Particle growth of nano-silica below the isoelectric point

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Current production of nano-silica

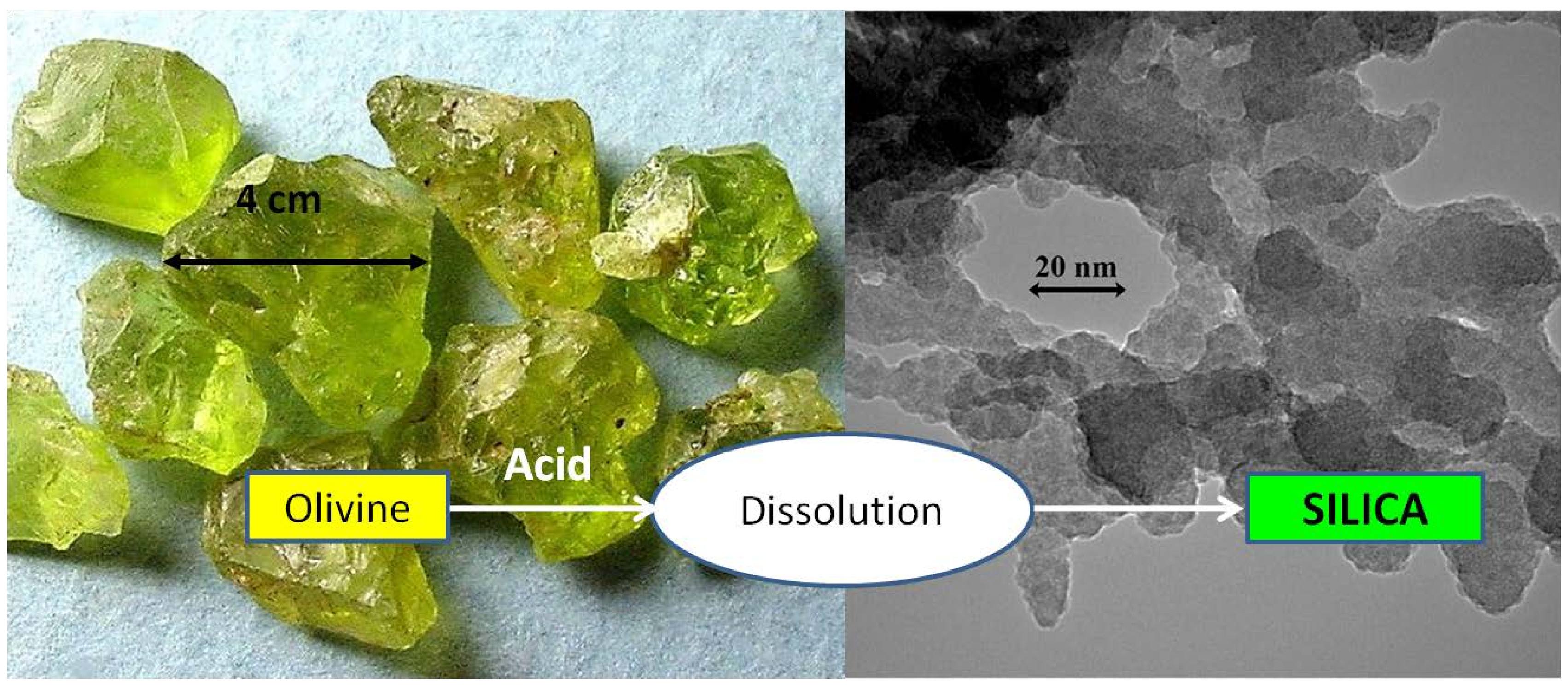
Nano-silica is one of the compounds that is boosting the field of nano-materials with an annual rise of 5.6 % reaching 2.8 million metric tons in 2016 and with a total value of $6.4 billion [1]. The current production methods involve steps with high temperatures. To reach these temperatures huge amounts of fuel are consumed making these processes: a) **non-sustainable** because of the scarcity of fuels; b) not environmentally friendly because of the huge amount of CO_2 emissions released; and c) expensive because of the fuel price.

Production of olivine nano-silica

Initial research has demonstrated that nano-silica can be produced by dissolving olivine in acid at **low temperatures**. The acid is neutralized by olivine mineral, according to:

$$(\mathrm{Mg,Fe})_2\mathrm{SiO}_4 + 4\mathrm{H}^+ \rightarrow \mathrm{Si(OH)}_4 + 2(\mathrm{Mg,Fe})^{2+}$$

The neutralization yields a slurry consisting of magnesium/iron salts, silica and unreacted silicates (more details in [2, 3, 4]).



Featured article and cover of the Chemical Engineering Journal [2]: *The properties of amorphous nano-silica synthesized by the dissolution of olivine.*

Experimental Methods

The **particle growth** of silica during the olivine dissolution (**negative pH**) was investigated using olivine. These experiments were carried out at 20 °C in a vigorously stirred reactor of two liters with sulfuric acid. The experimental variables were the concentration of sulfuric acid and surface area of olivine (see Table 1). The silica particle size (or cluster size) was measured with a Malvern ZS after passing the samples through a filter of 1 μm in order to avoid the presence of olivine particles.

Table 1. Conditions of the nano-silica polymerization experiments.

Experiment	m_{ol} (g/L)	$[Si]_{eq}$ (mmol/L)	d_{50} (μm)	SSA_G (m²/g)	SA_T (m²)	$[H^+]$ (mol/L)	T (°C)
NS-PO-2	50	307	116	0.09	9.0	4.0	20
NS-PO-3	50	307	116	0.09	9.0	2.0	20
NS-PO-4	100	613	116	0.09	18.0	3.9	20
NS-PO-5	70	429	116	0.09	12.6	3.9	20
NS-PO-6	70	429	116	0.09	12.6	4.1	20

$[Si]_{eq}$ refers to the equivalent concentration of silica from the olivine amount, SSA_G geometric specific surface area, and SA_T total geometric surface area of the olivine in the reactor.

Results

Figure 1 the concentration of silica produced during the dissolution of olivine in the polymerization experiments. Figure 2 presents the average particle size of silica over time.

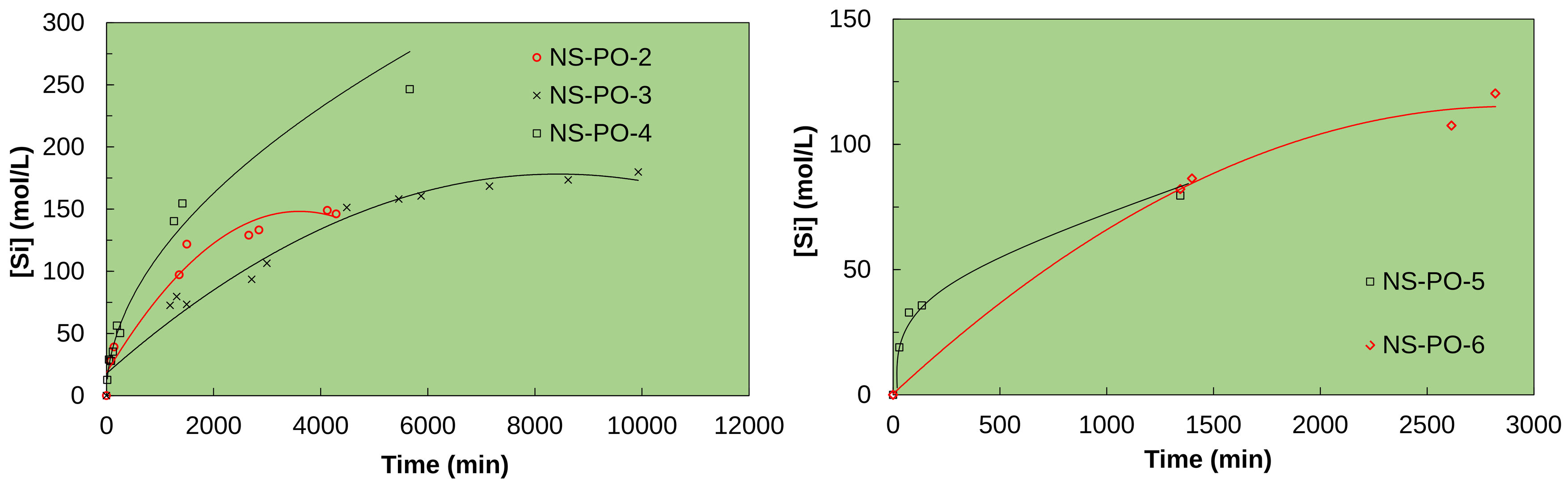


Figure 1. Silica produced over time for the particle growth experiments.

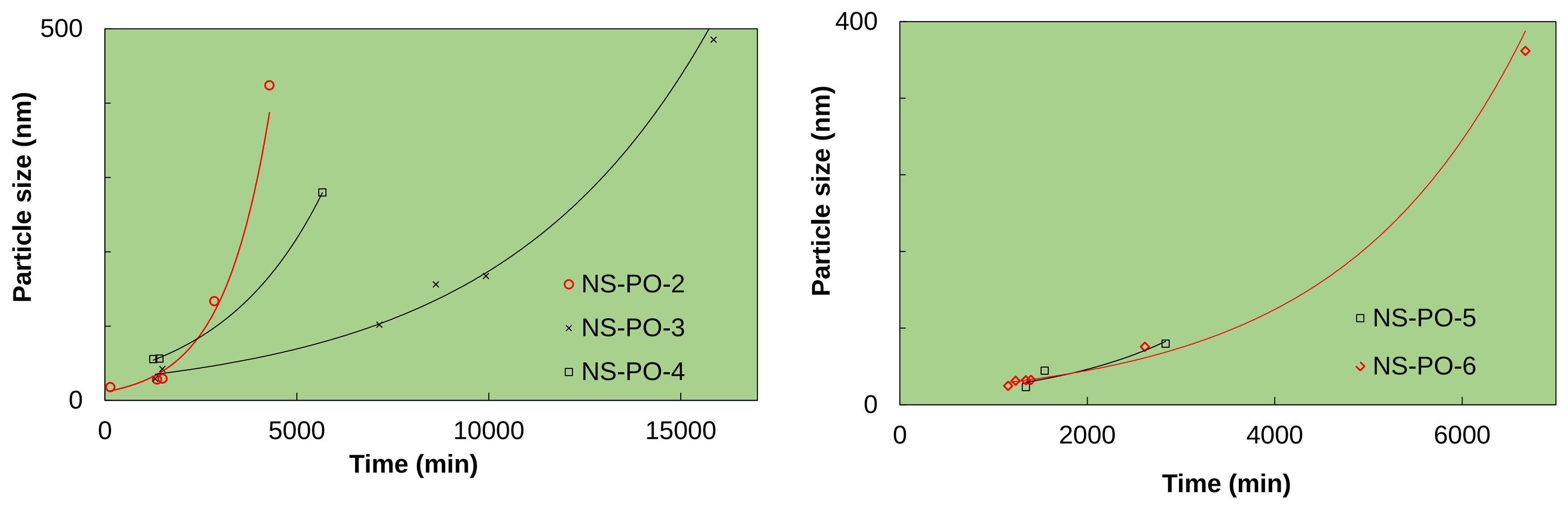


Figure 2. Growth of silica particles during the dissolution of olivine.

The cluster size of silica increased exponentially with time. The growth rate of silica accelerated with the increase of the hydrogen ion concentration and amount of nano-silica released.

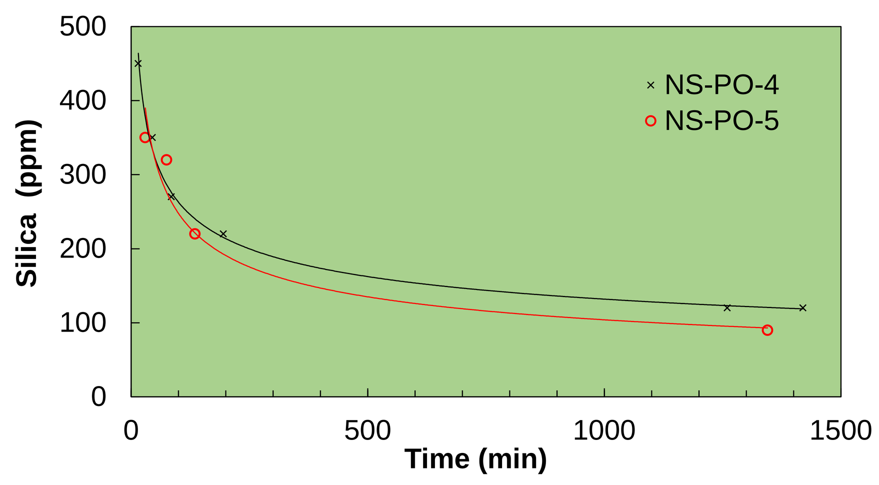


Figure 3. Concentration of soluble silica in the solution at early reaction times.

The evolution of the silica solubility reaches a maximum at the early stages of the experiment. Subsequently, the concentration of soluble silica slowly decreases over time due to the nucleation and formation of colloids, reaching a constant value around 100 ppm.

Conclusions

The cluster size of olivine silica grows up to 420 nm after 4300 minutes of reaction at 20 ˚C in 2M H_2SO_4 solution. The particle growth should be much faster under the production conditions of olivine nano-silica (90 ˚C and 3M H_2SO_4), which cause olivine to dissolve within 4-6 hours.

Olivine nano-silica does not gel. This behavior of olivine silica can be due to three reasons:

1) silica polymerizes fast at 90 ˚C in 3M H_2SO_4 solution, forming particles above 100 nm in a short time;
2) the concentration of small silica colloids is low;
3) the reactor is vigorously stirred.

References

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