

Production and Application of Olivine Nano-Silica in Concrete

Mardiana Oesman¹ and Haryadi²

¹Civil Engineering Department of Politeknik Negeri Bandung, Indonesia

²Chemical Engineering Department of Politeknik Negeri Bandung, Indonesia

E-mail: mardianaoesman@gmail.com, haryadi@polban.ac.id

Abstract. The aim of this research was to produce nano silica by synthesis of nano silica through extraction and dissolution of ground olivine rock, and applied the nano silica in the design concrete mix. The producing process of amorphous silica used sulfuric acid as the dissolution reagent. The separation of ground olivine rock occurred when the rock was heated in a batch reactor containing sulfuric acid. The results showed that the optimum mole ratio of olivine- acid was 1: 8 wherein the weight ratio of the highest nano silica generated. The heating temperature and acid concentration influenced the mass of silica produced, that was at temperature of 90 °C and 3 M acid giving the highest yield of 44.90%. Characterization using Fourier Transform Infrared (FTIR) concluded that amorphous silica at a wavenumber of 1089 cm⁻¹ indicated the presence of siloxane, Si-O-Si, stretching bond. Characterization using Scanning Electron Microscope – Energy Dispersive Spectroscopy (SEM-EDS) showed the surface and the size of the silica particles. The average size of silica particles was between 1-10 µm due to the rapid aggregation of the growing particles of nano silica into microparticles, caused of the pH control was not fully achieved.

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 increase density, reduce porosity and bleeding, and improve the bond between cement matrix and aggregates. 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. 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 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. However, initial research [2,4,8,9] has demonstrated that nano-silica could be produced for a low price and a sustainable method by the dissolution of olivine in acid.

Initial research [4,8,10] has revealed that nano-silica can be produced by dissolving olivine in acids. The acid is neutralized by olivine mineral, following: $(\text{Mg, Fe})_2 \text{SiO}_4 + 4\text{H}^+ \rightarrow \text{Si}(\text{OH})_4 + 2(\text{Mg, Fe})^{2+}$. The neutralization yields a mixture of a magnesium/iron salt solution, silica, unreacted olivine and inert minerals. 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 cake can be stored in this form, dried or redispersed for application in concrete. The



nano-silica produced has a specific surface area between 100 and 300 m²/g and a particle size between 10 and 25 nm. These particles are agglomerated in clusters forming a mesoporous material with an average pore diameter around 20 nm. The impurity content is below 5%, and the silica yield of the process in the range of 54–83%. When the separation of the silica is carried out by filtration, the textural properties of the material have a direct influence on the separation efficiency. The texture and specific surface area of nano-silica depends on several factors of the process, the main ones being the kinetics of the dissolution of olivine and the washing steps of the nano-silica. Thus, the properties of this nano-silica can be tailored by changing the process conditions [3].

Porroet *al.* [7] investigated the effect of the size of SiO₂ nanoparticles used at different dosages on the performance of cement pastes. It was demonstrated that the compressive strength of the cement pastes increased with the reduction of the particle size. This improvement was attributed to the formation of larger C-S-H silicate chains in mixtures with nano-SiO₂, as seen in figure 5. Nano silica is one of the blending materials used to improve the properties of concrete. Nanosilica concrete is stickier than normal concrete due to large surface area of nanosilica, also it has better permeability resistance.

2. Methodology

This research was aimed to obtain a specific amorphous silica in the rock olivine (Mg, Fe)₂SiO₄). The experiment comprised of two phases. The first phase was to make amorphous nano silica from the ground olivine rock using sulfuric acid as the reagent dissolution fluid according to Lazaro [3]. The ground olivine rock was supplied from Pomalaa region, South Sulawesi. Experiments were carried out at the following temperatures: 70, 80 and 90 °C. The olivine rock smoothed with 0.2 mm sieve passes and was used of 10 gram on each experiment for various temperatures. The optimum point of olivine-sulfuric acid ratio must first be determined at which the olivine-acid mole ratio of how much the maximum weight of silica is gained. The yield was obtained by varying the reaction temperature and the concentration of acid used for the reaction. Acidity was controlled, because the pH should be in the range of 0.5 to 1.0. After the heating process for 4 hours, resulting slurry of silica minerals. Then the silica mud could be washed into slurry of silica. Once the minerals dissolved in the acid have been removed, then decantation process was done. This solution was then taken to be filtered using Whatman 42. The washing and filtering processes were repeated four times until the washing pH was in the range of 6 to 7. Then, silica mud was dried in an oven at 110°C for 2 hours. Silica was sized between the micrometer to nanometer range that was characterized using SEM-EDS to observe the size and the surface microstructures. FTIR instrument was used to characterize the functional groups of silica particles produced.

The second phase was compressive strength tests of concrete specimens. The nanoolivin silica was applied in concrete mix design as cement substitution. There were two types of silica size those were 700 nm - 950 nm (type I), and 1000 nm - 10,000 nm (Type II). The specimens were cubic with 150 mm side length. Besides nano-silica, fly ash was also used as a substitute for cement. Mix concrete design based on ACI 211.1-97 with the value of slump was 50mm, and water-cement ratio was 0.3. The compression strength was design at 40 MPa in 28 days. The maximum coarse aggregate size was 13 mm. The concrete specimens without nano silica were constructed to be used as a reference to compare the behavior of the specimens. The compressive strength testing performed at the age of 7 days and 28 days using UTM.

Table 1. Optimization of molar

Molar ratio of Olivine: Acid	Yield of Silica, (%)
1 : 4	16,90
1 : 5	27,90
1 : 6	25,00
1 : 7	29,20
1 : 8	44,50
1 : 10	39,90
1 : 12	31,20

Table 2. Optimization of temperature

Operation Temperature, °C	Yield of Silica, (%)
70	30,60
80	44,60
90	44,90



Figure 1. Dried silica mud

3.Result and Discussion

3.1 Process of nano-silica production

In this research there were two steps to get optimum condition for silica production from ground Olivine rocks followed by dissolution namely molar ratio of Olivine over acid concentration and operation temperature. The series of molar ratio for Olivine to concentration of sulfuric acid was conducted to obtain the optimum condition for silica production using 3M sulfuric acid at 80°C and the results are listed in Table 1. It is indicated that yield of silica tends to increase in accordance with the increasing of sulfuric acid quantity. The maximum weight of silica produced was in condition: 1 mole olivine reacts with 8 moles of sulfuric acid at temperature of 80°C producing 44.50 % yield of silica. For operation temperature variation, it shows that the maximum operation temperature for dissolution was 90°C which is close to the finding of Lazaro, et.al [3], as shown in Table 2. In addition, the result of silica separation process from the ground olivine rock was dried mud as shown in figure 4. The increasing temperature and sulfuric acid concentration results in an increase in the mass and surface area of nanosilica [6]. Separation bonding silica from olivine is controlled by surface reaction and is dependent on the surface area of olivine, the hydrogen ion activity, and temperature. Thus, increasing the surface area of olivine, the hydrogen ion activity and the reaction temperature will increase the rate of reaction [2].

3.2 Characterization of Nanosilica by FTIR

Fourier Transform Infrared (FTIR) investigation aims to determine the characteristics of nanosilica by observing the functional groups in the silica sample. The infrared spectrum of silica produced from Olivine can be seen in figure 2. The main peak at 3446.7 cm^{-1} is observed which is assigned the silanol groups (Si-OH) and adsorbed water. A sharp peak at 1639 cm^{-1} assigned for C-O stretching vibration caused due to the atmospheric CO_2 adsorbed by the amorphous nanosilica. A strong band at 1089 cm^{-1} is caused by the presence of siloxane (Si-O-Si) stretching that suggest the local bonding structure of Si and O atoms at nanoparticles size. A peak corresponding to silanol groups (Si-OH) stretching is observed at 947 cm^{-1} . A sharp and intense peak at 796 cm^{-1} is caused by the presence of Si-O bending vibrations. The peak at 461 cm^{-1} is assigned by the Si-O out plane bending vibrations. The functional groups indicate specific functional groups contained in nano-silica. The silica separation from olivine rock has been successfully done by observing at the FTIR spectrum. The FTIR results can be summarized that the silica resulting from the extraction process of olivine rock has the functional group Si-OH (silanol), Si-O-Si (siloxane) and the OH group (hydroxyl) with the presence of adsorbed water in silicaparticle.

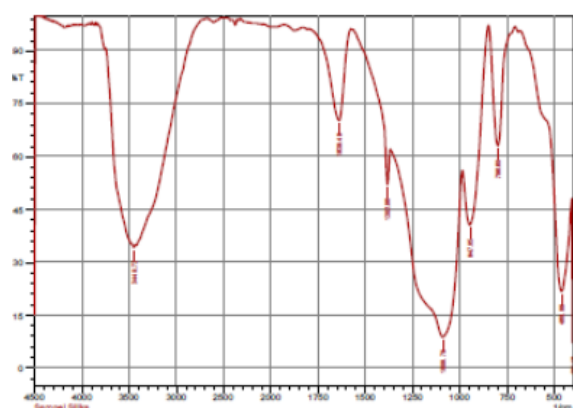


Figure 2. The analysis results of functional groups with FTIR ratio

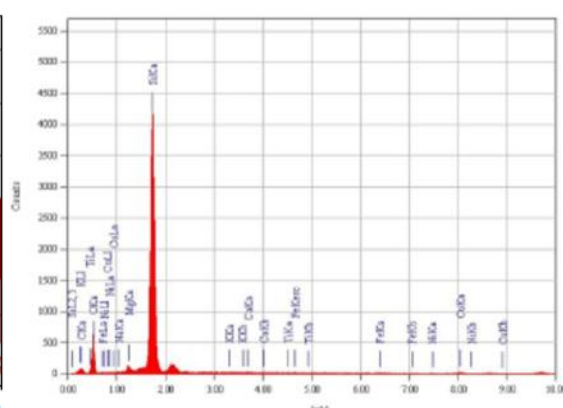


Figure 3. EDS spectrum of silica product of functional groups with FTIR ratio

3.3 Characterization of silica by SEM-EDS

The mass percent of each dried compounds in a silica sample characterized using SEM-EDS. SEM-EDS analysis performed to obtain the surface morphology of the sample with a very high resolution. Figure 3 shows EDS spectrum with a variety of elements and compounds in the silica sample. It shows that the compounds are dominated by SiO_2 for about 82.3 % followed by C, CuO, MgO of 11.9, 2.9 and 1.5 % by mass respectively. Figure 4 shows the morphology of silica particles extracted from olivine rocks after dissolution process observed by SEM-EDS with a magnification of 500 times. The figure shows the scale of the large chunk silica size is 500 μm . One large chunk is a collection of several small-sized silica particles are fused. Actually, expected amorphous silica obtained with an average size in nanometers. This occurred due to the nature of the silica particles that related to Ostwald ripening, in which the larger particles grow at the expense of smaller particles [2]. Particles are first formed at nanometer-sized and form a ball up micro-sized particles, through the mechanism of aggregation. This should be addressed during the reaction process; the acid concentration must be maintained at concentrations below 0.1 mol / L by controlling pH through addition of $\text{Na}_2\text{B}_4\text{O}_7$ at regular intervals [2]. Figure 3 also displays the silica with a magnification of 300 times viewable size of 10 μm silica indicating various silica particle size in the range of 100-1000 nm.

3.4 Compressive test of nano-silica concrete.

The results of compressive strength were conducted at ages of 7 days and 28 days. Table 3 shows the strengths of concrete with silica (type I and II) at the age of 7 days were 60% strength at 28 days. It is consistent with the results of research in general that is approximately 60-70% of concrete strength 28 days. The table indicates that the highest compressive strength achieved by the specimen without silica. This is not consistent with the predictions expected in this study, which is to achieve a high compressive strength concrete. This happened because the conditions predicted silica size obtained from the process of making nanosilica has not been reached properly.

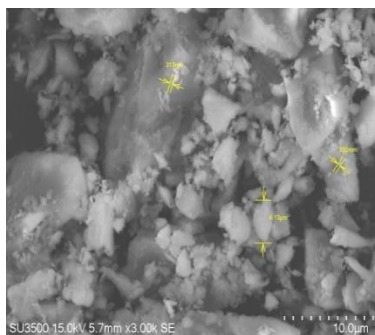


Figure 4. SEM image of nanosilica extracted from Olivine rock

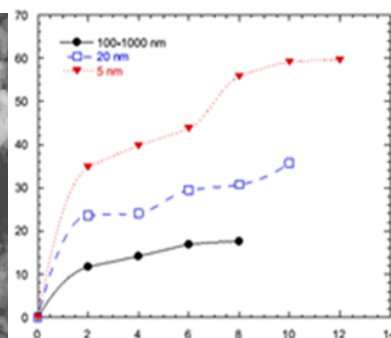


Figure 5. The effect of the nanosilica size to f_c [7]

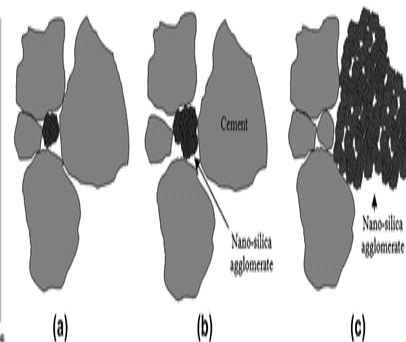


Figure 6. Illustration of the filling effect of the nano-silica agglomerates [5]

Porro et. al.[7] said that compressive strength of concrete with silica as substitution of cement can be increase if the silica size is under 100nm, as shown in figure 5. Actually, the product of silica size from the first phase of this research was in the range of 100-1000 nm so that the compressive strength of the concrete in this research was less than the concrete without silica. Moreover, Kong et al. [5] described the effect of particle size on the nano concrete, namely (a) small clumps of nano particles behave as a filler which remove the water trapped in the fresh pasta, (b) larger nanoparticles cannot behave as a filler, which led to an increase in cavities, and (c) large nanoparticles can absorb water which initially may affect viscosity paste. From these statements, it can be predicted how the nano silica condition that occurs in this study. Nanosilica condition can agglomerate into micro and even macro size, so that they cannot behave as a filler as expected. Thus, the silica can not decrease the

porosity happened, instead to an additional porosity formed. This causes the concrete has a high porosity; density occurring impact is low, and the low concrete strength (figure 6). Therefore, the study of silica nanoscale manufacturing process must be continued; so it can be applied to the manufacture of nano silica concrete to achieve a high performance concrete.

Tabel 3: Compressive strength

Specimens	7 days	28 days
Type I (nano)	12.57 MPa	22.93 MPa
Type II (micro)	16.00 MPa	25.53 MPa
Without Silica	24.78 MPa	34.97 MPa

Conclusion

The mole ratio of olivine-optimum acid is 1: 8 wherein the weight ratio of the highest nanosilica generated. Effect of heating temperature and acid concentration influence the weight of silica produced where at 90°C and acid produces 3 Molar yield the highest of 44.90%. Characterization using FTIR concluded that amorphous silica at wavenumber of 1089 cm⁻¹ corresponding to stretching vibration of siloxane bond, Si-O-Si. Characterization using SEM-EDS displays the average size of the silica particles is 1-10 µm due to the rapid aggregation of the growing particles of nanosilica into microparticles where pH control is not fully achieved. The average size of silica particles in the range 0.7-10 µm has not reached the optimum of nanosilica concrete. Therefore, it needs to conduct more research to get silica particle size below 0.1 µm for preparing high performance concrete.

References

- [1] A.M. Neville, 1996, Properties of concrete, Fourth Edition, John Wiley & Sons.
- [2] A.Lazaro, H.J.H, 2011, Brouwers, A new method for the production of colloidal nano-silica, Colloids and Materials, *The 1st symposium on Colloids and Materials*, Amsterdam.
- [3] A. Lazaro, H.J.H. Brouwers, G. Quercia, J.W. Geus, The properties of amorphous nano-silica synthesized by the dissolution of olivin, *Chemical Engineering Journal* 211-212, 2012, 112–121.
- [4] D.J. Liefstink, 1997, The preparation and characterization of silica from acid treatment of olivine, PhD thesis, Utrecht University.
- [5] D. Kong, Y.Su, X.Du, Y.Yang, S.Wei, S.P. Shah, Influence of nano-silica agglomeration on fresh properties of cement pastes, *Construction and Building Materials*, **43**, 2013, 557–562.
- [6] L.P. Singh, A. Goelb, S.K. Bhattacharyya, G. Mishraa, 2015, Improving the durability of cementitious materials using silica nanoparticle. *Nanotechnology in Construction*.
- [7] Porro, A., Dolado, J.S., Campillo, I., Erkizia, E., de Miguel, Y., Sáez de Ibarra, Y., Ayuela, A. 2005, Effects of nanosilica additions on cement pastes: Applications of nanotechnology in concrete design, Thomas Telford, London.
- [8] R.C.L. Jonckbloedt, 1997, The dissolution of olivine in acid, a cost effective process for the elimination of waste acids, PhD thesis, Utrecht University.
- [9] R.D. Schuiling, 1986, A method for neutralizing waste sulphuric acid by adding a silicate”, US 1987/4707348.
- [10] Van Herk, J., Pietersen H.S., Schuiling R.D., 1989, Neutralization of industrial waste acids with olivine — The dissolution of forsteritic olivine at 40–70 °C”, *Chemical Geology*, **76**: p 341.
- [11] Gorrepati, E., Wongthahan, P., Raha.S., and Fogler, H S., Silica Precipitation in Acidic Solutions: Mechanism, pH Effect, and Salt Effect, *Langmuir*, **26 (13)**, 2010, pp 10467-10474.