The effects of mass variation potassium chloride (KCl) on characteristics of nanosilicone from natural sand through the magnesiothermic method

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Abstract. Synthesis of Nanosilicon has been carried out from Natural sand with magnesiothermic method. Silica of natural sand was extracted by NaOH 10 N and HCl 6 N. Ultrasonication of silica with KCl has been done with a ratio of SiO₂ : KCl (1: 7.5 and 1: 12.5). Continuously, silica converted to nanosilicon by using magnesiothermic method with a ratio of SiO₂ : Mg 1: 2 heated up to 800ºC for 6 h. Nanosilicon was purified with deionized water and ethanol, HCl 5 N and HF 10%. The results of XRD analysis of nanosilicon of ratio of SiO₂ : KCl (1: 7.5 and 1: 12.5) each 88.8% and 73.0% by using Match application. The distribution of particle sizes were determined by using Scherrer’s equations 28.56 nm - 170.57 nm and 12.70 nm - 93.32 nm.

1. Introduction
Natural sand in and around river bed plays an important ecological. Silica sand is a by-product obtained as a result of cement manufactured by wet process. Silica sand acts as a filler material that is inert but enhances the process of hydration by physical activity[1].

95% of the earth’s crust is made up of silica and silicates. Silicon dioxide, commonly known as silica, occurs in several crystallographic forms. Quartz, cristobalite and tridymite are some of the crystalline forms of silica, and they are interconvertable at suitable temperature[2].

Silicon in the form of nano is used by [3] as a material anode on Ion-Lithium batteries. Nanosilicon can be prepared from silica by using several method, namely aluminothermic [4], carbothermic [5], and magnesiothermic. Magnesiothermic method is the method commonly used for nanosilicon preparation due to temperature used in the reduction process no too high (650-800 °C) [6].

Reducing silica to nanosilicon magnesiothermic release of heat at 586.7 kJ [7]. The heat released will be absorbed by silicon particles so that it will form agglomeration between the particles and resulting in large particle sizes. To reduce agglomeration between the particles is used NaCl salt as a heat-reducing agent in the silica reduction reaction magnesiothermic[3]. Size distribution of nanoparticles by 75% and a particle diameter of 20 nm.

However, [3] uses silica from halocye sludge with comparison of different SiO₂ : NaCl from Wu namely (1: 1) produces nanosilicon with a purity of 70% and diameter of 20-30 nm. NaCl salt can be replaced with KCl salt because it has as an agent the at absorbent in the silica reduction process magnesiothermic basis. This research performed by [8] and [9] that was obtained with using the magnesiothermic method at a SiO₂ : KCl ratio (1:10). On [8] nanosilicon obtained
through the purification stage with HCl, CH3COOH, and HF has a purity of 40.4% and a diameter particle 42.993 nm - 58.567 nm. Whereas, silicon nanoparticles are generated [9] through stages purification with deionized water, HCl and HF have purity 86.6% in diameter particles of 49.43 nm - 83.95 nm. Based on the background above variation in the addition of KCl are believed to be able influence distribution particle nanosilicon. Therefore, this research will focus on influence the ratio of KCl salt addition, i.e. more bigger and smaller than 1:10 which is 1: 7.5 and 1: 12.5 which continues with the process purification using deionized water, HCl and HF.

2. Experimental

2.1. Materials

Materials used in this research is quartz, NaOH pa Merck, HCl pa Merck, HF, deionized water, distilled water, Mg Merck powder, ethanol pa Merck.

2.2. Instruments

The instruments used in this research includes: glassware, hotplate stirrer, magnetic bar, balance sheet analytical, thermometer 110, tube centrifuge, centrifugator, tube rack, paper filter whatman No.42, indicator universal, ultrasonication, XRD Philips PW 3050 with Cu-Kα radiation which used (1.540598 Å). Scanning Electron Microscopy (SEM) JED-2300 SEM JEOL.

2.3. Preparation of Quartz Sand

100 grams of quartz sand mashed using a pestle a mortar and sifted with a 150 sieve mesh. Then washed with distilled water repeatedly and dried inside oven.

![Figure 1. 150 mesh quartz sand](image)

2.4. Preparation of Silica from Sand Quartz

150 mesh of quartz sand as much as 100 grams was put in beaker and dissolve with 400 ml NaOH 10 N while stirring with magnetic stirrer and heated at temperature 130 ° C for 4 hours then being cooled and filtered out. Filtrate obtained was added with HCl 6 N to form gel until pH= 7, then being allowed to stand for one night. The gel formed was centrifuged for 15 minutes with a speed of 6500 rpm then filtered. The formed gel is washed with distilled water and dried at 110 ° C.

2.5. Ultrasound of Silica

Silica as much as 3 gram was dispersed in a beaker contains 150 ml the mixture of 27.93 g of KCl and deionized water while stirring at a frequency of 42 kHz for 1 hr. After the process ultrasonication, the mixture was kept for a long time 1 night, then the filtrate was decanted and dried solids in the oven at a temperature of 110 ° C. Repeated procedure same in the ratio of silica and KCl 1: 12.5 with a mass of silica as much as 3 grams and KCl as much as 46.56 grams.

2.6. Reduction of Ultrasound Silica Results become nanosilicon

Ultrasound silica as much as 3 gram mixed with magnesium powder as much as 2.4 grams in a porcelain cup, then the mixture was planted for 6 hours at a temperature of 800 ° C then being allowed
to stand for one night. Nanosilicon from the results. Then, the result of reduction was purified with deionized water and ethanol, HCl 5N, and HF 10%.

2.7. Material Characterizations
Nanosilicon was characterized by XRD Philips PW 3050 with Cu-radiation The Ka used (1.540598 Å). Scanning Electron Microscopy (SEM) Tested with JEOL JED-2300 SEM.

3. Result And Discussions
Isolate silica from quartz sand had been prepared by dissolving quartz sand measuring 150 mesh in 400 ml of NaOH 10 N for 4 hours. This treatment can produce silica because silica can dissolves in NaOH to form Sodium Silicate (Na₂SiO₃). After that, it was filtered, then the filtrate from the results filtering added HCl 6 N to pH 7 and formed silica gel. Silicon oxide obtained was 49.88 grams.

Figure 2. Silica solids obtained

Silica obtained was cultivated at a frequency of 42 kHz for 4 hours as much as 3 grams into deionized water wherein respectively the solution contains 27.93 grams on the ratio (1: 7.5) and 46.56 grams of KCl in the ratio (1: 12.5) and left to stand for 24 hours. The process of planting during 24 hours aims to precipitate ultrasound silica particles. After being cooled down for 24 hours top layer formed, where the top layer decanted and the lower layer is dried in the oven at 110 °C.

Next, the reduction stage ultrasound silica with metal magnesium. Ultrasonic silica reduced with magnesium powder on 1: 2 mole ratio (3 gram: 2.4 gram) in an electric furnace at 800 °C for 6 hours using a saucer krus. Heating temperature of 800 °C aims to reduce.

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\text{Mg(s)} + \text{SiO}_2(s) \xrightarrow{\text{T=800 °C}} \text{Si(s)} + 2\text{MgO(s)}
\]

Nanosilicon obtained from reduction results was purified using deionized water to remove KCl which is attached to nanosilicon crystals, and deionized water and ethanol for remove the remaining KCl salt attached to nanosilicon particles. Addition of ethanol in purification nanosilicon was used to bind water which is found in the crystal of nanosilicon.

Solids resulting from purification stage I added to HCl 5 N for eliminate products that don't desirable like the rest of the Mg and yield side of the silica reduction process magnesiothermic such as Mg₂Si, and MgO [7]. Metal scraps magnesium that did not react with silica reacts with HCl to form MgCl₂ solution and H₂ gas MgO salt that was formed from magnesiothermic reduction of silica easily soluble in HCl 5 N produced a solution of MgCl₂[7]. Side product of Mg₂Si that formed from the reduction of silica in a manner magnesiothermic easily dissolves in HCl 5 N and produces silane gas SiH₄[10]. Solids resulting from purification stage II added with HF 10% for removing residual SiO₂ which did not reduce, because silica is inert against all acids except HF. Remainder irreducible silica reacts with 10% HF solution forms an acid solution hexafluorosilicate[7]. Next, purified by using HCl 5 N for the purpose to remove the remaining Mg, MgO and Mg₂Si formed during the process reduction takes place [7].
The reduction results added to the inside XRD test in this study done to determine the content elements and compounds in material, size crystal, hkl crystal field, particles agglomerated, and crystal lattice constants.

![Figure 3. Nanosilicon on the ratio of (a) 1:7.5 and (b) 1:12.5](image1)

The nanosilicon crystal structure in the SiO$_2$ : KCl ratio (1:7.5) was analyzed using an X-ray diffractometer Philips PW 3050. Cu-Kα radiation that used (1.540598 Å). Figure 4 (a) to show diffractogram nanosilicon on ratio of 1:7.5 that is angle nanosilicon that appears are on corner peaks of 28.5950; 47.3400; 56.1712; 69.1809; 76.4370 which is approaching data from The Join Committee of Powder Diffraction Standards (JCPDS) nanosilicon. The compounds contained in Figure 3 (a) can be analyzed by adjusting the peaks angle of Figure 4 (a) with data content of elements and compounds in Match-Phase Identification From Powder Diffraction Data can be seen in Figure 5.

From the Match data obtained nano-Si content of 88.8% and content of the actor in the form of silica 11.2%. The size of nanosilicon particles at ratio 1:7.5 determined with using equation Scherrer’s [11] and obtained Nano-Si particle sizes range between 28.56 nm - 170.57 nm. And the value of h$^2$ + k$^2$+ l$^2$ respectively 3, 8, 11, 16 and 19 and hkl value is 111; 220; 311; 400; and 421. And it has lattice constant 5.4222 Å. Figure 4 (b) shows that nanosilicon powder in comparison 1:12.5 has an angle emerging are on the corner peaks 27.0621; 47.4596; 55.3611; 71.0262; 78.1198 which approaches the JCPDS data nanosilicon. The compounds in figure 3 (b) can be analyzed by adjusting the peaks angle of Figure 4 (b) with data compounds content using the application Match-Phase Identification From Powder Diffraction Data. Diffractogram analysis results of the application Match-Phase Identification From Powder Diffraction Data can be seen in Figure 6.
Figure 5. The diffractogram of nano-Si by using Match 1:7.5

From the results of Match the nano-content Si at a ratio of 1: 12.5 obtained is 73% and impurity content in the form silica by 27%. The size of nanosilicon particles at a ratio of 1: 12.5 was determined by using equations Scherrer’s thus obtained particle size ranges from 12.69 nm - 93.23 nm. The values of $h^2 + k^2 + l^2$ are 3, 9, 12, 18 and 22 and hkl value 111; 221; 222; 330; and 332. And has constants lattice 5,7087 Å.
Conclusion
The effect of variation in KCl mass against nanosilicon from the results of silica reduction magnesiothermic with natural sand the ratio of silica: KCl (1: 7.5) and (1: 12.5) where at a ratio of 1: 7.5 produce nanosilicon purity of 88.8% and 1: 12.5 of 73%. The characteristics of nanosilicon with XRD at SiO$_2$: KCl ratio (1: 7.5) has a particle size of 28.56 nm - 170.57 nm and SiO$_2$ ratio : KCl (1: 12.5) has a particle size 12,6959 nm - 93,3238 nm.

Acknowledgment
The authors are gratefully acknowledge Laboratory of Institut Teknologi Sepuluh Nopember, Surabaya for running XRD.

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