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Green Building, MATERIALS AND CIVIL ENGINEERING

VIVEK PRATAP CHAUHAN

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Green Building, Materials and Civil Engineering

Preface

Green building is the practice of creating structures and using processes that are environmentally responsible and resource-efficient throughout a building's life-cycle from siting to design, construction, operation, maintenance, renovation and deconstruction. This practice expands and complements the classical building design concerns of economy, utility, durability, and comfort. Green building is also known as a sustainable or high performance building. Generally, green homes are healthier, more comfortable, more durable, and more energy efficient and have a much smaller environmental footprint than conventional homes.

Civil engineers are often responsible for specifying, designing and manufacturing the materials with which they build their structures. Studies in construction materials are intended to make structural, transportation and foundation engineers aware of the fundamental properties of the materials they use.

The construction materials engineering provides a broad understanding of the composition, microstructure, and engineering behavior of various materials used in civil engineering applications.

This book, a reference tool for researchers, engineers, and academics as well as industry professionals, presents research results and development activities in Materials, Environment and Civil Engineering.

Editor

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Chapter 1

Synthesis of a Green Nano-Silica Material Using Beneficiated Waste Dunites and Its Application in Concrete

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ABSTRACT

Nano-silica, one of the substances boosting the field of nanomaterials, can be produced by dissolving olivine in acid. The dissolution of olivine

is a convenient alternative route to the existing methods of nano-silica production (neutralization of sodium silicate and flame hydrolysis) because the olivine dissolution is a low temperature process making this method cheaper and greener. Furthermore, this process can use waste olivine materials for the production of nano-silica. The produced nano-silica has a specific surface area between 100 and 400 m^2/g; a primary particle size between 10 and 25 nm, which is agglomerated in clusters; and an impurity content below 5 wt.%. In addition, olivine nano-silica can be classified as a pozzolanic material with an activity index of 101%. The optimum replacement level of olivine nano-silica in conventional vibrated concrete is around 5% by volume resulting in: 1) a compressive strength increase of 20%; 2) a CO_2 emission reduction of 3%. Therefore, the use of the olivine nano-silica in CVC does not only improve the compressive strength but also reduce the CO_2 emissions.

INTRODUCTION

Current Production of Nano-Silica

At present, a wide range of silica products (see Figure 1) are manufactured industrially for a diverse array of applications. Silicas are mainly used for reinforcing, thickening and flattening purposes. World demand for specialty silicas, which include precipitated silica, fumed silica, silica gel and silica sol, will rise 6.3 percent per year to 2.7 million metric tons in 2014 [1].

There are two main routes for the productions of synthetic amorphous silica: the thermal route and the wet route [2]. In the thermal route, also called flame hydrolysis, highly dispersed silicas are formed from the gas phase at high temperatures. Silicon tetrachloride, which is the usual raw material, is continuously vaporized, mixed with dry air, then, with hydrogen and finally fed to a burner where it is hydrolyzed in an oxygen-hydrogen flame. The flame temperature depends on the properties of the burner and the desired characteristics of nano-silica. Moore patented a cooled plug burner to produce pyrogenic silica in a temperature range between 1000°C and 1200°C [3].

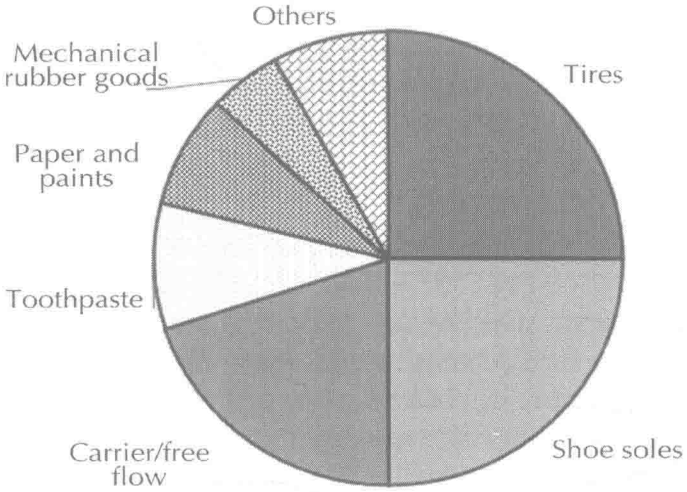

Figure 1: Worldwide consumption and use of precipitated silica in 1999 [5].

In the wet route or sol-gel process, a waterglass solution is mixed with acid (e.g. sulfuric acid) releasing the silica. Waterglass is produced by melting quartz sand with soda from temperatures of 1000°C to 1300°C [4]; subsequently, the resulting solid waterglass is hydrothermally dissolved in water. 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 it is produced at temperatures of about 2000°C [6,7].

In the above production methods, a high-temperature process is involved. To reach these temperatures, huge amounts of fuel are consumed making these processes: a) unsustainable because of the scarcity of fuels; b) environmental unfriendly because of the huge amount of CO_2 emitted; and c) expensive because of the fuel price.

This paper is structured in two parts: first, the production of olivine nano-silica using beneficiated waste dunite; and second, the application of olivine nano-silica in concrete. Here, we demonstrate that the dissolution of olivine is an optimal method to produce an amorphous nano-silica. This method is greener and cheaper than the conventional production methods because the reaction temperature is between 50°C and 95°C. The reaction is exothermic [8], and because of waste dunites, after beneficiation, it can be used as a silica source. The use of nano-silica in conventional vibrated concrete can reduce the CO_2 emissions by 3% and increase the compressive strength by 20%.

Application of Nano-Silica in Concrete

Concrete is the most widely used construction material and consists of water, aggregates and cement. World production of cement increased up to 3.6 billion tons in 2011 [9]. Nano-silica in concrete is not yet commonly applied, but silica fume, which is considered a microsilica, has already been used in concrete for several years to make high-performance concrete. The use of microsilica in concrete continues to increase despite its relatively high cost because of its pozzolanic behavior and its content of fine particles. These two features of the microsilica confer some benefits to the concrete. The pozzolanic behavior refers to the reaction between silica and portlandite, $Ca(OH)_2$, to produce CSH (calcium silicate hydrate) gel, which is the main phase contributing to the concrete's strength.

Also, because of its small particle size, micro-silica fills the voids between the cement particles; this improves the packing factor and reduces the porosity. Besides the above mentioned features, nano-silica has the following effects on cement pastes and concrete mixes: acceleration of the setting, cement matrix densification and improvement of the interparticle transition zone (ITZ) of aggregates (filling effect).

Because of the pozzolanic reaction, micro-silica can replace cement (1 part silica instead of 3 to 4 parts cement) for medium-strength concrete, while the strength is unaffected by the replacement [10]. Considering that the main difference between nano-silica and micro-silica is their particle sizes—assuming pozzolanic behaviors in each are similar—nano-silica will react faster with the cement due to its smaller particles. Therefore, the replacement of cement by nano-silica should considerably reduce the CO_2 emissions of the concrete. That is important because the cement industry is one of the industrial sectors that releases large amounts of CO_2 into the environment accounting for 8% of global CO_2 emissions [11]. In addition to this interesting application, the largest use of micro-silica is for producing concrete with enhanced properties, such as high early strength or low permeability.

Olivine Silica Production

Before beginning this section, it is necessary to clarify the difference between olivine and dunite for readers unacquainted with geology terms. Olivine refers to the mineral $(Mg,Fe)_2SiO_4$ and dunite refers to a rock where 90% of the volume is made up of olivine. The remaining 10% present in dunite ores can consist of pyroxenes, amphiboles, micas, carbonates, serpentines, etc. In many weathering and dissolution studies, pure olivines were used [12-14], but in this study, and our previous work [15], dunite had been used because we focused on the commercial production of olivine nano-silica.

The dissolution of olivine in acid at low temperatures (between 50°C and 95°C) produces amorphous silica:

$$(\mathrm{Mg,Fe})_2\,\mathrm{SiO}_4{+}4\mathrm{H}^+ \rightarrow \mathrm{Si}(\mathrm{OH})_4{+}2(\mathrm{Mg,Fe})^{2-} \tag{1}$$

The dissolution yields a slurry consisting of a mixture of magnesium/iron sulfates, amorphous silica, unreacted olivine and inert minerals. The silica can be separated from the resulting suspension by washing and filtration. A flow chart of this process is presented in Figure 2. The colloidal chemistry of silica strongly depends on the amount of salt and the pH of the solution. At the pH levels of the olivine silica process (−0.5 to 1), a colloidal solution of silica is usually unstable, and the silica particles polymerize [4].

In addition to the low temperature of this procedure (below 95°C), it is remarkable that the process is exothermic with a reaction heat of 223 KJ per mole of olivine [8]. The energy generation during the olivine nano-silica process for an adiabatic reactor is shown in Table 1. When 1.5 moles of olivine react with sulfuric acid, the temperature of the mixture will increase to 84°C. Therefore, the reaction generates more than enough energy to keep the system at the desired temperature (between 50°C and 90°C) provided the reactor is sufficiently large and well insulated.

MATERIALS AND METHODS

The chemical composition of different dunites analyzed by X-ray fluorescence (XRF) is shown in Table 2. The first three dunites were from Norway, and the others were from Greece. The Greek dunites were a waste material generated from the magnesite mining activities in Gerakini. The loss of ignition (LOI) of GR-PROMGM-1 and GR-PROMGM-3 is too high, which is presumably related to the presence of serpentine and carbonate minerals, but not to olivine. These waste rocks were beneficiated by dense media separation, resulting in samples GR-PROMGM-4, −8 and −10, with a LOI below 2.5%. The olivine content of these samples was determined by X-Ray diffraction (XRD), XRF and thermogravimetric (TG) techniques. The olivine content was about 89 % for the Norwegian dunites whereas in the Greek dunites it was lower (see Table 2). The samples after beneficiation, PROMGM-4, −8 and −10, doubled the olivine content of the original non beneficiated waste material.

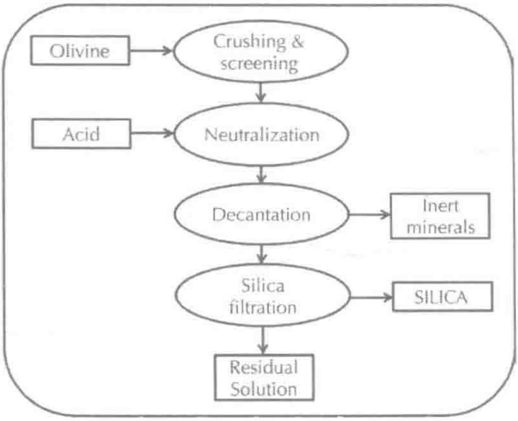

Figure 2: Flow chart of the olivine process.

Table 1: Energy generation during the olivine nano-silica process

H_r (kj/mol)	n_{ol} (mol)	V_{H2SO4} (l)	$[H_2SO_4]$ (mol/l)	X	Q (kj)	T (°C)
223	1.5	1	3	100	333.5	84

Table 2: Chemical composition of the different dunites

Dunite	g_0	Fe_20_3	$Si0_2$	Cr_20_3	Al_20_3	NiO	NInO	CaO	Na_20	LOI	Other Oxides	Olivine
NO-CRS-1	47.41	7.84	41.42	0.31	0.75	0.33	0.12	0.34	0.06	1.29	0.13	88.4
GL50	49.32	7.32	41.44	0.31	0.46	0.32	0.09	0.15	0.02	0.59	0.00	88.9
GR-PROMGM-1	41.62	8.63	41.46	0.5	0.52	0.3	0.15	0.69	0.09	5.92	0.12	44.0
GR-PROMGM-3	34.47	7.95	43.51	0.45	1.78	0.25	0.14	1.33	0.33	9.6	0.19	29.0
GR-PROMGM-4	43.93	9.01	43.60	0.44	0.56	0.32	0.13	0.70	0.00	1.33	0.00	75.0
GR-PROMGM-8	43.79	8.90	42.67	0.41	0.59	0.31	0.13	0.65	0.00	2.55	0.00	75.0
GR-PROMGM-10	45.12	8.79	41.92	0.42	0.54	0.31	0.12	0.83	0.00	1.95	0.00	75.0

Nano-silica production experiments were carried out at 50°C, 70°C and 90°C with olivine particles of 125 - 150, 250 - 300 and 500 - 600 μm in a stirred, thermostated reactor of one liter. The reagents used were 500 ml of 3 M sulfuric acid and the stoichiometric amount of olivine, previously dried. The neutralization reaction continued until the $[H^+]$ was below 0.1 mol/l when it was stopped. Then the suspension was separated from the solid residue by sedimentation. Subsequently, the remaining slurry was washed and filtered to obtain the clean amorphous nanosilica (more details can be found in [15]).

The nano-silica produced was characterized by nitrogen physisorption, transmission electron microscopy (TEM), X-ray fluorescence (XRF), and combustion infrared analysis (determination of sulfur content). A Micromeritics TriStar 3000 equipment using N_2 with a soaking time of 240 min above 100°C was used for the gas physisorption analysis [16] in order to remove the physisorbed water. The physisorbed water is completely removed from the silica at 200°C, but all the silanol groups still remain [17]. The presence of remaining water decreases the adsorption of nitrogen on the surface of the solid material. The difference in the SSA_{BET} between an olivine nano-silica with a soaking temperature of 120°C and 190°C was around 20% for an olivine nano-silica of 345 m^2/g with a soaking temperature of 190°C. In this study two soaking temperatures for olivine nano-silica are used in order to compare the results of Greek dunite with Norwegian dunite, which were analyzed at 120°C in our previous study [15]. The specific surface area, SSA_{BET}, was calculated using the BET [16, 18]. The specific external surface area, SSA_E, and the specific micropore surface area, SSA_{MP}, were calculated using the t-plot method [19, 20] from the slope of the t-plot curve [21]. The particle size of the nano-silica was calculated from the geometrical relationship between surface area and mass given by

$$d\left(nm\right) = \frac{6000}{SSA_{BET} \cdot \rho} \tag{2}$$

where d is the particle size of nano-silica considered to be spherical (nm), 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.

RESULTS

Olivine Nano-Silica from Norwegian Dunite

The experiments performed with Norwegian dunite are presented in Table 3 together with the amount of reagents, the molecular ratio of hydrogen ion versus olivine, the average particle size of olivine (d_{OL}) and the reaction temperature. The values of the specific surface area, pore size and particle size of olivine nano-silica (equation (1)) are collected in Table 4. Figure 3 shows a TEM picture of sample NS-7 [15]. The chemical composition of the nano-silica produced in these experiments is shown in Table 5. The total sulfate, the sulfate limit for the application of silica in concrete "norm NEN – EN 13263-1 + A1" and the number of filtration steps of the olivine nano-silica are shown in Figure 4.

Table 3: Initial conditions of the nano-silica production experiments

Title	$m_{H2so,}$(g)	Moi (g)	Ratio W/01	do) (pm)	Treactor (°C)
NS-1	589.1	109.8	4.5	138	48.7
NS-2	593.5	125.0	4.0	200	52.0
NS-3	555.8	121.7	3.8	400	55.0
NS-4	532.7	112.6	4.0	313	70.2
NS-5	593.9	122.9	4.0	400	70.7
NS-6	594.2	113.1	4.4	550	69.9
NS -7	593.7	119.4	4.2	275	87.7
NS-S	592.3	121.5	4.1	400	S6.2

Table 4: Properties of olivine nano-silica produced using Norwegian olivine

Title	SSABEr (m^2/8)	SSAie (m^2/8)	SSAE (m^2/8)	dp A (mu)	dp_D (mu)	Darr (nm)
NS-1	131	27	104	21	21	26
NS-2	150	27	123	1S	17	22
NS-3	165	43	122	1S	18	22
NS-4	21S	52	166	1S	17	16
NS-5	19S	5S	139	19	19	20
NS-6	179	47	132	28	24	21
NS-7	266	72	194	25	22	14
NS-8	185	36	149	18	17	18

'Soaking temperature was 120°C.

The maximum sulfate content (SO_4) from the norm is 2.4% or 0.8% expressed as sulfur content.

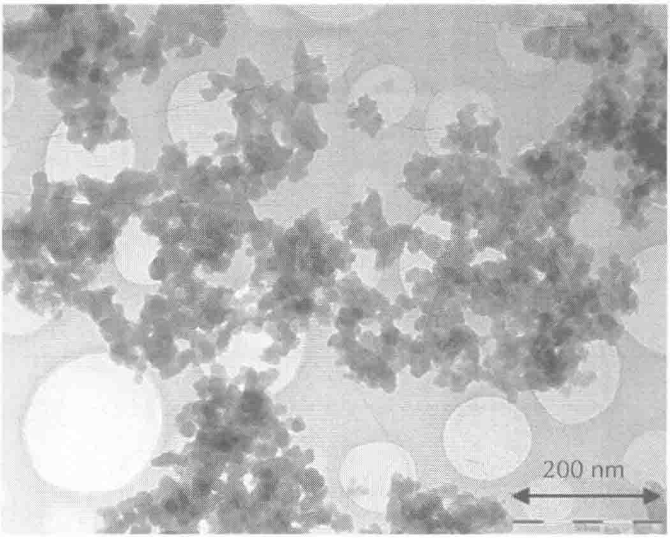

Figure 3: TEM picture (89 kx) of the olivine nano-silica NS- 7 [15].