Influence of the Production Process Conditions on the Specific Surface Area of Olivine Nano-Silicas

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The production of nano-silica by the olivine route is a cheaper and greener method than the commercial methods (neutralization of sodium silicate solutions and the flame hydrolysis) because of the low cost of raw materials and the low energy requirements. The produced olivine nano-silica has a specific surface area between 100-400 m²/g and primary particles between 10 to 25 nm (agglomerated in clusters). The process conditions and the ripening process influence the properties of nano-silica in the following ways i) the cleaner the nano-silica is the higher the specific surface area is; ii) the higher the filtration pressure is the higher the surface area is (unless the pressure is so high that the voids of the material collapse reducing drastically the SSA); iii) the ripening process diminishes the specific surface of nano-silica by two thirds and could be even further reduced. Thus, modifying the process conditions and/or adding an Ostwald ripening process, nano-silicas with different specific surface areas can be synthesized.

Keywords: Olivine, Nano-Silica, Specific Surface Area, Porous, Particle size.

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1. INTRODUCTION

At present, a wide range of silica products is manufactured industrially for various applications. Amorphous silicas are mainly used for reinforcement of elastomer products, thickening of liquid systems such as paints, thermosetting resins, and printing inks, and as fillers in silicone rubber [1]. World demand for specialty silicas, which includes precipitated silica, fumed silica, silica gel and silica sol, was 1.9 million metric tons in 2009 and will rise to 2.7 million metric tons in 2014 with a total value of $5.8 billion [2], making it one of the most used nano-materials. Nowadays, the two most important commercial processes in the production of nano-silica are the neutralization of sodium silicate solutions with acid and the flame hydrolysis. Both processes are expensive and not environmentally friendly because of the price of the raw materials and the energy requirements. Nano-silica could be applied even more widely if a new industrial, low cost production process could be developed.

Initial research [3-6] has demonstrated that nano-silica can be produced by dissolving olivine in acids. The acid is neutralized by olivine mineral, according to

$$(Mg,Fe)_2SiO_4 + 4H^+ \rightarrow Si(OH)_4 + 2(Mg,Fe)^{2+}.$$
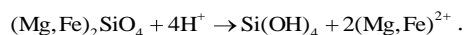
The neutralization yields a slurry consisting of a mixture of magnesium/iron sulfate, silica, unreacted olivine and inert minerals (see Fig. 1). Once the reaction is complete, the unreacted olivine and inert minerals are removed from the final suspension by sedimentation. Subsequently, the silica can be cleaned from the resulting mixture by washing and filtering. After the filtration, a cake with a 20 % solid content of nano-silica is obtained.

This nano-silica has a specific surface area (SSA) between 100 and 400 m²/g (see Table 1) and primary particles between 10 and 25 nm. These particles are agglomerated in clusters (see Fig. 2), forming a porous material with an average pore diameter between 17 and 28 nm. The impurity content depends on the washing steps, being able to obtain a material above 98 % of purity. Because of the good properties of the olivine nano-silica and the low energy requirements, the olivine dissolution process is a convenient alternative to the commercial methods of nano-silica production.
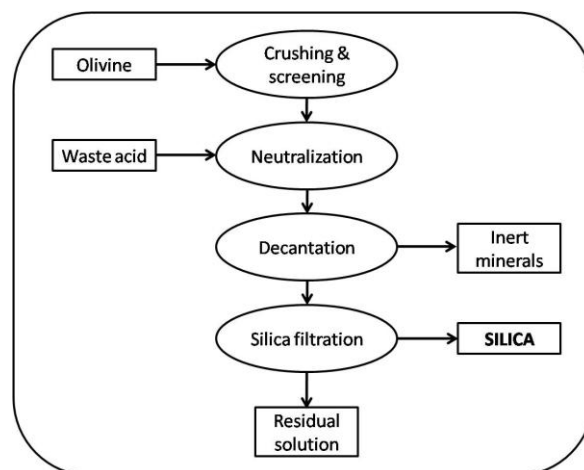

Fig. 1 – Schematic process flow diagram of the olivine process

The SSA, both internal and external, is a crucial parameter for nanomaterials, conferring special properties to these types of materials. That is because materials with a huge surface area possess a huge surface energy and, thus, are thermodynamically unstable or metastable [7]. Therefore, the application of these materials strongly depends on this parameter, making it one of the

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most relevant parameters to study in the field of nano-materials. In the case of olivine nano-silica, there is a lack of data about how the specific surface area is affected by the production process conditions.

Table 1 – Surface area, particle size and pore size of different nano-silicas.

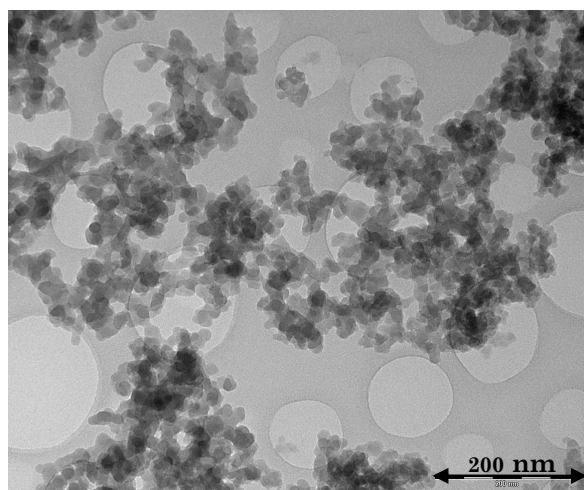| Parameters	Pyrogenic	Precipitated	Olivine Route
Purity SiO$_2$ (%)	>99.8	>95	>95
SSA$_{BET}$ (m^2/g)	50-400	30-500	100-400
d (nm)	5-50	5-100	10-25
d$_p$ (nm)	None	>30	>10
Reference	Ecetoc	Ecetoc	Lazaro

Fig. 2 – Transmission electron microscope photograph (89 kx) of the olivine nano-silica.

The specific surface area of olivine nano-silica depends on the kinetics of the reaction of olivine, the pressure during filtration and the amount of magnesium sulfate in the porous solution. Likewise, the kinetics of the dissolution of olivine depends on the temperature, surface area of olivine and hydrogen ion activity. In addition, it is possible to alter the specific surface area of olivine nano-silica by post treatment such as the Ostwald ripening. The Ostwald ripening consists of a hydrothermal treatment at basic pH to dissolve the small silica particles and to deposit them on the bigger ones.

The main purpose of this research is to establish the influence of the process conditions and Ostwald ripening on the specific surface area of olivine nano-silica.

2. METHODOLOGY

Experiments were carried out in a vigorously stirred glass thermostated reactor of one liter. The reagents used were 500 ml of 3 M sulfuric acid and an stoichiometric amount of olivine, previously dried. The ground olivine rock used in this study was from Norway with a purity content of 89 percentage in mass of olivine with the composition (Mg$_{1.84}$Fe$_{0.153}$Ni$_{0.007}$)SiO$_4$.

The neutralization reaction was stopped when the

concentration of [H$^+$] reached 0.1 mol/l. After that, the solution was separated from the solid residue by sedimentation. Subsequently, the slurry was washed and filtered either using a vacuum pump or a filter press.

The ripening experiments were carried out in the thermostated reactor with a NH$_4$OH solution of pH 10 at 90 °C during 6 hours. The pH was measured at regular intervals and was adjusted to the set value in case of deviation.

The nano-silica produced was characterized by gas physisorption, and transmission electron microscopy (TEM). A Micromeritics TriStar 3000 equipment using N$_2$ and with a soaking time of 240 min at 190 °C was used for the gas physisorption analysis [8]. The physisorption analyses were carried out three times with a standard deviation below 5 %. The specific surface area, SSA$_{BET}$, the specific micropore surface area, SSA$_{MP}$, and the pore size distribution were calculated using the BET [9], t-plot [10,11] and BHJ methods [12], respectively. The particle size of the nano-silica was calculated from the geometrical relationship between surface area and mass given by

$$d \text{ (nm)} = \frac{6000}{SSA_{BET} \cdot \rho} , \qquad (1)$$

where d is the particle size of nano-silica considered to be spherical (nm), ρ the density of the material, 2.2 (g/cm^3) for nano-silica, and SSA the surface area (m^2/g). This particle size is an average value, considering that the particles are spherical.

3. RESULTS

Different olivine silicas were synthesized using different process conditions. The process conditions studied are the number of washing steps (washing and filtration), which are filtered using a vacuum pump, the filtration pressure and the addition or not of a hydrothermal post-treatment to the silica. Table 2 shows the specific surface area, the particle size (calculated from equation 1) and the pore size of these silicas. The adsorption isotherm and the t-plot are showed in Figures 3 and 4, respectively.

There is an increase in the specific surface area with the number of washing steps. During the washing and filtration, the sulfate salts, which are soluble, are being removed from the silica. The sulfate salts are adsorbed on the surface area of the silica and the cleaning can be regarded as an extraction of the salts from the silica. The sulfate salts do not contribute significantly to the overall surface area, but to the overall weight of the sample. Thus, the presence of salts in silica reduces the specific surface area. From the results of the SSA for NS-3F and NS-4F can be observed that the relative increase of the SSA$_{MP}$ is higher (increase of 110 %) than the increase of the SSA$_E$ (increase of 15 %). For the next washing steps, the same trend can be observed; however, it is more difficult to appreciate it due to the lower content of salts. A plausible interpretation to explain this trend would be to consider that the sulfates are located mainly in the mesopores, making more difficult the entrance of the gas

into these pores. In order to test this hypothesis, more results need to be carried out about.

Samples NS-6F and NS-HP were filtered as many times as necessary to reach a high purity level, the only difference between them being the pressure of filtration. However, there is a clear difference in the specific surface area. This phenomenon is due to the compression effect on the bulk structure of the silica. This phenomenon is in agreement with what Madeline stated about the influence of a pressure on the voids of cake of nano-particles [13]. Because the specific surface area does not decrease but increase, it means that the filtration pressure is high enough to compress the voids of the material but not enough so the voids collapse. If the filtration pressure would be higher, the voids could collapse, resulting in a drastic drop of the SSA_{MP}. Thus, the filtration pressure is a key parameter influencing the specific surface area.

During the ripening process the SSA drops by two thirds, compared with data of clean nano-silica filtered under vacuum (NS-6F). This drop is due to the removal of small particles and increase of the big particles of silica because of the difference in solubility of the particles of different diameter [14]. Therefore, the ripening process is an interesting alternative for reducing the specific surface area of nano-silicas. The specific surface area could be further decreased by adding gradually new nano-silica as has been described by Iler [14].

4. CONCLUSIONS

The process conditions of the olivine nano-silica production have a great influence on the specific surface area of this material. Thus, modifying the process conditions, nano-silicas with different specific surface areas can be synthesized. In addition, treatment of the olivine nano-silica by Ostwald ripening can be a useful method to reduce the specific surface area below 150 m²/g.

The process conditions and the ripening process influence the properties of nano-silica in different ways. The cleaner the nano-silica is the higher the specific surface area is, reaching values around between 300 and 400 m²/g for olivine silicas with low content of salts. The higher the filtration pressure is the higher the surface area is. That is due to a reduction of the voids volume. However, if the pressure is too high, the voids of the material can collapse reducing drastically the SSA. The ripening process diminishes the specific surface of nano-silica by two thirds and could be even further reduced if the material would be treated gradually.

Table 2 – Surface area, particle size and pore size of different olivine nano-silicas.

Sample	SSA_{BET} (m²/g)	SSA_{MP} (m²/g)	SSA_E (m²/g)	d (nm)	d_p (nm)
NS-3F	233	58	175	11.7	14.5
NS-4F	324	122	202	8.4	13.9
NS-5F	346	142	204	7.9	13.7
NS-6F	348	142	206	7.8	14.6
NS-HP	433	125	308	6.3	14.7
NS-RIP	125	20	105	21.8	18.9

F refers to washing/filtration steps, HP to high pressure filtration and RIP to Ostwald ripening process.
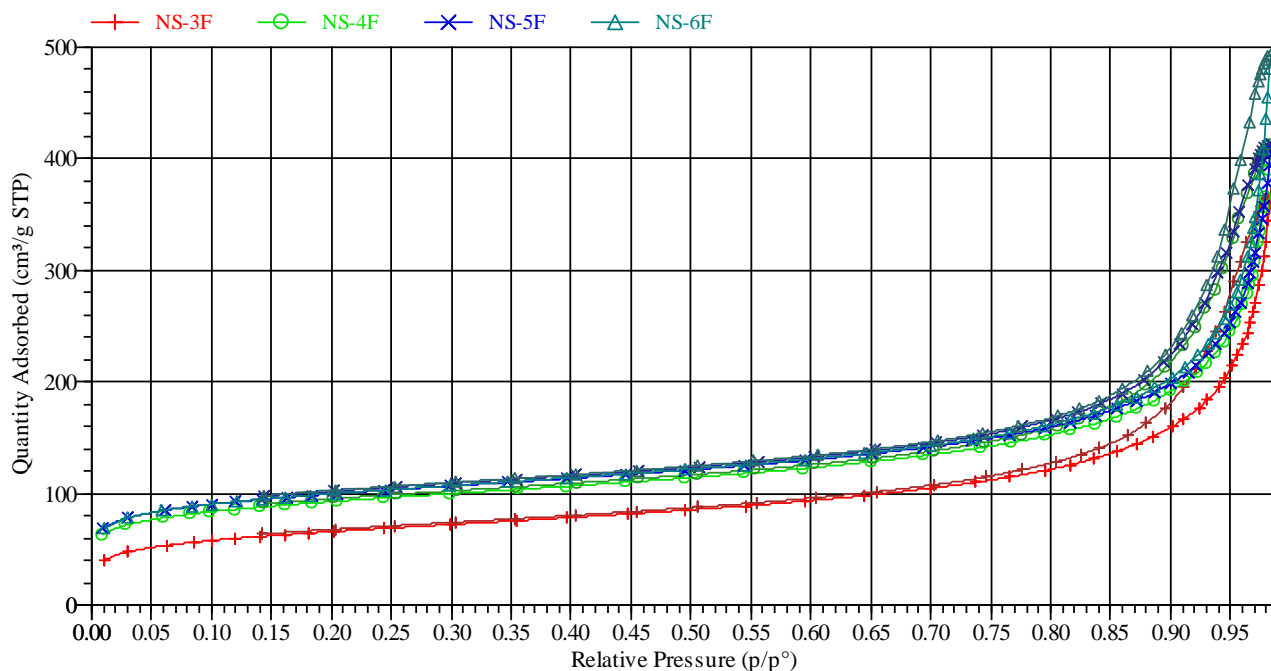

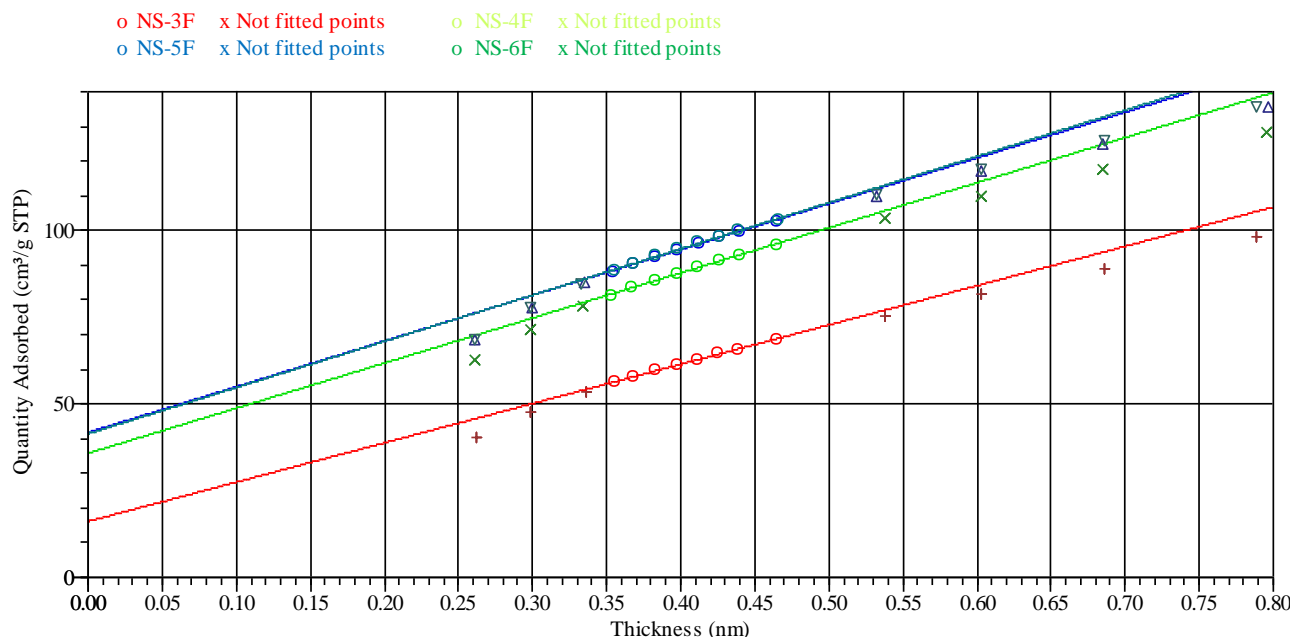**Fig. 3** – Adsorption isotherm of the olivine silicas with different number of filtration steps

o NS-3F   x Not fitted points   o NS-4F   x Not fitted points
o NS-5F   x Not fitted points   o NS-6F   x Not fitted points

Fig. 4 – t-plot curves of the olivine silicas with different number of filtration steps

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