CALCINATION PROCESS OF DIATOMITE FROM BAHIA STATE

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ABSTRACT

Diatomite (also known as diatomaceous earth) is a sedimentary rock of marine or lacustrine deposition. It consists mainly of an accumulation of siliceous frustules (shells) or skeletons of diatoms, which are microscopic plants of freshwater and saltwater origin. Diatomite is largely used in many filtration processes found in beverage and pharmaceutical industries, as well as a filler for paints, paper and insulation products. The diatomite studied in this work was obtained from the Brazilian, north-eastern state of Bahia. The Bahia State diatomite studied presented a high content of both organic matter and clays, which were removed during the beneficiation process. This process comprises the steps of scrubbing, sedimentation, drying, calcination and pneumatic classification of the diatomite. Among these, calcination is the most important step because it is responsible for defining the main technological characteristics of the final product.

During the calcination process of diatomite, that occurs in the range of 800-1,000 °C, the organic matter is burned, leading to the formation of a white material containing melted fine particles of diatomite, as well as iron oxides which are aggregated and removed during pneumatic classification step. In order to produce diatomite with the exact specifications required for the market, the operational variables of the calcination step (i.e. temperature, retention time and Na₂CO₃ flux addition - an alternative used in industries to diminish silicon melting point) must be properly controlled. It is the main goal of this investigation to optimize the operational variables of the calcination process of diatomite.

Calcination experiments using diatomite were performed in a rotary kiln pilot plant at the Center for Mineral Technology (CETEM) in Brazil. During these experiments, the influence of the calcination process variables such as temperature (range of 800-1,000 °C), retention time of the material into the kiln (45-55 minutes) and flux addition (0 – 4%) were studied. It was aimed to determine a set of operational conditions that would produce high quality diatomite. The results found in this investigation showed that, in order to produce diatomite with better particle size distribution, brightness and filtration rates, proper control of the calcination process is necessary.

INTRODUCTION

Chemically, diatomite is essentially amorphous hydrated or opaline silica with varying amount of impurities such as clay minerals, organic matter, silica sand and metal salts. Non-silica components (e.g. aluminium, iron and other oxide compounds) are present in diatomite in the range of 5-15% w/w. The level of soluble impurities in diatomite affects its end-use properties. Table I shows a typical chemical analysis of diatomite from Bahia State. In Figure 1, typical frustules of calcined diatomite from Bahia State (ship shape) are presented.

Table I: Chemical characterisation of diatomite run of mine from Bahia State (calcined basis)

<table>
<thead>
<tr>
<th>Contents</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>88.0 – 90.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.5 – 9.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.54 – 0.72</td>
</tr>
<tr>
<td>Lost ignition</td>
<td>3.0 – 4.5</td>
</tr>
</tbody>
</table>

Porosity is an important property for diatomite particles. The porous structure of diatomite particles is a result of skeletons variation in sizes and forms. The special nature of the skeletons, combined with the chemical stability and inertia, make diatomite an ideal filter aid material. As a matter of fact, the largest industrial application of diatomite takes place in
filtration processes. Particularly, about 80% of calcined diatomite are used as filter aid material in Brazil.

Figure 1 - Frustules of calcined diatomite from Bahia State

Examples of industrial applications in filtration include: beer, wine, oils, pharmaceuticals and water systems. Diatomite may also be used as polishing and cleaning agent and due to its high water and oil absorption, it may be used in many chemical technical products. Because diatomite presents brightness up to 90%, low bulk density, high surface area and is chemically inert, it is also employed industrially as a filler. In the paints industry, diatomite is used as a flattening agent and also employed to increase product consistency and improve surface structure. The high porosity of diatomite decreases its required drying time and prevents crack formation. Example of industrial applications include: paints, rubber, plastics, polishing agent, catalyst support and insulating material.

The reason why is very important to investigate the operational variables, as temperature, retention time and flux addition is because with the optimisation of the calcination process it is possible to produce a better diatomite, with technological characteristics to each market, being for filtration or for filler.

MATERIAL AND METHODS

Diatomite from Bahia State, in northeastern of Brazil, has been studied in this work, in order to improve the industrial beneficiation process used by CIEMIL Company, especially calcination step.

In order to study the calcination process and its operational variables, two different kinds of tests were performed: bench scale muffle furnace experiments and pilot plant rotary kiln experiments, designed to simulate similar conditions found in the industrial calcination process.

Material handling

Crude diatomite from CIEMIL Company were received by CETEM, in 25 drums. From each drum, a sample was taken and homogenised, resulting in 25 samples of 2 kilograms each. These samples were used for the bench scale experiments, chemical analysis and mineral characterisation.

Muffle furnace tests

Two sets of experiments in the muffle furnace were performed. The first set of experiments was based on washed and dried diatomite (processed in hydroclassifier), while the second one was based on diatomite run of mine. Table II presents the experimental plan used in this work.

Table II - Calcination experiments in the muffle furnace.

<table>
<thead>
<tr>
<th>Retention time (h)</th>
<th>T (°C)</th>
<th>Moisture (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>800</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>800</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>900</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>900</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>800</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>800</td>
<td>76</td>
</tr>
<tr>
<td>1</td>
<td>900</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>900</td>
<td>76</td>
</tr>
</tbody>
</table>

The moisture level of 76% is relative to the run of mine material. Another value of temperature was also investigated, 1,000 °C.

Sodium carbonate (Na₂CO₃) flux addition was also investigated for all temperature levels, in varying amounts of 1, 2, 3, 6 and 9% and also no flux whatsoever. These mass percentages are based on material with 13% of moisture which is the ideal value to have a good mix between diatomite and Na₂CO₃ powder.

In the experimental procedure, representative samples of diatomite were put in melting pots which were dried during 30 minutes at 120°C before the experiments. After placing the sample into the muffle furnace, a temperature drop of about 50°C was noticed, requiring 1 to 2 minutes in order to restore the temperature to the desired operating level. The muffle furnace experiments were a preliminary step for
performing the calcination experiments in CETEM rotary kiln pilot plant. The parameters used in the rotary kiln were based on the results obtained in the muffle furnace experiments.

**Calcination in a rotary kiln pilot plant**

The calcination was conducted in a 0.9 m long and 0.26 m diameter rotary kiln. Feeding of diatomite was conducted with a screw feeder connected to the kiln. The heating of the kiln is provided by electrical resistances, disposed in shells around the calcination chamber.

In order to perform calcination with flux addition, the diatomite and Na$_2$CO$_3$ were firstly blended in a V-homogenizer during 10 minutes. After calcination, the calcined product was sieved to remove slag particles and other coarse particles.

Three different temperatures and four different levels of flux addition were investigated. The rotation speed and the slope of the rotary kiln determine the retention time. Two different slopes at the same rotation speed of the kiln were used. A 15% load (volume) for the screw feeder, to allow that diatomite had enough motion and time to be properly calcined.

Table III shows the main variables studied in the rotary kiln calcination experiments.

<table>
<thead>
<tr>
<th>Na$_2$CO$_3$ Addition (%)</th>
<th>Temperature (°C)</th>
<th>Retention time (slope)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>800°C</td>
<td>0.9°</td>
</tr>
<tr>
<td></td>
<td>900°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000°C</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>800°C</td>
<td>0.9°</td>
</tr>
<tr>
<td></td>
<td>900°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000°C</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>800°C</td>
<td>0.9° and 1.5°</td>
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<tr>
<td></td>
<td>900°C</td>
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<td>1000°C</td>
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<tr>
<td>4</td>
<td>800°C</td>
<td>0.9° and 1.5°</td>
</tr>
<tr>
<td></td>
<td>900°C</td>
<td></td>
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<tr>
<td></td>
<td>1000°C</td>
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</tbody>
</table>

Operational conditions for the rotary kiln pilot plant:

- Rotation speed of the kiln – 4.6 r.p.m.
- Rotation speed of the feeding screw – 1.5 r.p.m.
- Load in the kiln – 15% in volume
- Diatomite moisture – 14%

In the first set of experiments in the rotary kiln, temperatures of 800°C and 900°C and Na$_2$CO$_3$ additions of 0.0, 2.0, and 3.0% were investigated. The slope was 0.9°. In the second set of experiments, temperatures of 800°C and 900°C and Na$_2$CO$_3$ addition of 4.0% were investigated. The temperature of 1000°C was also investigated.

In the third set of experiments, the slope was increased to 1.5°. The temperature of 900°C and Na$_2$CO$_3$ additions of 0.0, 2.0, 3.0 and 4.0% were investigated.

When the experiments in the rotary kiln pilot plant were conducted, a steady state was desirable. The aim was to take all the samples during steady state. The samples at each temperature and at each Na$_2$CO$_3$ addition were taken with an interval of 80 minutes. Accumulation of material in the kiln during the calcination disturbs the steady state. Therefore, the inner walls of the kiln were cleaned during the experiment. Mass balances were carried out at each experiment to confirm the steady state. In all experiments 2.0 kg of diatomite were used to feed the kiln during 3.0 (three) hours.

**RESULTS AND DISCUSSION**

After processed in the rotary kiln pilot plant, the calcined material was sieved in order to remove slag coarse particles. Particles over 150 microns were discharged as tailing. The calcined diatomite in the rotary kiln was not air classified, such as in the normal industrial procedure, after diatomite calcination step. Comparison between the final product of CETEM rotary kiln and CIEMIL Company (or any other manufacturer) may be misleading, if no consideration is taken to the fact that the rotary kiln products have not been classified.

The calcined products were submitted to chemical analysis, mineralogical characterization, particle size analysis, brightness determination, filtration tests and water and oil absorption experiments. Results obtained in this work were compared with commercial products obtained from CIEMIL Company, Celite and Celite Hyflo.

During the experiments, the retention time in the rotary kiln, the angle of inclination and rotary kiln
rotation speed were varied. The retention times used during the experiments were 47 and 54 minutes. The rotation speed of the kiln was 4.6 r.p.m. and this was the fastest possible rotation speed of the kiln. A slower rotation speed was not tested because it would result in a longer retention time.

A typical temperature profile in the kiln at $T=800^\circ$C is shown in Figure 2. The temperatures were measured before calcination with the rotary kiln empty.

The operating temperature in rotary kiln was set at $800^\circ$C, $900^\circ$C or $1,000^\circ$C, but the real temperature measured by a thermocouple located at the central part of the calcination chamber was about 100 - 200°C higher than the desired temperature. This is attributed to combustion of organic matter during the calcination.

![Figure 2: Typical temperature profile in the CETEM rotary kiln pilot plant](image)

**Chemical analysis**

Chemical analysis of products resulted of rotary kiln calcination are given as follows. Fe$_2$O$_3$ content was found to be low (about 0.45% w/w) in all of the products analysed. The products presented high content of Al$_2$O$_3$, varying from 7 to 14% w/w among the samples. The amorphous SiO$_2$ content differed from 63 to 77%, the kaolinite content from 8% to 14% and the quartz content from 4% to 9%. The K$_2$O and CaO contents are very low, almost non-existing. Trace of elements Mg, P, Ti, Cr, Ni, Cu, Rh, U, Mn, Zr, Ce, V, Se, Cs, Tb and S were found.

**Mineralogical characterization**

Mineralogical characterization of CIEMIL products, commercial products, rotary kiln calcination product and run of mine diatomite were undertaken. The mineralogical characterization was conducted by using X-Ray diffraction and Scanning Electron Microscope (SEM).

The X-ray analysis showed that the rotary kiln products consist mainly of amorphous silica. Quartz and cristobalite were verified in the products whose calcination was performed at high temperatures ($900 - 1,000^\circ$C) and with high flux addition (4%). Figure 3 shows a typical X-ray diffraction spectrum of a calcined diatomite at $900^\circ$C and 4% in flux addition.

The peaks observed in the X-ray diffraction spectrum result from an exceeding temperature in the calcination process, which has an increased effect with the high percentage of flux addition, which allows changes in silicon structure, appearing cristobalite phase.

![Figure 3 - X-ray diffraction spectrum of calcined diatomite](image)

**Particle size analysis**

Particle size analysis of CIEMIL Company products, commercial products, muffle furnace products and rotary kiln products obtained at CETEM were determined using the Malvern 260 Laser Diffraction Particle Size Analyser. The specific surface area was also determined using the Malvern Analyser.

CIEMIL Company, commercial and rotary kiln calcined products were also wet sieved using sieves with nominal apertures of 150, 106, 75, 53 and 45 micra.

The Malvern analysis of calcined products from the second set of the muffle experiments shows that the particle sizes increase when temperature and Na$_2$CO$_3$ addition is increased.

The Malvern analysis of the rotary kiln calcined products shows that the average particle size increases when temperature and flux addition are increased (Figure 4).
The rotary kiln calcined products were also wet sieved using nominal apertures of 150, 106, 75, 53 and 45 microns. At 900°C temperature, angle of inclination 1.5°, the average particle size increases when Na₂CO₃ addition increases but for the other two sets of experiments, it was not possible to detect clearly an increase in the average particle size.

The calcined diatomite which resulted from the 6% and 9% Na₂CO₃ addition experiments could not be investigated because the high amount of Na₂CO₃ addition and high retention time (1h) led to a partial melting of the calcined product.

Brightness

Brightness of diatomite was measured in a Carl Zeiss ELREPHO Photometer with a filter of 457 nm. It was possible to observe the improvement of the diatomite colour as a result of its calcination. Run of mine, washed and dried diatomite presented a dirty grey colour, which changed to a clear pink or white colour after calcination. Figure 5 shows the brightness of calcined diatomite for the experiments carried out in the rotary kiln pilot plant.

Filtration tests

Filtration tests of the CIEMIL Company, commercial and rotary kiln calcination products were undertaken. The filtration tests were repeated three times for each sample.

The filtration tests were conducted with a funnel connected to a vacuum system. A filter textile was placed in the funnel in order to support the filter cake. A certain amount of diatomite (relative to a pot with 72 cm³) was mixed with 200 ml of water and added to the funnel. This was conducted to achieve a regular cake. When the mixture level passed a fixed mark in the funnel, the clock was started and another litre of water was added to the funnel. When the water level passed the fixed mark again, the clock was stopped and the filtration time was obtained.
Filtration test during a longer time was also conducted. In this analysis, the same equipment as previous was used. Five litres of water were filtered and the filtration time for each litre was observed. Filtration rate data for calcined diatomite in rotary kiln experiments at different temperatures and different amount of Na₂CO₃ addition are shown in Figure 6.

The filtration rate is higher for calcined diatomite at 900°C than at 800°C. This was observed for all products obtained at these temperatures with different Na₂CO₃ addition. For calcination at 800°C, a maximum filtration rate was achieved at 3% of Na₂CO₃ addition. In addition, at 900°C (inclination 1.5°), a maximum filtration rate was achieved at 3% of Na₂CO₃ addition and this was observed to be the highest filtration rate achieved. The filtration rate is 1.5 higher at 900°C (inclination 1.5°) and 3% of Na₂CO₃ addition than at 800°C.

For all temperatures, the filtration rates were found to increase more between 2-3% of Na₂CO₃ addition than between 3-4%. The highest enhancement was observed between 2-3% of Na₂CO₃ addition and at 800°C.

A filtration rate test during a longer time was undertaken for products obtained with 3% of Na₂CO₃ addition and for diatomite just washed and dried. The results are shown in Figure 7. It can be seen that filtration rate is higher for the calcined diatomite, because in these products particles are coarser than in crude diatomite. The filtration rates are higher for calcined diatomite at 900°C than at 800°C, but with an exception at the volume of 1 litre of water.

As expected, coarser particles provided a higher flow rates and while lower flow rates were observed for smaller particles. The small particles in the rotary kiln products that were not removed by classification gave to calcined material a lower flow rate in the filtration tests. A higher flow rate would have been possible to achieve if product was classified. Regarding natural diatomite, flow rate is low due to the presence of a great amount of small particles.

In the filtration tests during a longer time with 5 litres of water (cf. Figure 7), it can be seen that the flow rate for crude diatomite is low, due to a lot of small particles content. In these filtration tests it is clear that calcined diatomite at 900°C has a higher filtration rate.

CONCLUSIONS

The calcination process of diatomite from Bahia State (Brazil) was investigated in this work. It was found that the average particle size increases with temperature and with Na₂CO₃ addition and this led to better filtration rates.

It was also found that beyond 6% flux addition of Na₂CO₃ the average particle size does not increase anymore. For the experiments conducted in CETEM rotary kiln pilot plant, the best filtration rates for the calcination process occurred at a temperature of 900°C, flux addition of 3% and a retention time of 47 minutes. Under these conditions, the calcined products showed similar technological characteristics to the commercial products, used as filter aid or filler.

Some of the rotary kiln calcined products could not be compared with CIEMIL Company products at
high filtration rates, because no size classification was performed.

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**BIBLIOGRAPHY**


