Nano-silica production by a sustainable process; application in building materials.

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Abstract
Concrete is the most widely produced manmade material. Current micro-silica is only applied in special cases, due to its high price, and nano-silica is not used in common practice yet. The neutralization of waste acids (either sulphuric or hydrochloric) with olivine produces tailored nano-silica [1][2]. The main factors that determine the rate of dissolution of olivine in acids at elevated temperatures are the olivine specific surface area, the temperature and the pH. The production parameters with a strong influence on the properties of the silica are the olivine composition and fineness, acid purity and concentration, temperature, releases of silica monomers rate and stirring speed. Nano-silica obtained by this process can be produced in large quantities, for low prices and by sustainable method so that mass application in concrete is within reach. It may replace cement in the mix, which is the most costly and environmentally unfriendly component in concrete. The use of nano-silica reduces the CO_2 footprint of the manufactured concrete products and improves the properties in hardened state. Thus a concrete with better performance, lower costs and environmentally sustainable is designed. The application of these concretes can be anywhere, both in infrastructure and in buildings.

1. Introduction

This paper presents a state of the art of the production of nano-silica, focusing on the nano-silica applied to concrete. It includes the present production of nano-silica, an overview of the olivine silica production process, experimental setup and first results and further research.

1.1 Production of nano-silica

At present a wide range of silica products is manufactured industrially for a diverse array of applications. Silicas are mainly used for reinforcing, thickening and flattening purposes. In 1999 the world precipitated silica production capacity was 1100 kilotons [3]. There are two main routes for the productions of synthetic amorphous silica.

Silica by sol gel process:
In the sol-gel process silica monomers are allowed to condense to colloidal particles. These particles form aggregates, which can age. An important reaction route is the procedure involving waterglass. Waterglass is produced by melting quartz sand with soda. Subsequently the solid waterglass is hydrothermally dissolved in water.

Pyrogenic Silica:
The term pyrogenic silica refers to highly dispersed silicas formed from the gas phase at high temperature. Silicon tetrachloride is the usual raw material for flame hydrolysis. It is continually vaporized, mixed with dry air and then with hydrogen, fed to a burner, and hydrolyzed.

Apart from silica produced by these processes, we also have to take into account the silica fume, because it is the main silica used in cement materials. Silica fume is a byproduct of the reduction of quartz for the production of silicon and ferrosilicon. It is a very fine powder consisting of noncrystalline silica spheres with an average diameter of ca. 0.1 μm and is produced at temperatures of about 2050 K. Silica fume is mainly used as an admixture in cement and concrete to improve strength and durability. Due to the small particle size and the large surface area (up to 30 m²/g), it acts both as a microfiller that reduces the porosity and as a pozzolan which reacts with the calcium hydroxide from the cement.

1.2   Concrete containing silica fume

The use of silica fume in concrete continues to increase despite its relatively high cost because its fine particles and its puzzolan behavior are particularly valued in making high performance concrete.

Silica particles are located in very close proximity to the aggregate particle that is, at the aggregate-cement paste interface. This zone is known to be a source of weakness in concrete, the reason being the wall effect which prevents the particles of Portland cement from packing tightly against the aggregate surface. Such packing is achieved by the particles of silica fume. A contributing factor is the fact that silica fume, reduces bleeding so that no bleed water is trapped beneath coarse aggregate particles. In consequence the porosity in the interface zone is reduced [4].

Silica fume is very reactive with calcium hydroxide, because of this, it is possible to use silica fume as a replacement for a small proportion of Portland cement. This is done on the basis of 1 part of silica fume per 5 parts of Portland cement by mass. When using this approach for medium strength concrete, the strength is unaffected by the replacement and the use of superplasticizers is not necessary.

By far the largest use of silica fume is for the purpose of producing concrete with enhanced properties, mainly high early strength or low penetrability. The maximum amount of silica that can be applied in concrete successfully is of about 10 per cent.

2. Overview of the olivine silica production

The olivine silica process will be described, using sulphuric acid as an example. A schematic process flow diagram is presented in figure 1. In the first section the acid is neutralized at elevated temperatures with ground forsteritic olivine rock. The reaction equation is:

$$(Mg, Fe)_2SiO_4 + 4H^+ \longrightarrow Si(OH)_4\,(s) + 2(Mg, Fe)^{2+}$$
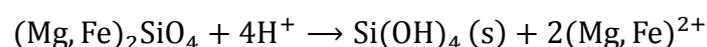
The reaction goes to completion (pH 9-10) even at room temperature but for an industrial application, the reaction rate has to be increased, e.g. by increasing the temperature or the surface area of the olivine. The neutralization yields a mixture of a magnesium/iron salt solution, precipitated silica and unreacted olivine. In the next process section the unreacted olivine and inert minerals are removed from the reaction suspension by a gravitational

separation. Subsequently the precipitated silica is separated from the solution by filtration and washing steps.
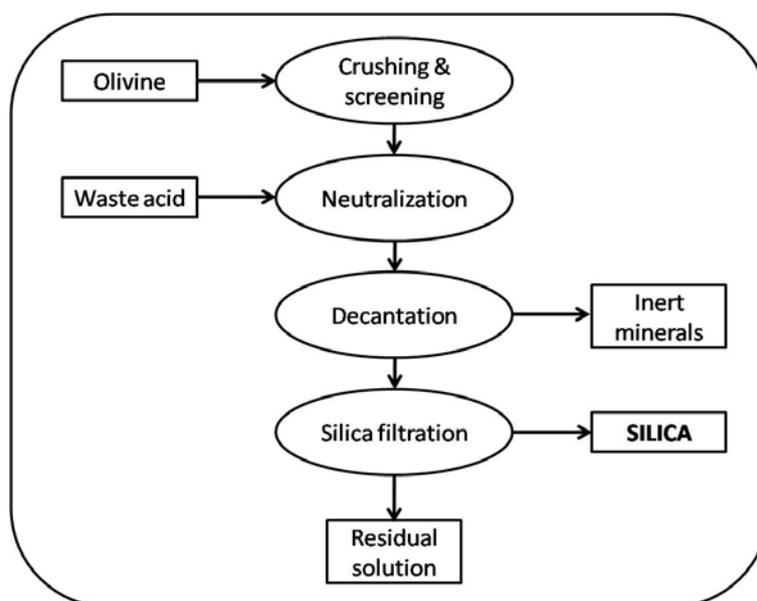

Figure 1. Schematic process flow diagram of the olivine process.

2.1 Dissolution of olivine

The dissolution of olivine can be subdivided in several processes. During the dissolution hydrogen atoms are transported from the bulk of the solution to the olivine surface by convection or diffusion. Subsequently they form an activated complex (surface species) and finally the reaction products, Mg^{2+} and $Si(OH)_4$, are transported away from the surface by convection or diffusion.

In studies under natural conditions, it was suggested that during dissolution precipitated layers could be formed. If a surface layer is present the dissolution process is controlled by diffusion. The distinction between control by diffusion and by surface reaction can be easily made by varying the stirring speed, which will only affect the diffusion-controlled rates. When the reactor is stirred a surface layer is not formed and the dissolution process is controlled by the surface reactions.

Several studies have been carried out to quantify the olivine dissolution rate under natural weathering conditions, all assuming that the olivine dissolution kinetics were controlled by surface reactions [5 [6]. The olivine dissolution rate is given by the general equation:

$$\frac{d[C_{ol}]}{dt} = -k_T \cdot S_{ol}^m \cdot A_{H^+}^n \tag{1}$$

Where C_{ol} is the olivine concentration, S_{ol} is the reactive olivine surface area, $A_H{}^+$ the hydrogen ion activity and k_T a constant depending on the temperature. The coefficients m and n are not equal to the stoichimetric coefficient in this reaction equation and have to be determined experimentally. The temperature constant, k_T, usually follows a Arrhenius relationship.

For the dissolution in 3M sulphuric acid two importants points have to be considered in relation to the dissolution under natural conditions. First the dissolution rate is much higher and secondly the silica monomers will start to polymerize as soon as their concentration

exceeds 100 mg/l [8]. In a non-stirred reactor the silica starts to precipitate close to the dissolve olivine grains.

Figure 2. A. shows a SEM picture of an olivine grain that has undergone dissolution in unstirred 3M H_2SO_4 at 25 °C. The olivine grain is totally covered by a layer of precipitated silica, which exhibits shrinkage cracks due to drying of the hydrous layer of precipitated silica. Figure 2. B. shows a SEM image of olivine grains that were stirred during disolution where it can be observed that these grains are free of the precipitated silica layers.
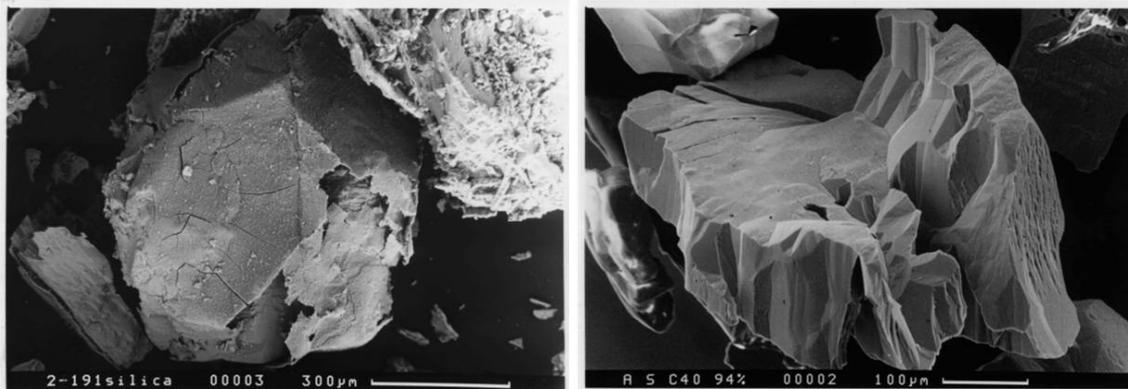

Figure 2. SEM pictures of partly dissolved olivine. A) Partly dissolved olivine grain covered by a layer of precipited silica. B) Partly dissolved olivine grain, showing etch pits and dissolution cracks.

In order to prevent the precipitation of silica on olivine grains vigorous stirring of the reaction mixture is required. Under these conditions the dissolution reaction is kinetically controlled by surface reactions.

2.2   Olivine silica kinetics

A kinetic model for the dissolution of olivine in sulphuric acid at elevated temperatures is presented in [1]. The effects of temperature, grain size fraction and amount of olivine on the neutralization rate have been quantified by carrying out a range of complete neutralization experiments.

For the interpretation of the experimental data, values of the hydrogen ion activity were required and were calculated using the Pitzer model.

The rate equation coefficients and constants were obtained by fitting an expression for the rate equation to the experimental data, obtaining the following equation:

$$\frac{d[H^+]}{dt} = -e^{\frac{E_{act}}{RT}} \cdot 10^8 \cdot 1,92 \cdot S_{geo} \cdot A_{H^+}^{0,33} \qquad (2)$$

With E_{act} being the activation energy of 66,5 kJ/mol, S_{geom} the geometrical surface area of the olivine grains calculated from the grain size distribution, and A_{H+} the hydrogen ion activity calculated with the Pitzer model. The equation was validated for the dissolution of Norwegian olivine (FO_{93}) with grain sizes from 63-300 μm in sulphuric acid at temperatures ranging 60-90 °C.

2.3   The development of the texture of the olivine silica

The formation of colloidal silica particles has been studied widely by Lieftink. The differences of the silica texture can be explained by assuming the following processes taking place in the reaction vessel:

1. Dissolution of olivine and related production of silica monomers.
2. Polymerization of monomer and subsequent nucleation of particles.
3. Particle growth by monomer addition and/or particle aggregation.

The silica texture generated during the dissolution of olivine is mostly determined by the dissolution rate of the olivine. The texture produced during a very fast dissolution remains stabler during the reaction than the texture produced during a slow dissolution. When the reaction is slower, particle growth occurs. Particle growth seems to proceed via a particle aggregation model. This model can explain the observed variation in the texture and the microporosity.

The final particle size is determined by the rate of formation of 2 nm particles and the aggregation of these particles. When the 2 nm particles are produced rapidly, the chance of aggregation of two small particles is larger than the chance of accommodation of small particles on the surface of a larger, growing particle. Therefore the growing of particles occurs when the concentration of small particles in the solution is not too high.

The proposed model by Lieftink provides the possibility for predicting the texture of the silica.

2.4   Previous results

By reacting 1 kg of sulphuric acid 3M with 190 g of Olivine at 90°C in a stirred reactor 65 g of nano-silica is produced. The features of the silica produced are a specific surface area of 100-500 m²/g, a mean particle size of 5-20 nm and specific surface area in micropores of 20-200 m²/g [1][2].

BET specific surface area and particle size of silica as function of temperature and reaction progress, for the neutralization of 3M sulphuric acid with coarse grained norwegian olivine are presented in figure 3 [1][2].
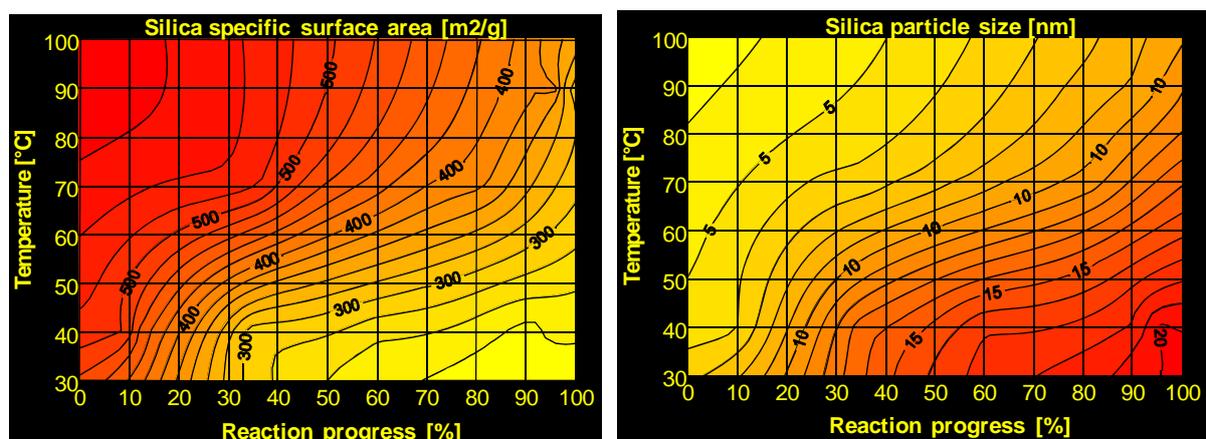

Figure 3. Properties of silica. A) BET specific surface of silica. B) Particle size of silica.

Silica produced by olivine dissolution has very low particle size and high surface area in micropores. This together with the low cost process of the olivine silica production (the materials are not expensive and the temperature reaction is of about 80 °C) makes the research of olivine silica production for cement materials quite interesting.

3. Setup and first results

The olivine silica setup consists in a stirred double-walled glass reaction vessel with an inner volume of 1 liter, with a thermostat bath that controls the reactor temperature through the outer wall. The lab scale setup for the production of olivine silica is presented in the figure 4. A. and the nano-silica produced with this setup at 70 °C and with a 3M sulphuric acid is presented in figure 4. B. The whiteness of the silica is an indicator that the content of the magnesium salt in the silica cake is zero or almost zero.

Figure 4. A) Lab scale setup for the production of olivine silica. Figure 4.B) Nano-silica produced in a stirred reactor at 70 °C and with a 3M sulphuric acid.

4. Further research

The following steps in the production of olivine silica will be:
1. Optimization of process conditions such as olivine particle size, reaction temperature and reactor type.
2. Chemical, physical and mechanical characterization of the produced nano-silica.
3. Tailoring silica in order to establish optimal silica properties and determine washing efficiencies and number of washing steps.
4. Application in concrete, including experiments in mix design, mix evaluation and optimization.
5. Full scale application to study the properties of concrete and structural concrete.

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