The Effect of Hydrothermal Treatment on Olivine Nano-Silica

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This paper provides an overview of the effects of ripening the olivine nano-silica to form particles with a lower specific surface area for optimal use in high performance concrete. The nano-silica was ripened using a hydrothermal treatment in a mixed batch reactor at 90 °C, pH ranging from 8 to 10 and a silica weight percentage of three and six percent. The specific surface area of the olivine nano-silica can be reduced by 62 percent by Ostwald ripening in 22 hours. This reduction corresponds to a 80 percent drop of the micropore surface area and a 57 percent drop of the external surface area. The different hydrothermal conditions did not affect the final specific surface area at the equilibrium. However, the use of a high energy mixer reduced the specific surface area by 52 percent in only five minutes. Despite the reduction in specific surface area, the aggregates of the original olivine nano-silica are not dissolved during the ripening process.

Keywords: Nano silica, Hydrothermal treatment, Ripening, Specific surface area, Particle size, Olivine.

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1. INTRODUCTION

The use of amorphous micro-silica in concrete continuous to increase and, it is particularly valued in making high performance concrete. The main beneficial effects of micro-silica in concrete are a higher strength and a lower permeability. This is due to the pozzolanic properties of micro-silica and the extremely fine particles located at close proximity to the aggregate particles [1].

Despite the beneficial properties of small silica particles in concrete, nano-silica is not yet used in common practice because it is often too expensive. However, initial research [2-6] has demonstrated that nano-silica could be produced for a low price and a sustainable method by the dissolution of olivine in acid.

The problem when using this nano-silica in concrete is the low workability of the concrete due to the high specific surface area (SSA_{BET}), between 200 and 400 m^2/g, and the three-dimensional network structure of the silica. The workability can be increased by adding more water, resulting in a lower compressive strength, or by adding superplasticizers, which are expensive. For optimal use in concrete a more spherical nano-silica with a lower SSA is needed.

The polymerization of silica has been widely studied by Iler [7] and can take place by aggregation of particles, creating the unwanted three dimensional networks as seen in Fig. 1 following path A, but also by the growth of spherical particles increasing in diameter, following path B of Fig. 1.

Between pH 7-10, the silica particles are negatively charged and repel each other, therefore the particles do not aggregate. This is only true if the salt concentration is low and does not reduce the charge repulsion [7]. Even though the particles do not aggregate, under these conditions, they still grow in size and reduce in number. This is due to Ostwald ripening where smaller, more soluble particles dissolve and silica is deposited upon larger, less soluble particles, creating bigger particles with a lower SSA [7]. The ripening of the particles stops when the difference in solubility between the largest and smallest

particles becomes negligible and equilibrium is reached [7]. But, the question is whether it is possible to ripen the nano-silica produced by the dissolution of olivine in acid. If so, then it is interesting to know what the effect of different ripening conditions is on the final SSA of the olivine nano-silica. The aim of this paper is to answer these questions and to have a better understanding of the effect of the ripening process on the olivine nano-silica.
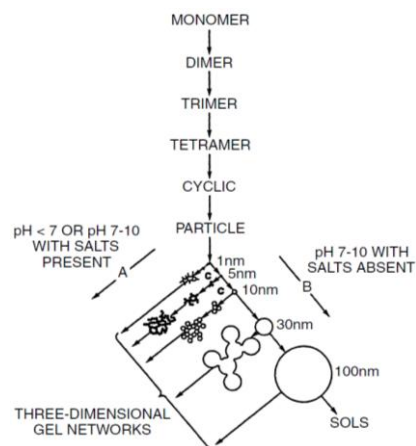

Fig. 1 – Polymerization pathway of aqueous silicate sols by Iler [7]

2. EXPERIMENTAL METHOD

The nano-silica cake used was supplied by Geochem. All the experiments where performed using a mixed batch reactor which was kept at the set temperature.

A base solution was added to the reactor to adjust the pH of the final solution. When the temperature reached the set temperature, the nano-silca cake was added. After 15 minutes the pH of the solution was measured and the pH was adjusted to the desired value.

The ripening process was conducted with two different bases, NH$_4$OH and NaOH; at different pH ranging from 8 to 11.3; and with a silica mass percentage of three and six percent.

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During the first experiments we observed that it took three hours before the 'lumps' of nano-silica cake where no longer visible in the solution. Therefore, in some experiments a high energy mixer was used to break the silica cake before adding it to the reactor.

During the ripening process, samples were taken at regular intervals to determine the pH of the solution and the SSA_{BET} of the silica. The silica samples were filtered to extract most of the water and dried in an oven at 110 °C for about 15 hours.

The nano-silica was characterized by gas physisorption. A 'Micromeritics TriStar 3000' equipment was used for the gas physisorption analysis [8]. The specific surface area (SSA_{BET}) and the specific micropore surface area (SSA_{MP}) were calculated using the BET [9] and t-plot [10,11] methods, respectively. The external surface area (SSA_E) was determined as the difference between the specific surface area and the specific micropore surface area

The particle size of olivine 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. Lieftink [4] stated that the correlation between the primary particle size, obtained from the TEM images and the SSA_E, is in good agreement for olivine nano-silica. The particle size distribution and d50 were determined as well by laser light scattering using a 'Mastersizer 2000'.

3. RESULTS

The experiment conditions are shown in Table 1 giving the average values of the reactor temperature, pH of the solution, the silica weight percentage and the base used.

Table 1 – Conditions during the ripening experiments

	T (ºC)	pH	SiO$_2$wt%	Base
RP-1	89.0	8.4	4.41	NH$_4$OH
RP-2	90.2	10	3.10	NH$_4$OH
RP-3	90.3	8.3	2.63	NaOH
RP-4	90.2	9.6	3.26	NaOH
RP-5*	90.2	10	6.57	NaOH

*High energy mixer used.

3.1 Gas physisorption analysis

Fig. 2 and Fig. 3 show the adsorption isotherm and the t-plot curve of the original olivine nano-silica used (in red) and the ripened olivine nano-silica of experiment RP-1 after 22 hours (in green), respectively.

The adsorption isotherm can be classified as a type IV with H1 or H2 hysteresis loop [12,13]. This adsorption isotherm classified as type IV, is typical for mesoporous materials and is related to capillary condensation taking place in mesopores [12]. Hysteresis H1 is associated with porous materials known to consist of agglomerates with narrow pore distributions, and H2 is associated with materials of not well-defined pore size and shape [11].
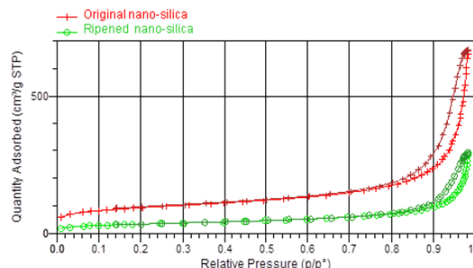

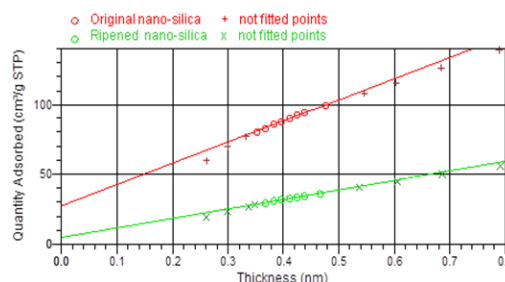**Fig. 2** – Adsorption isotherms of the original and ripened olivine nano-silica

Fig. 3 – t-plot curves of the original and ripened olivine nano-slica.

3.2 Specific surface area

The SSA_{BET} of the nano-silica during the different ripening experiments is shown in Table 2. The SSA_{BET} can be reduced by 62 percent, from 330 m^2/g to 125 m^2/g.

The SSA_{MP} of the original nano-silica and the average SSA_{MP} of the ripened nano-silica are 100 m^2/g and 20 m^2/g, respectively. This is a reduction of the micropore surface area of 80 percent. The SSA_E of the original nano-silica and the average SSA_E of the ripened nano-silica are 230 m^2/g and 100 m^2/g, respectively. This is a reduction of external surface area of 57 percent. This means that in terms of percentage the micropore surface area is reduced more than the external surface area during the ripening process.

Table 2 – SSA_{BET} in m^2/g of the ripened nano-silica.

t (h)	RP-1	RP-2	RP-3	RP-4	RP-5	RP-6
0	332	334	-	-	-	-
0.2	-	-	-	-	160	-
1.5	-	-	181	-	-	198
3	-	150	-	-	-	-
6	141	135	131	133	139	-
22	124	-	-	-	-	-

The SSA_{BET} of the experiments RP-1, RP-3 and RP-5 are shown in

Fig. 4 as they give a representative view of the overall results.

All the ripening experiments result in a similar SSA_{BET} of around 130 m^2/g after six hours. This is because the ripening process reaches equilibrium when the difference in solubility between the smallest and the largest particles becomes negligible [7]. Because the same initial nano-silica, with the same particle size distribution, has been used in all the experiments, the same equilibrium with a similar final particle size is reached.

To reduce the SSA_{BET} even further, relatively small,

and thus more soluble, particles need to be added gradually to the solution, as described by Iler [7]. Consequently, the ripening process continues further until the equilibrium is reached once again.

3.3 Particle size and zeta potential

The average particle size calculated with equation 1 is 22 nm and the d_{50} determined by laser light scattering is 18 µm. This indicates that the nano-silica particles are still present as larger aggregates.

The zeta potential of the nano-silica particles during the ripening process was -47 mV, indicating a good stability if the only force taken into account is the electrostatic force. This means that there is most likely no further aggregation of the silica particles during the ripening process. This indicates that the original olivine nano-silica already consists of relatively large aggregates which have not dissolved during the ripening process.

4. CONCLUSIONS

The olivne nano-silica can be ripened by hydrothermal treatment, reducing the specific surface area up to 63 percent. However, the different ripening conditions: a pH from 8 up to 11.3; a silica weight percentage of three or six percent; or the use of NaOH or NH_4OH, do not have a significant effect on the final specific surface area.

Using the high energy mixer at room temperature does lower the specific surface area almost instantly by 52 percent, but does not influence the final specific surface area.

In order to reduce the specific surface area even further and to reduce the aggregates present in the original olivine nano-silica, a different ripening process is needed.

5. FURTHER RESEARCH

Further research will focus on the ripening process in multiple steps, where more relatively small silica particles will be added to a previously ripened suspension. Adding the 'active' silica results in a significant difference in solubility between the smaller 'active' silica and the larger, ripened 'growth' particles. Thus, the ripening process continues until the active silica has disappeared and equilibrium is reached once again.

Because the nano-silica particles are present as relatively large aggregates, the effects of dissolving all the silica in solution and slowly lowering the solubility in order to form new spherical particles which grow by nucleation and polymerization (path B of Fig. 1).
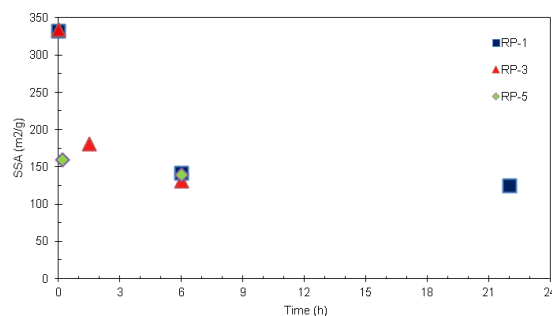
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Fig. 4 – SSA$_{BET}$ of the ripened nano-silica for RP-1, RP-3 and RP-5

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