclave from Büchi Kiloclace Type 3E, at 175 °C with 117 bar pure grade CO$_2$ in the presence and the absence of additives such as sodium bicarbonate, oxalic acid, and ascorbic acid in duration of 2–4 h. Sample amount ranging from 100 to 300 g was added to the 1000 mL solution with a mixing rate of 600 revolutions per minute in different experiments. After the reaction, the liquid had very low content of metal cations and was analyzed via the ICP OES analysis. The characterization of the solid products was restricted to the XRD analysis and XRF analyses.

![Figure 5 – The formation of the silica passivating layer](image)
The presence of magnesite and silica was confirmed using the SEM analysis of the solid product, as shown in Figure 7.

As illustrated by Figure 7, the SEM-analysis confirmed that very small particles of SiO₂ and magnesite are formed as rhombohedrons or hexagonal prisms at the surface of partially carbonated magnesium silicate. The challenge of future work is the separation of the formed
silica particles from the product and the determination of the ratio of the formed silica.

**Conclusion**

The acidic leaching of lateritic ores, high silicon bauxite, and eudialyte leads to the formation of silica gel which hinders the leaching process in order to recover nonferrous metals and rare earth elements. Adding sodium fluoride and using dry digestion offer a possibility to prevent gel formation. The second possibility is the carbonation of olivine in water solution under high pressure in an autoclave in the presence of additives such as hydrogen becarbonate, oxalic acid, and ascorbic acid at 175°C. The formed silica particles are between 200 and 500 nm and have a spherical form. The influence of the parameters such as temperature and pressure, pH-Value and concentration of additives has high importance in controlling the synthesis of nanosilica particles. Furthermore, the best parameter combinations will be studied in future work in order to offer an experimental design for the synthesis of silica particles.

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Сажетак:
Увод/сврха: Растварање обојених метала из оксидних руда, као што су латерити, боксити са високим садржајем силицијума и еудиалит, коришћењем киселина повезано је са стварањем гела од силицијум-диоксида.
Методе: Сличност са понашањем силицијум-диоксида у хидрометалуршким процесима, као што су растварање при атмосферском и високом притиску, таложење, неутрализација и филтрирање, од великих значаја за извлачење метала из раствора.
Резултати: Избегавање формирања гела омогућено је коришћењем растварања великим концентрацијама киселина („суво растварање”) и апсорцијом угљен-диоксида од оливина при високом притиску у аутоклаву.
Закључак: Припрема финог праха силицијум-диоксида из оливина у воденом раствору постигнуто је на 175°C и 120 бара за 4 сата у аутоклаву коришћењем додатака као што су натријум-бикарбонат и оксална киселина.
Кључне речи: силицијум, хидрометалургија, гел, силицијум-диоксид.