Synthesis and evaluation of the size and morphology of SiO$_2$ nanoparticles in ICP RF plasma reactors

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Synthesis and evaluation of the size and morphology of SiO2 clusters and nanoparticles in ICP RF plasma reactors

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Contents

- Project objectives
- Introduction
- Results
- Conclusion
Objectives

- Thermal plasma production of SiO2 nanoparticles in an evaporation condensation process

- Identification of the critical parameters affecting the size, morphology and aggregation level of the powder
  (*Using laser scattering as a complimentary technique to SEM and BET*)

- Showing how thermal plasma method can be used as an efficient method to control the size and the morphology of the nanoparticles
  (*Using CFD modelling by Fluent and FPM to understand the effect of quench and reactor configuration*)
Introduction

- Concepts
- Study tools
- Experimental operating conditions
Formation and growth of nanoparticles by different mechanisms

[H. Fissan 2001-2002]

The final size and morphology of the particles depends on the temperature and time history of the flow inside the reactor [Friedlander S.K. 1999]
Note to the complementary nature of different characterization techniques

Image analysis by SEM

\[20 \text{ nm} < d < 130 \text{ nm}\]

Aggregate size distribution measurement by Laser scattering

\[D(4,3) = \sum w_i \times d_i\]

\[D(1,0) = \sum n_i \times d_i\]

\[100 \text{ nm} < d < 800 \text{ nm}\]

Specific surface area measurement by nitrogen absorption BET method

\[D(3,2) = \sum s_i \times d_i\]

\[= \frac{6}{\rho \times SSA}\]

\[d = 50 \text{ nm}\]
### Raw powder feed characterization

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma Gas and Flow rate</td>
<td></td>
</tr>
<tr>
<td>- Central Gas</td>
<td>Argon, 22.5 slpm</td>
</tr>
<tr>
<td>- Sheath gas</td>
<td>Oxygen, 65 slpm</td>
</tr>
<tr>
<td>Feeding Rate and Mechanism</td>
<td>4.5 - 27 g/min SiO₂ (50% weight suspension of SiO₂ in methanol</td>
</tr>
<tr>
<td></td>
<td>D(3,2) = 290 nm</td>
</tr>
<tr>
<td>Plasma Power Plate Efficiency</td>
<td>40 kW</td>
</tr>
<tr>
<td></td>
<td>45 %</td>
</tr>
<tr>
<td>Reactor Pressure</td>
<td>90 kPa</td>
</tr>
<tr>
<td>Quench gas flow rate</td>
<td>270 - 450 slpm</td>
</tr>
</tbody>
</table>

**Experimental: operating process conditions**
Result

Effect of feed injection rate
Result of quench gas injection
Numerical results
Controlling the nanostructure
Result

- Effect of feed injection rate
- Result of quench gas injection
- Numerical results
- Controlling the nanostructure
Result

Effect of feed injection rate

Uncontrolled Feed injection

Controlled Feed injection
Injection rate = 6.5 g/min

**Effect of feed injection rate** (powders collected from the filter)

The effect of feed rate on the equivalent diameter \( D(3,2) \) as calculated from BET results.

**Aggregates size distribution of the synthesised particles without quench.**

Injection rate = 4.5 g/min

Injection rate = 6.5 g/min
Result

**Effect of feed injection rate**
(powders collected from the reactor wall)

Variation of particles diameter, as deposited on the reactor wall at different feeding rates $D(3.2)$, calculated from BET measurements.
Result

- Effect of feed injection rate
- Result of quench gas injection
- Numerical results
- Controlling the nanostructure
Solid bridging of nanometric particles with unevaporated particles and creation of large aggregates
Result \[ \implies \] Effect of quench gas injection

Aggregate and particle size distribution, results of laser Scattering. a: with quench b: no quench. (Powder collected from the filter).
Result

- Effect of feed injection rate
- Result of quench gas injection
- Numerical results
- Controlling the nanostructure
Calculation domain used for the numerical simulation

(Goortani et al., 2006)
Result  Numerical results

Particles size distribution along the reactor wall for 4.5 g/min feed rate and 270 slpm quench gas injection (Goortani et al., 2006)
Explanation of effect of quench gas injection: creation of particles of lower diameter (temperature gradients) with higher level of aggregation (streamlines)

(Goortani et al., 2006)
Result

**Numerical results** (An explanation for the presence of the minimum in the experimental observations)

Particles with the minimum diameter

Top: Contours of diameter, colored by size.

Down: Vectors of velocity, colored by temperature

Vectors of velocity along with the particle diameter in the reactor chamber

*Goortani et al., 2006*
How can we design the quench gas inside the thermal plasma reactor to control the nanostructure?
Result

- Effect of feed injection rate
- Result of quench gas injection
- Numerical results
- Controlling the nanostructure
Controlling the nanostructure

**RADIAL TOP QUENCH:**
Highly aggregated porous nanostructure

**RADIAL BOTTOM QUENCH:**
Partially sintered nanoparticles

**ALUMINA WALL REACTOR:**
Non-aggregated nanospheres
Numerical assumptions and boundary conditions

a) Boundary Conditions

<table>
<thead>
<tr>
<th>Boundary Type</th>
<th>Assumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Torch inlet- Velocity</td>
<td>$V = V_0(1-x^2/r^2)$; $V_0 = 45$ m/s , $0 &lt; x &lt; 5$ cm</td>
</tr>
<tr>
<td>2) Torch inlet- Temperature</td>
<td>$T = T_0(1-x^2/r^2)$; $T_0 = 6500$ K $0 &lt; x &lt; 5$ cm</td>
</tr>
<tr>
<td>3) Wall</td>
<td>Alumina wall, Radiation beginning at 300 K, $\varepsilon = 0.6$ , Thickness = 0.5 cm</td>
</tr>
<tr>
<td>4) Outlet</td>
<td>Pressure Outlet, $P = 95000$ KPa, equilibrium pressure distribution</td>
</tr>
</tbody>
</table>

b) Mixture of materials properties

<table>
<thead>
<tr>
<th>Material</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Ar</td>
<td>Boulos M.I. [20]</td>
</tr>
<tr>
<td>2) O$_2$</td>
<td>Boulos M.I. [20]</td>
</tr>
<tr>
<td>2) Ar- O$_2$ mixture</td>
<td></td>
</tr>
<tr>
<td>a) Density</td>
<td>- Volume weighted average</td>
</tr>
<tr>
<td>b) $C_p$</td>
<td>- Mixing law</td>
</tr>
<tr>
<td>c) Thermal conductivity</td>
<td>- Mass weighted</td>
</tr>
<tr>
<td>d) Viscosity</td>
<td>- Mass weighted</td>
</tr>
<tr>
<td>e) Diffusivity</td>
<td>- Constant dilute approximation</td>
</tr>
</tbody>
</table>

c) Other Fluent settings

<table>
<thead>
<tr>
<th>Solver</th>
<th>Segregated, 3 dimensional, Steady state, Double precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscous model</td>
<td>Standard $K - \varepsilon$ turbulent model</td>
</tr>
<tr>
<td>Operating conditions</td>
<td>$1.013\times10^5$ pa at the torch inlet</td>
</tr>
</tbody>
</table>
Radial top quench

Highly aggregated porous nanostructure

Quench gas injection holes

Quench injection tube

Supporting and transferring tube

Plasma Gas (Central and Sheath Gases)

Feed (SiO2 Suspension) and Atomizing Gas

Quench injection tube

Reactor Body

L1

L2
Radial top quench ➔ Highly aggregated porous nanostructure

Calculation domain used for the numerical simulation

Temperature profiles (K) at various reactor cross sections
Radial top quench  ⇔  Highly aggregated porous nanostructure

Velocity profile (m/s) at the plane of quench gas injection

Velocity vectors (m/s) in the reactor top corner
Variation of particles diameter $D(3,2)$, as deposited on the reactor wall. Comparison of the predicted FPM-3D results with experimental BET measurements $D(3,2)$.

Particles size distribution on the reactor wall. Results of FPM 3-d. (The results converged after 85000 iterations. About 45 days on the Pentium IV Intel processor.)
Radial top quench  ➞  Highly aggregated porous nanostructure

Aggregates size distributions, powders collected from the filter (Blue Graph)
Radial bottom quench

Calculation domain of radial-bottom quench reactor.
Radial bottom quench  ➡️  Partially sintered nanoparticles

Temperature profiles (K) at various reactor cross sections

Velocity vectors (m/s) in the reactor top corner
Aggregates size distributions, powders collected from the filter

(Green Graph)
Alumina wall reactor \[\rightarrow\] Non-aggregated nanospheres

Calculation domain used for the numerical simulation
Alumina wall reactor ➰ Non-aggregated nanospheres

Temperature profiles (K) at various reactor cross sections

Velocity vectors (m/s) in the reactor downstream
Alumina wall reactor  

Non-aggregated nanospheres

a

b

500 nm

2 μm

c

10 μm
Aggregates size distributions, powders collected from the filter
(Red Graph)
Fibrous nanostructure: Powder collected from the top reactor wall
Conclusion
Conclusion

When the feed rate increases from 4.5 to 27 g/min the BET equivalent diameter of the particles $D(3,2)$ increases from 37 to 65 nm. However the product is essentially aggregates of the size between 1-3 micron.

Result 1

Result 2

In the presence of quench, a significant decrease in BET diameter of the particles to 25 nm was observed. However the size of the aggregates increased.

Result 3

The presence of high temperature regions inside the reactor increases the evaporation efficiency.

$$\eta_{Evpn\cdot Alumina} > \eta_{Evpn\cdot radial\cdot bottom} > \eta_{Evpn\cdot radial\cdot top}$$
More fluid recirculation leads to more collisions between the particles and consequently more levels of aggregation among particles are observed.

\[
d \text{radial-top quench} > d \text{radial-bottom quench} > d \text{Alumina}
\]
### Conclusion

3 categories of aggregates

<table>
<thead>
<tr>
<th>a) Nanoparticle-nanoparticle sintering</th>
<th>b) Nanoparticle-microparticle sintering</th>
<th>c) Microparticle microparticle sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>500 nm</td>
<td>1 μm</td>
<td>2 μm</td>
</tr>
</tbody>
</table>

Rapid cooling of vapors stops the growth of nanoparticles and generates high temperature gradients. This explains the observed behavior in the results of SEM and BET:

\[ d_{\text{radial-top quench}} < d_{\text{radial-bottom quench}} < d_{\text{Alumina}} \]
1) Thermally insulated wall extending the high temperature regions.

2) Gradual expansion entrance preventing fluid recirculation.

3) Radial quench injection through 16 nozzles for fast quench: high temperature gradients.

Synthesis of non-aggregated silica nanospheres in the size range D(3,2) of 10-50 nm.
Thanks!

Merci!

спасибо!