

# CLASSIFICAÇÃO NANOMÉTRICA DE CARBONETO DE SILÍCIO EM PÓ\*

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## Resumo

Partículas de carbeto de silício (SiC) com diferentes tamanhos e formas são separadas em frações granulométricas distintas para garantir a qualidade do produto final. O SiC de alta qualidade é obtido quando a granulometria está na faixa nanométrica. A eficiência do processo de classificação é fundamental para a qualidade do produto final, com valor de mercado do SiC chegando a US\$ 3,3 bilhões em 2022, o Brasil é um dos maiores produtores de SiC bruto, mas precisa importar metal em granulometrias mais finas para uso industrial. O objetivo deste estudo é desenvolver um método eficiente para o fracionamento nanométrico de pós de carboneto de silício. Os resultados mostraram que foi possível obter SiC com diâmetro inferior a 2  $\mu\text{m}$  e aumentar a eficiência do processo em até 68%. Múltiplos dispersantes químicos foram testados para o processo de centrifugação para desagregar a solução e aumentar o rendimento, com destaque para o carbonato de sódio.

**Palavras-chave:** Carbeto de silício; Classificação; Centrifugação; Dispersantes .

## NANOMETRIC SILICON CARBIDE POWDER CLASSIFICATION

### Abstract

SiC particles with different sizes and shapes are separated into distinct granulometric fractions to ensure the quality of the final product. High-quality SiC is achieved when the granulometry is in the nanometer range. The efficiency of the classification process is critical to the quality of the final product, with the market value of SiC reaching US\$3.3 billion in 2022, Brazil is one of the largest producers of raw SiC, but the country needs to import carbide in finer granulometries for industrial use. The aim of this study is to develop an efficient method for nanometric fractionation of silicon carbide powders. The results showed that it was possible to obtain SiC with a diameter below 2  $\mu\text{m}$  and increase the efficiency of the process by up to 68%. Multiple chemical dispersants were tested for the centrifugation process to disaggregate the solution and increase the yield, with sodium carbonate standing out.

**Keywords:** Silicon carbide; Classification; Centrifugation; Dispersants.

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## 1 INTRODUCTION

The classification of silicon carbide (SiC) is a crucial process in the production of advanced materials that are widely used in various industrial applications, such as electronics, automotive, aerospace, and energy [1]. The classification involves separating SiC particles with different sizes and shapes into distinct granulometric fractions to meet industry specifications and ensure the quality of the final product [2].

One of the most common techniques for SiC classification is the use of centrifuges [3]. These machines are capable of separating particles based on their mass and size, applying centrifugal force to separate lighter particles from heavier ones [4]. Additionally, centrifuges can be adjusted to produce different granulometric fractions [5], making them a valuable tool in the production of high-quality SiC, which is achieved when the SiC granulometry is in the nanometer range [6].

This topic is of great importance to industries that produce and use SiC - in 2022, the market value of this compound was US\$3.3 billion [7] - as the quality of the final product depends directly on the efficiency of the classification process [8]. Brazil is one of the largest producers of raw SiC [9], however, it is necessary to import carbide in finer granulometries for use in industry [10].

The focus of this paper was to improve the methodologies developed by previous research, with improvements of over 60%, including the action of dispersants in centrifugation.

## 2 DEVELOPMENT

### 2.1 Materials and Methods

The main silicon carbide powder used was the 1200F from the company SiCBRAS, with particle size distribution and chemical analysis provided by SiCBRAS. The composition of the powder is shown in the table 1:

Compound	SiC	Si	C	$Fe_2O_3$	$SiO_2$	$Al_2O_3$
Fraction	94,27	1,39	0,33	0,89	2,56	0,56

Table 1 - Chemical analysis carried out by 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 varying openings available in the laboratories of IME and CETEM were used, as well as a sieve shaker from the

PRODUTEST, model TWB. In dry sieving, carried out at IME, the samples were dried in an oven, weighed, and manually disaggregated before each pass through the sieves. After classification, the populations were weighed again using a Gehaka balance with 4 decimal places of precision, and the results were recorded. The same drying and weighing process was repeated for wet sieving performed at CETEM, with similar equipment in equivalent laboratories. From the wet sieving, the finest fraction was collected for further separation. This fraction was manually quartered at CETEM, making a conical pile followed by a longitudinal pile of the sample. After homogenization, samples of 25 g and 50 g were collected, stored, and identified from half of the quartered mass, while the other half was kept intact.

To perform the centrifugations, samples with 10% by mass of SiC in water were prepared, completing a volume of 40 ml for the laboratory centrifuge. 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 and its concentration being varied according to table 2:

Dispersant	Dosage (g/ton)
<i>NaOH</i>	500, 1.000
<i>Na<sub>2</sub>CO<sub>3</sub></i>	500, 1000
<i>Na<sub>2</sub>SiO<sub>3</sub></i>	500, 1000
meta- <i>Na<sub>2</sub>SiO<sub>3</sub></i>	500, 1000
<i>(Na<sub>2</sub>PO<sub>3</sub>)<sub>6</sub></i>	500, 1000

Table 2 - Table Dispersant and dosage

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 by the use of 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.

Particle size analysis was performed on all fractions resulting from wet sieving and on all supernatant fractions from centrifugation. The samples were sonicated for disaggregation, and a Malvern Mastersizer 2000 equipment was used for DTP.

Zeta potential tests were carried out for SiC with d<sub>0.9</sub> of 20 μm (product of wet sieving) and for SiC with d<sub>0.9</sub> 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, comparing the two graphs. For this, a Malvern instrument 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

In the pilot configuration, an initial screening was carried out with 250  $\mu\text{m}$ , 125  $\mu\text{m}$ , 53  $\mu\text{m}$ , and 25  $\mu\text{m}$  sieves. However, the presence of a non-passing population through the 250  $\mu\text{m}$  sieve indicated the need for dehumidification followed by powder deagglomeration, given the theoretical particle size. The screening was redone, and no non-passing fraction was observed through the first sieve, with the screening without prior deagglomeration treatment called "A1" and with this treatment, "A2," producing samples of 20 g and 18 g, respectively.

To verify the influence of the vibration factor of the agitator and the maximum mass that can be sieved at once, screenings B1 and B2 were carried out, where with 125  $\mu\text{m}$ , 62  $\mu\text{m}$ , and 25  $\mu\text{m}$  sieves, 99.98 g and 100.27 g of previously dried and manually deagglomerated powder were sieved with 10 and 5 vibrations (agitator settings), respectively.

The results showed not only the impossibility of dry screening of large samples for the used sieves but also the positive relationship between the amplitude of the apparatus vibration and the separation process's improvement.

The qualitative explanation for this impossibility is the sieves' clogging during the screening, where particles with sizes close to the opening sizes can become trapped, interrupting the vertical mass flow and causing undue accumulation of mass on a sieve, even if the upper layers of the powder have a smaller particle size than the opening size because their passage to the sieve is impossible.

Two more screenings, C1 (50 g) and C2 (25 g), were performed sequentially with samples dried in an oven and manually deagglomerated. At the end of C1, carried out with 125  $\mu\text{m}$ , 62  $\mu\text{m}$ , and 25  $\mu\text{m}$  sieves, the absence of a non-passing population through the 125  $\mu\text{m}$  sieve was verified, indicating that the used mass is within the limit for this sieve, justifying the removal of this sieve for screening C2. However, the clogging of the 62  $\mu\text{m}$  sieve was evident in the C1 screening due to the high percentage of retained mass. The C2 screening, with 62  $\mu\text{m}$  and 25  $\mu\text{m}$  sieves, presented more promising results, although possible clogging of the 62  $\mu\text{m}$  sieve again, with relatively much higher fine populations.

Table 3 compares the results of screenings A1 and A2, while table 4 compares the results of screenings B1 and B2, and table 5 compares the results of screenings C1 and C2.

Powder fraction :	A1 Screening	A2 screening
+250 $\mu\text{m}$	2,76%	0%
+125 $\mu\text{m}$	4,79%	2,27%
+53 $\mu\text{m}$	87,34%	95,07%
+25 $\mu\text{m}$	5,12%	1,84%
-25 $\mu\text{m}$	0%	0,83%

Table 3 - Results related to screenings A1 and A2.

Powder Fraction :	B1 Screening	B2 Screening
+125 $\mu\text{m}$	37,75%	70,34%
+62 $\mu\text{m}$	48,67%	25,02%
+25 $\mu\text{m}$	13,31%	4,37%
-25 $\mu\text{m}$	0,27%	0,27%

Table 4 - Results related to screenings B1 and B2.

Powder Fraction :	C1 Screening	C2 Screening
+125 $\mu\text{m}$	0%	-
+62 $\mu\text{m}$	85,26%	52,65%
+25 $\mu\text{m}$	13,85%	45,16%
-25 $\mu\text{m}$	0,89%	2,19%

Table 5 - Results related to screenings C1 and C2.

At the CETEM pilot plant, a mass of approximately 4 kg was sieved, divided into 1 kg samples through sieving. Sieves with openings of 20  $\mu\text{m}$  (625 mesh) and 38  $\mu\text{m}$  (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  $\mu\text{m}$  (bottom) was manually quartered and separated into smaller samples. The resulting passing and non-passing masses were related, as shown in table 6:

Sieves (mesh)	+400	+625	Bottom	Total
Mass (g)	192,86	297,21	3.488,79	3.978,86
Mass( %)	4,85	7,47	87,68	100

Table 6 - Results related to sieving

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 population also includes a relationship between the percentage in volume of the sample whose particles are smaller than certain diameters, shown in Table 7:

Particle Diameter:	Finest fraction:
1,445 $\mu\text{m}$	21,48%
1,660 $\mu\text{m}$	25,57%
1,905 $\mu\text{m}$	30,48%
2,188 $\mu\text{m}$	36,18%
2,512 $\mu\text{m}$	42,61%
2,884 $\mu\text{m}$	49,63%

Table 7 - Malvern results related to sieving

Using Lagrange interpolation, it is possible to mathematically approximate, through a polynomial, the fraction of particles with a diameter smaller than 2  $\mu\text{m}$ , 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  $\mu\text{m}$ .

In the tests using dispersants, two product properties were comparatively analyzed: the mass obtained after centrifugation (process yield) and the product granulometry (d0.9). 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), justified by previous research. The masses used were 4.30 g of wet-sieved SiC that passed through the screens.

Dispersant	Recovered Mass	Expected Recovered Mass	Yield	Relative Yield
None (blank)	0,2023 g	1,393 g	14,52%	100%
$\text{Na}_2\text{SiO}_3$ 500 g/ton	0,2255 g	1,393 g	16,19%	111,47%
$\text{Na}_2\text{SiO}_3$ 1.000 g/ton	0,2818 g	1,393 g	20,23%	139,30%
Meta - $\text{Na}_2\text{SiO}_3$ 500 g/ton	0,2605 g	1,393 g	18,70%	128,77%
Meta - $\text{Na}_2\text{SiO}_3$ 1.000 g/ton	0,2474 g	1,393 g	17,76%	122,29%
$\text{Na}_2\text{CO}_3$ 500 g/ton	0,3390 g	1,393 g	24,34%	167,57%
$\text{Na}_2\text{CO}_3$ 1.000 g/ton	0,3031 g	1,393 g	21,76%	149,83%

Table 8 - Results related to centrifugation D1.

Dispersant	Recovered Mass	Expected Recovered Mass	Yield	Relative Yield
None (blank)	0,2388 g	1,393 g	17,14%	100%
$(Na_3PO_3)_6$ 500 g/ton	0,2014 g	1,393 g	14,46%	84,34%
$(Na_3PO_3)_6$ 1.000 g/ton	0,2067 g	1,393 g	14,84%	86,56%
NaOH 500 g/ton	0,2421 g	1,393 g	17,38%	101,38%
NaOH 1.000 g/ton	0,2165 g	1,393 g	15,54%	90,66%

Table 9 - Results related to centrifugation D2.

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%, considerably low values compared to those found in previous research. This is justified by the percentage value of mass below 2  $\mu\text{m}$  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  $Na_2SiO_3$  500 g/ton.

Knowing that all dispersants tested in D1 had a positive effect on the material classification, it is still possible to establish an order of increasing efficiency, in which sodium metasilicate showed intermediate yield with both concentrations, sodium silicate showed low yield when at 500 g/ton and good yield when at 1,000 g/ton, and finally, sodium carbonate showed very good yields with both concentrations, especially when at 500 g/ton, where it increased the recovered mass by two-thirds. Regarding the ideal amount of dispersant used, there was no universal result, depending on the chemical used, since in metasilicate and sodium carbonate, there was a higher yield with a lower concentration, while in silicate, this happened with the higher concentration. In D2 centrifugation, in contrast to D1, the addition of reagents resulted in a loss of process yield, except for sodium hydroxide at 500 g/ton, which generated a result considered indifferent, with 1% more mass than its equivalent in blank.

It is also concluded that sodium hexametaphosphate acted more "strongly" (by decreasing yield more) at low concentrations, and sodium hydroxide did so at higher concentrations (in magnitude, the dispersant at 1,000 g/ton generated a greater difference compared to the blank sample), contributing to the conclusion about the particularity of the relationship between 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 1 and 2, respectively.

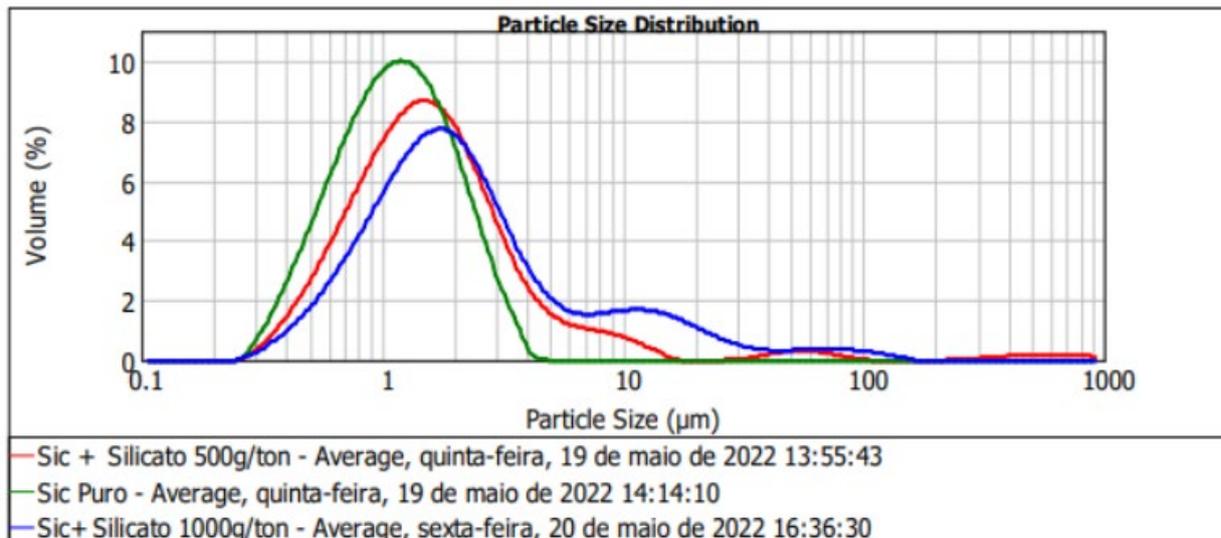


Figure 1 - Overlapping results of 3 Malvern tests on samples from centrifugation D1.

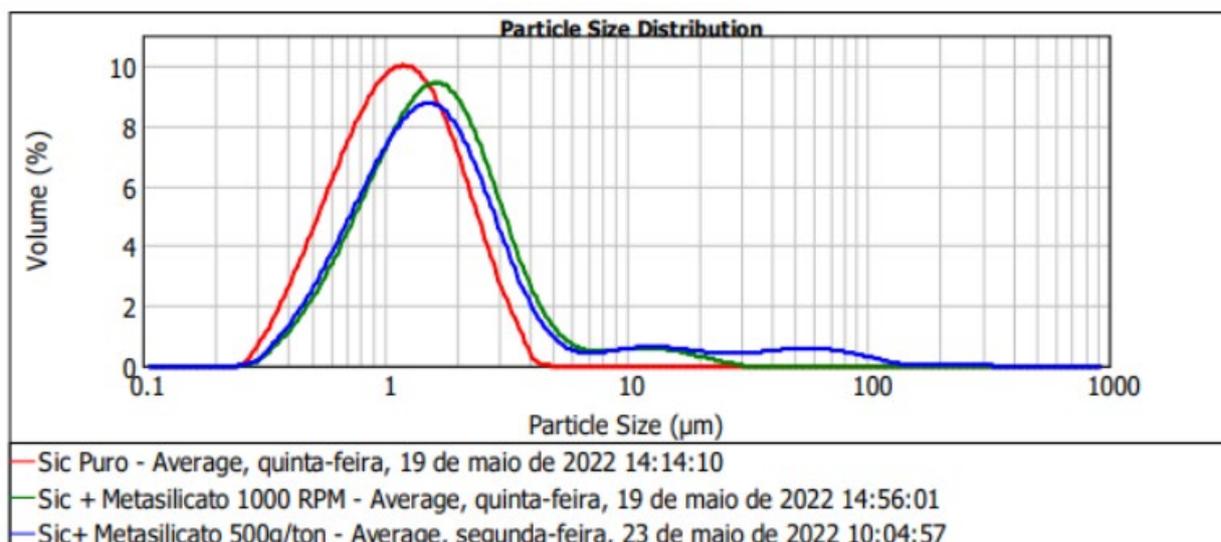


Figure 2 - Overlapping results of 3 Malvern tests on samples from centrifugation D1.

For the particle sizes of  $-20 \mu\text{m}$  and  $-2 \mu\text{m}$ , 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 Figures 3 and 4, but it is important to note the difference in behavior of the two curves for high pH values.

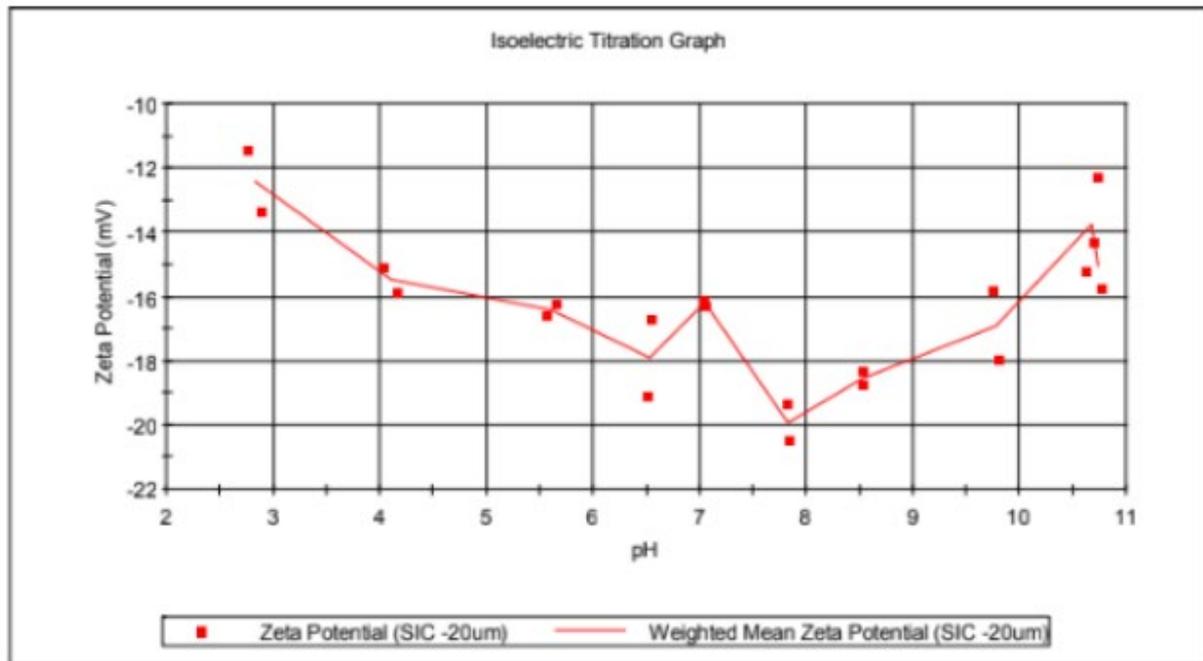


Figure 3 - Zeta potential for SiC with particle size of -20  $\mu\text{m}$

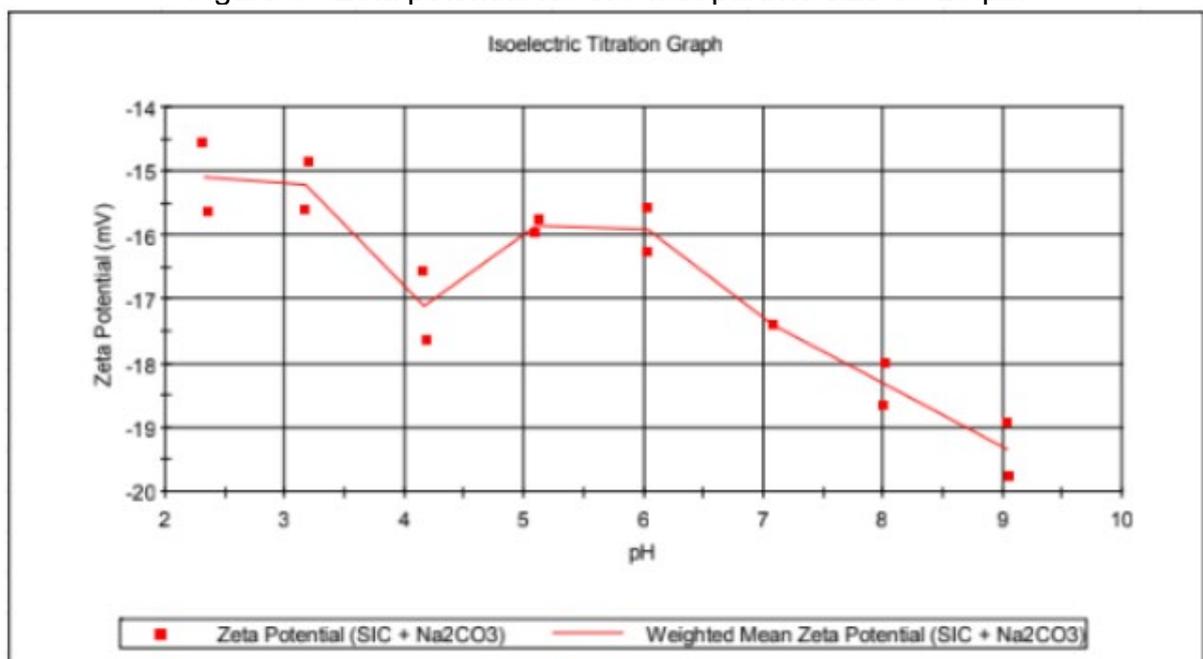


Figure 4 - Zeta potential for SiC with particle size of -2  $\mu\text{m}$

### 3 CONCLUSION

It was possible to conclude that:

- From the dry sieving tests carried out, it was concluded that 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.

- 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.
- No isoelectric point was identified in any of the samples and more analysis is necessary on the other samples

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