Spheroidization of Nanometric Waste Glass Powder for Use in Cementitious Materials via the Technology of RF Induction Plasma Torch

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Abstract: Because of its high throughput, Inductively-Coupled Plasma (ICP) torch can commercially provide an added value to waste glass (WG). It vaporizes WG into spheroidized glass powder (SGP) that could be used as a cementitious material. Changing the WG feed rate and pressure induce variations on the particle size distribution and chemical composition. Using Field Emission Gun Scanning Electron Microscopy (FEGSEM), Brunauer, Emmet and Teller (BET) method, nano-micro phases separation (ICP-MS), low WG feed rate and pressure increase the nanometric phase of SGP (NSGP). Adding <5% SGP in replacement of cement in a mortar give a filler effect at early age (<7 days) and a pozzolanic effect on a long term (>28 days), which increases by ≈10% the compressive strength of mortar.

Keywords: RF Plasma spheroidization, waste glass, glass nanoparticles, cluster coalescence, cementitious materials.

1. Introduction

Durability and sustainability of concrete infrastructures is becoming of critical importance for the construction industry. The current trend is to blend submicron aluminosilicate supplementary cementitious materials (SCMs) with ordinary Portland cement (OPC). Well known SCMs are silica fume, fly ash and slag. The cement hydration reactions -the core of concrete-making- involve numerous chemical species reacting to form hierarchical structures ranging from nanometers to millimeters [1-3]. Briefly, it generates hydrated calcium silicate gels (C-S-H), responsible for concrete performance (mechanical resistance and low permeability) and hydrated lime (Ca(OH)₂:CH), a weak binder that is responsible of the porosity and permeability of concrete. On the other hand, the hydration of SCMs triggers pozzolanic reactions during the hydration of OPC. Instead of producing lime as for the case of hydration of OPC, pozzolanic reactions consume CH to produce C-S-H gels. These C-S-H gels and unreacted SCMs fill the capillary pores in concrete, thus enhancing the mechanical resistance and decreasing the permeability of concrete [4-6].

Utilizing spheroidized nanoparticles, especially nanosilica [7-9], is one way that could stimulate the hydration reactivity and improve the rheological properties of concrete due to their fine size and spherical shape. Nano-size, large specific surface and dispersed nanosilica particles ensure high contact surface and optimum reactivity with CH generated from the hydration of OPC. They act as a nucleation site for lime produced from the hydration of cement, but also for the growth of hydration product around them, particularly for high-stiffness C-S-H. This then catalyzes and increases the kinetic of cement hydration to yield C-S-H at early age [7-9]. More important, these nanoparticles have the appropriate fineness to percolate into the capillary pores of cementitious materials and thus act as a nanofiller.

In order to engineer nanosilica, waste glass powder (WG), as starting material, is vaporized and spheroidized using the inductively-coupled thermal plasma torch technology into spheroidized glass powder (SGP). This paper discusses the effects of the WG feed rate and the reactor pressure on the size and morphology SGP and the influence of adding SGP in a cementitious matrix on the compressive strength of cement mortars.

2. Plasma equipment

In Figure 1, a powder feeder supplies ball milled WG into the injection probe of a PL-50 induction thermal plasma torch (Tekna Plasma System Inc.). The plasma torch is attached at the top extremity of a vertical stainless steel water-cooled cylindrical
reactor. Downstream, a filter consisting of 4 porous metal cylinders separates the particles from the exhausted gas stream. Produced SGP are distinctly collected on the walls of the reactor and filter.

Figure 1: Induction plasma system for the spheroidization of waste glass.

Table 1 lists the investigated operating parameters for the synthesis of SGP. The experiments were conducted by using argon (Ar) as central plasma-forming gas and oxygen (O₂) as sheath gas.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torch Power</td>
<td>50 kW</td>
</tr>
<tr>
<td>Central plasma gas</td>
<td>Ar: 25 slpm</td>
</tr>
<tr>
<td>Plasma sheath gas and flow rate</td>
<td>O₂: 75 slpm</td>
</tr>
<tr>
<td>Reactor pressure</td>
<td>40 and 88 kPa</td>
</tr>
<tr>
<td>Powder feeding rate</td>
<td>3.5, 4.5, 6.0 g/min</td>
</tr>
</tbody>
</table>

3. Material characterization

WG is observed using Scanning Electron Microscopy (SEM: Hitachi S-3400N). The SEM acceleration voltage and emission current are respectively set to 5.0 kV and 60 μA. Given their nanometric size, SGP is analyzed using a Field-Emission Gun SEM (FEGSEM: Hitachi S-4700). The FEGSEM acceleration voltage and emission current are respectively set to 3.0 kV and 10 μA.

Figure 2 shows that WG particles possess random edged morphology with a PSD ranging below 100 μm, which was confirmed using laser granulometry (Fritsch Analysette 22 COMPACT). In Figure 3, SGP possessed a spherical morphology with a bimodal size range: it is composed of a large fraction of nanometric SGP (NSGP) particles of 0.025-0.200 μm in diameter and few micrometric SGP (MSGP) particles of 1-5 μm in diameter.

The NSGP content was determined by the nano-micro phases separation. This procedure implies of weighting 0.5g of powder samples in methanol in a 100 ml beaker. The resulting solution was then put in an ultrasonic bath for 5 minutes. As a result, the NSGP was suspended in methanol, while the MSGP precipitated in the bottom of the beaker. The NSGP suspension was then decanted from the MSGP. The NSGP suspensions and MSGP were dried in an oven at 105°C and weighted to determine the NSGP content.

When measuring the specific surface area, the BET apparatus was preliminary degassed for 1 hour under vacuum at 110°C. The measurements were performed on 5 points using N₂ as the absorbing gas. The specific surface area measurements were thereafter converted into an equivalent diameter value using the following equation:

\[ D(3,2) = \frac{6 \times 10^9}{\rho \times SSA} \]

Where \( \rho \) is the density of SGP (2300 kg/m³), SSA, the specific surface area in m²/kg, and D(3,2), the equivalent diameter in nm.

The chemical composition of SGP is analyzed using Inductively-Coupled Plasma-Mass Spectroscopy (ICP-MS). Prior the analyses, SGP were digested...
and completely dissolved in an acid solution (HNO₃, HCl, HF, H₃BO₃) in a closed Teflon vessel using a microwave reaction oven (CEM Mars X).

4. Effect of WG feed rate
NSGP were synthesized at 40 kPa at 3 different WG feed rates: 3.5, 4.5 and 6.0 g/min. The BET measurements in Table 2 demonstrate an increase of the particle size as the WG feed rate increases. The increase of the WG feed rate from 3.5 to 4.5 g/min suddenly decreases the SSA by about twice and doubles the equivalent diameter (D(3,2)). An increase of the WG feed rate to 6.0 g/min further decreases the SSA by about 3 times and triples D(3,2). As for Goortani et al. [10], a high WG feed rate may increase the partial pressure of glass vapor in the plasma flame that increases the coalescence of glass clusters into SGP, leading to the formation of larger particles. Moreover, the high WG feed rate induces a strong cooling of the plasma flame, reducing the plasma flame enthalpy, as well as the residence time of the glass clusters and vapor [11-12]. Also, one has to note that operating at a WG feed rate of 6.0 g/min leads to frequent impulsion feeding that results in instantaneous high loadings and cooling of the plasma flame. This consequently reduces the ability of the plasma flame to vaporize WG and yield a higher MSGP content.

5. Effect of WG feed rate
NSGP were synthesized at two plasma reactor pressures: 40 and 88 kPa. The BET measurements in Table 2 demonstrate an increase of the particle size as the pressure increases. The use of a high pressure reduces by ≈70% the SSA and increases by more than 3 times the equivalent diameter (D(3,2)). Despite this trend includes only 2 data points, the difference in the particle size is notable. With respect to WG, SGP shows a lower concentration of Na₂O and a higher concentration of SiO₂. This is also reflected in the Na₂O/SiO₂ ratios. These concentration variations in SiO₂ and Na₂O measured along the different plasma system zones are attributed to the differential nucleation temperature of SiO₂ and Na₂O. The boiling points of SiO₂ and Na₂O are respectively 2230°C and 1950°C [13]. The CaO/SiO₂ and Al₂O₃/SiO₂ ratios, not shown in Table 3, remain relatively constant through the different collection zones to 9 and 2 respectively, because of their relatively high boiling points of CaO and Al₂O₃: 2850°C and 2977°C respectively.

6. Chemistry of SGP
ICP-MS was used to measure the chemical composition of SGP. Table 3 exhibits the chemical composition of WG and SGP synthesized at a pressure of 40 kPa and a WG feed rate of 3.5 g/min. It shows the chemical composition of the major oxides contained in WG and SGP (SiO₂, Na₂O, CaO and Al₂O₃) collected in the different zones in the plasma system and their respective ratio with respect to the SiO₂ content. In our case, the concentrations of MgO, K₂O and Fe₂O₃ are not presented, because they only account for less than 1% respectively.

7. Compressive strength of mortars
Cubic mortars were made according to ASTM standard test methods C109/C109M using a General Use (GU) cement and Ottawa sand. The water to cementitious material ratio (w/cm) was set to 0.4 and the sand to cementitious material ratio (S/cm) to 2.75. SGP are introduced in mortars at a 0% (control), 1%, 5% and 10% cementitious material

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**Table 2:** Measured SSA and calculated D(3,2) values from BET, wt.% NSGP and particle size for SGP-N₂ as function of WG feed rate and pressure

<table>
<thead>
<tr>
<th>Feed rate (g/min)</th>
<th>Pressure (kPa)</th>
<th>SSA (m²/kg)</th>
<th>D(3,2) (nm)</th>
<th>wt.% NSGP</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>40</td>
<td>16 430</td>
<td>150</td>
<td>98</td>
</tr>
<tr>
<td>4.5</td>
<td>40</td>
<td>8 550</td>
<td>301</td>
<td>86</td>
</tr>
<tr>
<td>6.0</td>
<td>40</td>
<td>5 770</td>
<td>446</td>
<td>81</td>
</tr>
<tr>
<td>3.5</td>
<td>88</td>
<td>5 090</td>
<td>506</td>
<td>59</td>
</tr>
</tbody>
</table>

**Table 3:** Chemical composition of SGP from ICP-MS.

<table>
<thead>
<tr>
<th>wt.%</th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>Na₂O/SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>WG</td>
<td>70.0</td>
<td>20.0</td>
<td>6.2</td>
<td>1.7</td>
<td>29</td>
</tr>
<tr>
<td>Reactor</td>
<td>77.1</td>
<td>13.9</td>
<td>6.6</td>
<td>1.2</td>
<td>18</td>
</tr>
<tr>
<td>Filter</td>
<td>78.9</td>
<td>11.6</td>
<td>7.1</td>
<td>1.2</td>
<td>14</td>
</tr>
</tbody>
</table>
Prior mixing the materials, SGP were dispersed in water using an ultrasonic probe. At the fresh state, the different mortar had their flow adjusted using a superplasticizer (SP) to meet the prescribed fluidity (between 100% to 115% flow). The mortars were allowed to harden at room temperature for 24 hours and were then cured in lime saturated water.

Figure 4 shows the compressive strength of mortar as a function of the curing time (1, 7, 28 and 56 days). At early age (<7 days), SGP 1% and 5% mortars show similar compressive strengths to the control. In the case of the control, the compressive strengths are given by the hydration of cement, whereas in the case of SGP mortars, by partially the filler effect of SGP and cement hydration. On a long term (>28 days), the compressive strengths of SGP 1% and 5% mortars increase, by ≈10% in case of the former, with respect to the control. This increase is attributed to the pozzolanic reaction, which is slower than the hydration of cement. At 56 days, the decrease of the compressive strength with respect to the increase of SGP% is attributed to the increasing water demand of SGP in the cementitious matrix. This is also reflected in the SP demand. The dosages of dry extract SP for the 1%, 5% and 10% SGP mortars were 0.4%, 0.5% and 0.7% of the quantity of cm to meet the prescribed fluidity. Adding SGP reduces the effective water for the hydration of cement and for the pozzolanic reaction. Moreover, an increase concentration of SGP in the cementitious matrix creates agglomerates and reduces the pozzolanic and filling effect of SGP.

Tests on mortars demonstrate that a small addition of SGP (<5%) increases the compressive strength comparatively to control cement mortars. The effect of SGP on compressive strength and reactivity can increase with a better dispersion. Their small size leads to an increase of the surface energy that tends to agglomerate the nanoparticles.

**References**


**Conclusions**

SGP were synthesized via the induction plasma spheroidization of WG for a potential application as a cementitious material. By optimizing the process parameters, notably the flow rate and the chemistry of quench and the sheath gas, the pressure and the WG feed rate, it is possible to influence the morphology, the size and the chemical composition of SGP. In fact, these process parameters influence the vapor pressure of precursors, the extension of the hot temperature zone of the plasma flame and the thermal gradients for the coalescence of SGP. A low WG feed rate introduced in the plasma torch decreases the precursor vapor pressure and reduces sudden cooling of the plasma flame. A low pressure inside the plasma reactor expands the hot temperature and increases the thermal gradients for the coalescence of small size SGP.