CENTRIFUGATION OF NANOMETRIC SILICON CARBIDE POWDER FOR GRANULOMETRIC CLASSIFICATION

CENTRIFUGAÇÃO DO PÓ DE CARBONETO DE SILÍCIO NANOMÉTRICO PARA CLASSIFICAÇÃO GRANULOMÉTRICA

CENTRIFUGACIÓN DE POLVO DE CARBURO DE SILICIO NANOMÉTRICO PARA CLASIFICACIÓN GRANULOMÉTRICA

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ABSTRACT

In this study, researchers focused on improving the quality of SiC particles, considering their different sizes and shapes. To ensure a high-quality end product, the particles were separated into distinct granulometric fractions, with a focus on the nanometer range. The efficiency of this classification process played a crucial role in determining the quality of the final product. SiC holds significant market value, reaching US$3.3 billion in 2022. Brazil stands as one of the main producers of raw SiC, but it still relies on imports for finer granulometries needed in various industrial applications. The main objective of the research was to develop a highly efficient technique for the nanometric fractionation of silicon carbide powders. After conducting experiments, the researchers successfully obtained SiC with a diameter below 2 μm. To achieve this, multiple chemical dispersants were explored for the centrifugation process, aiming to disaggregate the solution and improve the overall yield, with sodium carbonate emerging as the most promising among the tested dispersants. By presenting these findings, the researchers contribute to advancing SiC production and its applications, especially in industries that require nanometer-sized SiC particles. The study not only enhances the quality of the final

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product but also reduces the country's dependence on imported carbide for industrial purposes.

**Keywords:** Silicon carbide; classification; centrifugation; dispersants.

**RESUMO**
Nesse trabalho, os pesquisadores se concentraram em melhorar a qualidade das partículas de SiC, considerando seus diferentes tamanhos e formas. Para garantir um produto final de alta qualidade, as partículas foram separadas em distintas frações granulométricas, com foco na faixa de nanômetros. A eficiência deste processo de classificação desempenhou um papel crucial na determinação da qualidade do produto final. O SiC tem um valor de mercado significativo, atingindo US$ 3,3 bilhões em 2022. O Brasil é um dos principais produtores de SiC bruto, mas ainda depende das importações de granulométrias mais finas, necessárias em várias aplicações industriais. O principal objetivo da pesquisa foi desenvolver uma técnica de alta eficiência para o fracionamento nanométrico de pó de carboneto de silício. Depois de realizar experimentos, os pesquisadores conseguiram obter SiC com diâmetro inferior a 2 μm. Para isso, vários dispersantes químicos foram explorados para o processo de centrifugação, visando desagregar a solução e melhorar o rendimento global, com o carbonato de sódio emergindo como o mais promissor entre os dispersantes testados. Ao apresentar esses achados, os pesquisadores contribuem para o avanço da produção de SiC e suas aplicações, especialmente em indústrias que necessitam de partículas de SiC de tamanho nanômetro. O estudo não só melhora a qualidade do produto final como reduz a dependência do país de carboneto importado para fins industriais.

**Palavras chave:** Carboneto de silício; classificação; centrifugação; dispersantes.

**RESUMEN**
En este estudio, los investigadores se centraron en mejorar la calidad de las partículas de SiC, teniendo en cuenta sus diferentes tamaños y formas. Para garantizar un producto final de alta calidad, las partículas se separaron en distintas fracciones granulométricas, con un enfoque en el rango de nanómetros. La eficiencia de este proceso de clasificación desempeñó un papel crucial en la determinación de la calidad del producto final. SiC tiene un valor de mercado significativo, alcanzando los US$3.300 millones en 2022. Brasil es uno de los principales productores de SiC crudo, pero todavía depende de las importaciones de granulometrías más finas necesarias en diversas aplicaciones industriales. El objetivo principal de la investigación fue desarrollar una técnica altamente eficiente para el fraccionamiento nanométrico de polvos de carburo de silicio. Después de realizar experimentos, los investigadores obtuvieron con éxito SiC con un diámetro inferior a 2 μm. Para lograr esto, se exploraron múltiples dispersantes químicos para el proceso de centrifugación, con el objetivo de desagregar la solución y mejorar el rendimiento general, con el carbonato de sodio emergiendo como el más prometedor entre los dispersantes probados. Al presentar estos hallazgos, los investigadores contribuyen a avanzar en la producción de SiC y sus aplicaciones, especialmente en industrias que requieren partículas de SiC de tamaño nanométrico. El estudio no solo mejora la calidad del producto final, sino que también reduce la dependencia del país del carburo importado para fines industriales.

**Palabras clave:** Carburo de silicio; clasificación; centrifugación; dispersantes.
1. Introduction

The classification of silicon carbide (SiC) plays a vital role in the production of advanced materials widely utilized in various industrial sectors, including electronics, automotive, aerospace, and energy (Germano, 2018). An example of these applications is that recent research has shown that adding 10% silicon carbide enhanced cement paste's mechanical properties. Compressive strength increased 36.3% compared to reference pastes, reducing surface abrasion wear. (Estolano et al, 2023)

This process involves segregating SiC particles with diverse sizes and shapes into distinct granulometric fractions to meet industry standards and ensure the final product's quality (Han et al, 2017).

Among the commonly employed techniques for SiC classification, centrifuges stand out in the recent studies of nanoparticles (De Sousa et al, 2015). These machines effectively separate particles based on their mass and size, using centrifugal force to differentiate lighter and heavier particles (de Sousa et al, 2015). Centrifuges can also be adjusted to produce different granulometric fractions (Rumpf 2020), making them instrumental in achieving high-quality SiC, especially when targeting the nanometer range (Izhevskyi et al, 2000).

This topic holds immense significance for SiC-producing and utilizing industries, considering the compound's market value of US$3.3 billion in 2022 (Grand View Research, 2020). The efficiency of the classification process directly impacts the quality of the end product (Kimoto, 2014). Although Brazil is a major producer of raw SiC (Morais, 2005), the country still imports carbide in finer granulometries for industrial use (Lima, 2006).

Various other separation methods for nanoparticles exist, including Electrophoresis, "High Field Flow Fractionation," and Chromatographic techniques (Costa, 2014). Electrophoresis involves charged particle movement in an electric field, facilitating separation based on their migration rates. "High Field Flow Fractionation" utilizes a high flow rate and perpendicular field to separate particles according to size and shape. Chromatographic methods
involve component separation based on affinity for a stationary phase, such as a solid support or a liquid.

Another important characteristic when classifying nanoparticles is the zeta potential, also known as electrokinetic potential, is the potential at a colloid particle’s slipping/shear plane under an electric field. It represents the difference in potential between the electric double layer (EDL) of mobile particles and the surrounding dispersant layer at the slipping plane. (S. Bhattacharjee, 2016)

This study’s primary focus was to enhance methodologies developed in prior research, particularly exploring the role of dispersants in centrifugation. The aim is to contribute to the advancement of SiC classification methods, ultimately benefiting industries reliant on this essential material.

2. Development

2.1 Materials and Methods

The composition of the silicon carbide powder used 1200 F SICBRAS is shown in the Table 1. The majority phase, with 94.27%, is SiC. The Si and C were originated from the initial sources to produce the material from the Acheson process (Acheson, 1893). The silica (SiO₂) superficial formation on the SiC particles is well known and Fe₂O₃ and Al₂O₃ are residues from the milling mediums (Acheson, 1893).

<table>
<thead>
<tr>
<th>Compound</th>
<th>SiC</th>
<th>Si</th>
<th>C</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction (Mass, %)</td>
<td>94.27</td>
<td>1.39</td>
<td>0.33</td>
<td>0.89</td>
<td>2.56</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Source: SiCBRAS

In this paper, several technical equipment and procedures were used, which can be divided into two groups: the classification group, which includes materials such as sieves and shaker, centrifuges, mortar and pestle, and ultrasound deagglomerators, as well as drying ovens and dispersants; and the characterization group, which includes the Malvern Mastersizer 2000 (DTP), the
XRD equipment, and the Malvern for measuring the zeta potential, as well as balances for measuring obtained masses.

For the initial classification of the sample, sieves with different openings were employed and it was utilized as a PRODUTEST sieve shaker (model TWB). In the dry sieving process, the samples were dried in an oven, weighed, and manually disaggregated before passing through the sieves. Following classification, the populations were re-weighed using a Gehaka balance with high precision (4 decimal places), and the results were carefully recorded. The same drying and weighing process was replicated for the wet sieving using similar equipment in comparable laboratories. From the wet sieving, we collected the finest fraction for further separation. This fraction was manually quartered involving the creation of a conical pile, followed by a longitudinal pile of the sample. After thorough homogenization, the samples were stored and identified at 25 g and 50 g from one-half of the quartered mass, while the other half was kept intact for future reference.

In the initial pilot setup (dry sieving), screening was conducted using sieves of 250 μm, 125 μm, 53 μm, and 25 μm. However, the presence of material retained by the 250 μm sieve indicated the necessity for dehumidification and subsequent deagglomeration to achieve the desired particle size. Following these adjustments, a second screening was performed, resulting in no material retained by the first sieve. The first screening (20g) was labeled "A1" and the second (18g), with treatment, labeled "A2".

To assess the impact of agitation intensity and the maximum amount of material sieved at once, screenings B1 and B2 were conducted. These screenings utilized sieves of 125 μm, 62 μm, and 25 μm, with 99.98 g and 100.27 g of previously dried and manually deagglomerated powder sieved under agitator settings of 10 and 5 vibrations, respectively. Analyzing the results of B1 and B2 and comparing them to A1 and A2, it becomes clear not only the impossibility of dry sieving of large samples for the sieves used but also the positive relationship between a higher vibration amplitude of the apparatus and a better separation process. As for the qualitative explanation of this impossibility, what occurs is a clogging of the sieves during sieving, where particles with sizes close to the sieve...
openings can become trapped, interrupting the vertical mass flow and consequently leading to undue accumulation of mass on a sieve. This can happen even if the upper layers of powder have a smaller particle size than the opening size, as their passage through is prevented.

Subsequently, two additional screenings of smaller masses, C1 (50 g) and C2 (25 g), were performed sequentially using samples dried in an oven and manually deagglomerated. In screening C1, with sieves of 125 μm, 62 μm, and 25 μm, no material was retained by the 125 μm sieve, indicating that the amount of material used was within the sieve's capacity. Hence, the 125 μm sieve was omitted in screening C2. However, clogging of the 62 μm sieve was evident during screening C1 due to a high percentage of retained mass. Screening C2, employing sieves of 62 μm and 25 μm, produced more promising results despite the possibility of clogging the 62 μm sieve again, with a relatively higher proportion of fine particles.

There is a significant difference in screening efficiency between wet and dry processes for finer powder fractions. It is possible to screen wet granulometries as small as 20 μm, which is not achievable with dry screening (Parin, 2003). On an industrial scale, dry screening is used for particles up to 1.7 mm, while wet screening is used for particles up to 50 μm (Luz et al., 2010)
For the wet sieving, a mass of approximately 4 kg was sieved, divided into 1 kg samples. Sieves with openings of 20 μm (625 mesh) and 38 μm (400 mesh) were used, a choice justified by dry sieving, where a similar configuration was most effective. The fraction with a diameter smaller than 20 μm (bottom) was manually quartered and separated into smaller samples.

Finally, to perform the centrifugations and get even thinner material, samples with 10% by mass of SiC (wet-sieved) in water were prepared, completing a volume of 40 ml for the laboratory centrifuge Eppendorf model 5810 R. In the benchtop centrifuge, a fixed rotation speed of 1000 rpm was used for all experiments, as well as a constant centrifugation time of 3 minutes, with the dispersant being sodium silicate, meta-sodium silicate, sodium carbonate, sodium hexametaphosphate and sodium hydroxide at dosages 500 and 1000 g/ton.
For each chemical dispersant, only one centrifugation was performed with all the different dosages simultaneously, including a sample without dispersant for comparison, so as not to interfere with the unique parameters of each centrifugation in comparing the increase in yield generated solely using the dispersant. In the current phase of the research, the concentration of the most promising dispersants is being varied to find the best solute-solvent ratio.

After centrifugation, the supernatant liquid was filtered, dried, weighed and subjected to particle size distribution analysis, DTP, using the Malvern Mastersizer 2000 model equipment.

Zeta potential tests were carried out for SiC with $d_{90}$ of 20 μm (product of wet sieving) and for SiC with $d_{90}$ of 2 μm (obtained by centrifugation) to verify not
only the colloidal stability of the total material before centrifugation but also for the fraction of interest (under 2μm), comparing the two graphs. For this, a Malvern Mastersizer 2000 with an automatic pH changer was used. Using acidic and basic reagents, the pH value of both samples was increased by 1, and the Malvern measured the zeta potential in duplicate.

2.2 Results and Discussion

The results for the dry sieving and wet sieving are the ones that follow in table 2 and table 3, respectively:

<table>
<thead>
<tr>
<th>Powder Fraction (μm):</th>
<th>A1 (20g)</th>
<th>A2 (18g)</th>
<th>B1 (100g)</th>
<th>B2 (100g)</th>
<th>C1 (50g)</th>
<th>C2 (25g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+250</td>
<td>2.76%</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>+125</td>
<td>4.79%</td>
<td>2.27%</td>
<td>37.75%</td>
<td>70.34%</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>+62</td>
<td>0</td>
<td>0</td>
<td>48.67%</td>
<td>25.62%</td>
<td>85.26%</td>
<td>0</td>
</tr>
<tr>
<td>+53</td>
<td>87.34%</td>
<td>95.07%</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>52.65%</td>
</tr>
<tr>
<td>+25</td>
<td>5.12%</td>
<td>1.84%</td>
<td>13.31%</td>
<td>4.37%</td>
<td>13.85%</td>
<td>45.16%</td>
</tr>
<tr>
<td>-25</td>
<td>0</td>
<td>0.83%</td>
<td>0.27%</td>
<td>0.27%</td>
<td>0.89%</td>
<td>2.19%</td>
</tr>
</tbody>
</table>

Source: the authors themselves

<table>
<thead>
<tr>
<th>Sieves (mesh)</th>
<th>+400</th>
<th>+625</th>
<th>Bottom</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (g)</td>
<td>192.86</td>
<td>297.21</td>
<td>3488.79</td>
<td>3978.86</td>
</tr>
<tr>
<td>Mass (%)</td>
<td>4.85</td>
<td>7.47</td>
<td>87.68</td>
<td>100</td>
</tr>
</tbody>
</table>

Source: the authors themselves

In the wet sieving process, the 3 resulting fractions were analyzed using Malvern for particle size distribution testing, with the final sieve-passing fraction being tested. The Malvern result for this (thinner) population also includes a relationship between the percentage in volume of the sample whose particles are smaller than certain diameters, shown in Table 4:
Using Lagrange interpolation, it is possible to mathematically approximate the fraction of particles with a diameter smaller than 2 µm, which was not explicitly provided by the equipment. As a result, it is obtained that 32.4% of the particles passing through the sieve have a maximum diameter of interest of 2 µm.

In the tests using dispersants, two product properties were comparatively analyzed: the mass obtained after centrifugation (process yield) and the product granulometry (d90). The centrifugations were performed at three different times during the research period, with different dispersants used in the first two (D1 and D2) under the same conditions, and in the last one (D3), only the dispersant that obtained the best result in phases D1 and D2 was used, varying the centrifuge parameters.

In both centrifugations D1 and D2, a rotation of 1,000 rpm was used for a duration of 1 minute (counting starts when the centrifuge reaches the desired speed). The masses used were 4.30 g of wet-sieved SiC that passed through the screens.
Table 6 - Results related to centrifugation D2.

<table>
<thead>
<tr>
<th>Dispersant</th>
<th>Expected Recovered Mass</th>
<th>Recovered Mass</th>
<th>Yield %</th>
<th>Relative Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>1,393 g</td>
<td>0,2388 g</td>
<td>17,14</td>
<td>100</td>
</tr>
<tr>
<td>Sodium hexa Metaphospate 500 g/ton</td>
<td>1,393 g</td>
<td>0,2014 g</td>
<td>14,46</td>
<td>84,34</td>
</tr>
<tr>
<td>Sodium hexa Metaphospate 1000 g/ton</td>
<td>1,393 g</td>
<td>0,2067 g</td>
<td>14,84</td>
<td>86,56</td>
</tr>
<tr>
<td>Sodium Hydroxide 500 g/ton</td>
<td>1,393 g</td>
<td>0,2421 g</td>
<td>17,38</td>
<td>101,38</td>
</tr>
<tr>
<td>Sodium Hydroxide 1000 g/ton</td>
<td>1,393 g</td>
<td>0,2165 g</td>
<td>15,54</td>
<td>90,66</td>
</tr>
</tbody>
</table>

Source: the authors themselves

As the first result of centrifugation D1, it is important to mention that with all dispersants and concentrations, a higher supernatant mass was obtained than in the tube without dispersants, as indicated by the "relative yield" value greater than 100%. In general, all process yields are between 14.5% and 24.5%. This is justified by the percentage value of mass below 2 μm expected, where in this work the value of 32.4% (previously cited) was used while previously 23.81% was used. By using the lower percentage, the expected recovered mass would be
1.024 g and the minimum and maximum yields would be 19.75% and 33.10%, respectively, in the blank sample and with Na2CO3 500 g/ton.

After conducting tests on various dispersants in D1, it is evident that all dispersants positively impacted the material classification. However, we can establish an order of increasing efficiency among them. Sodium metasilicate exhibited an intermediate yield at both concentrations tested. Sodium silicate showed a low yield at 500 g/ton but a good yield at 1,000 g/ton. On the other hand, sodium carbonate demonstrated very good yields at both concentrations, with exceptional results at 500 g/ton, where it increased the recovered mass by two-thirds. The ideal amount of dispersant varied depending on the specific chemical used. While metasilicate and sodium carbonate showed higher yields with lower concentrations, silicate yielded better results with higher concentrations.

In D2 centrifugations, unlike D1, the addition of reagents led to a loss of process yield, except for sodium hydroxide at 500 g/ton, which yielded a result considered indifferent, with 1% more mass than its equivalent in the blank sample. It was observed that sodium hexametaphosphate had a stronger impact on the yield at low concentrations, while sodium hydroxide exhibited its effect at higher concentrations, with the dispersant at 1,000 g/ton generating a greater difference compared to the blank sample. This emphasizes the particular relationship between dispersant action in the mixture and the ideal concentration of dispersants. Comparative Malvern results (particle size distribution analysis) between blank and D1 and D2 dispersant tests are also included in Figures 4 thru 10. These findings provide valuable insights into the varying efficiency of dispersants and their concentrations during the classification process.

It’s also worth noting that any particle sizes above 10 µm indicated by the Malvern results imply material agglomeration, given that it has previously passed through sieves with openings smaller than this value and, according to the Malvern result for pure SiC, there is no significant population in this particle size range.
Figure 4 - Malvern analysis SiC pure, D1 centrifugation

Figure 5 - Malvern analysis SiC + Silicate 500g/ton, D1 centrifugation

Figure 6 - Malvern analysis SiC pure + Silicate 1000g/ton, D1 centrifugation

Source: the authors themselves
CENTRIFUGATION OF NANOMETRIC SILICON CARBIDE POWDER FOR GRANULOMETRIC CLASSIFICATION

Figure 7 - Malvern analysis SiC pure + NaOH 500 g/ton, D2 centrifugation

Source: the authors themselves

Figure 8 - Malvern analysis SiC pure + NaOH 1000 g/ton, D2 centrifugation

Source: the authors themselves

Figure 9 - Malvern analysis SiC + Metasilicate 1000g/ton, D2 centrifugation

Source: the authors themselves
For the particle sizes of -20 μm and -2 μm, zeta potential tests were performed in the pH range between 2.5 and 11. No isoelectric point was identified in any of the samples, whose results are shown in Figure 11, but it is important to note that the dispersant solution has higher zeta potential at higher pH.

Figure 11 - Zeta potential for SiC with particle size of -20 μm and -2 μm
3. Conclusion

It was possible to conclude that:

a) from the dry sieving tests carried out, it is impossible to fractionate fine particles with acceptable yield and on a laboratory scale by this method, although there are ideal configurations for increasing efficiency;

b) sodium carbonate at 500 g/ton was the dispersant that provided the best result for centrifugation, and the next steps of the research are to find a concentration that further improves the results;

c) no isoelectric point was identified in any of the samples and more analysis is necessary on the other samples;

d) more studies are on the way, with tests of carbonate in different amounts, as well as variation of centrifugation parameters, such as speed and temperature.

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