Currently, there is a tendency to use less silica rich ores given the depletion of high-quality resources. The raw kaolin treatment of Tamazert (Eastern Algeria) produces, by hydrocyclone process, approximately 80 % of siliceous by-products. These siliceous wastes, which are stored in the open air, constitute a significant environmental problem. This research work aims to improve the quality of siliceous by-products, more particularly, to a process for the elimination of iron oxides and aluminium to make this raw material usable industrially as well as solving environmental issues. The collected by-products, were characterized by different techniques, such as X-ray fluorescence (XRF) and X-ray diffraction (XRD). XRF confirmed that the by-products east siliceous, with content going up to 82 % of SiO₂.

The by-product resulted from the raw kaolin treatment, mainly contains varying amounts of impurities such as iron oxide, titanium oxide and alumina. In all cases, the presence of these impurities affects the color and the physical properties of the mineral, and so lowers the economic value and limits the industrial application. In this framework, the classified fraction (–500)–(+100) µm was directed to attrition scrubbing followed by magnetic separation technique and chemical treatment by sulphuric acid with different concentrations. The results of the beneficiation tests of by-product indicate that using the attrition scrubbing alone not provides a suitable product for glass manufacture. The magnetic separation was tested with attrition on the useful fraction ((–500)–(+100) µm). The non-magnetic attritional fraction concentrates less than 0.45 % of Al₂O₃ and 0.05 % of Fe₂O₃. This low content coupled with a remarkable percentage in silica of 97.98 %. The tests by attrition and leaching with 40 % of sulphuric acid show, on the one hand, significant results with a high percentage of silica (>98.5 %) against 0.04 % Fe₂O₃ and 0.66 % Al₂O₃, and on the other hand, that the enriched product meets the standards required by glass making.

Keywords: Tamazert raw kaolin, siliceous by-products, mineral processing, silica, glass.

1. Introduction

After the hydrocyclonage process, two products are obtained: the kaolin intended for ceramics manufacture and siliceous by-products stored in the open pit pose an environmental problem on the El-Mila region (Jijel). The glass industries require a fairly high degree of sand purity, which nature does not offer in large quantities. For this purpose, the processing of siliceous by-products does not require any grinding and the particles are mostly in liberated form, which are the added advantages of treating this siliceous by-products. The oldest known use of the silica is as a glass-manufacturing raw material. Presently, the silica is a versatile industrial mineral also finds in various applications such as photovoltaic industries, ceramic, electronics, and foundry [1]. In glass making industries silica, sand content ranges from 94.5 to 99 % of the whole composition. In this field, the content of iron (Fe₂O₃) is very important to determine the quality of both silica sand and produced product. Thus, the permissible Fe₂O₃ content in household glass is no more than 0.05 %, in clear glass 0.012–0.02 %, crystal glass 0.023–0.035 %, light engineering and medical glass not more than 0.07 %. The content of Fe₂O₃ in sheet glass is permitted within the limits of 0.09–0.20 % [2]. Iron oxide is the predominant impurity in silica raw materials and the most harmful, can be removed via physicochemical methods such attrition, as froth flotation, gravity separation and magnetic separation [3–5]. The leaching has been tested, as it is more effective, especially for extremely content low iron [6]. Sometimes, combinations of these methods are needed generally [7].

When the objective of enrichment is to produce high purity silica, the attrition sand product was further subjected to gravity separation using «Wilfley» shaking table. As a result, with the mentioned combined processes iron content was reduced to 0.018 % and alumina oxides contents were decreased to 0.09 % [8].

Silica sandstone was experimented by using two different methods them for removal of impurities. The magnetic separation method removes about 65 % of iron oxide
from sand and decreases the Fe$_2$O$_3$ content from 0.28 % down to 0.1 % and leaching was also showed that using of hydrochloric acid result a better removal of iron oxide after 150 min of treatment at temperature 90 °C with a 3 mol/L, a concentrate obtained final of 99.16 % SiO$_2$ with a content of 0.01 % Fe$_2$O$_3$ [9].

According [10] a method of leaching by several acids, such as HF, H$_2$PO$_4$, H$_2$C$_2$O$_4$, HNO$_3$ and H$_2$SO$_4$ has been presented to investigate mainly there effect on the iron and aluminium removal. The results obtained show that sulfuric acid is one of the best leaching agents for the removal of iron and aluminium impurities from the quartz sand. The optimal leaching rates for iron and aluminium are up to 97.9 % and 94.2 %, respectively.

A sand ore containing 97.9 SiO$_2$ and 0.06 Fe$_2$O$_3$ has been processed by bioleaching alone and combination of magnetic separation and bioleaching for the processing of a feed size fraction of (–850)–(+150) μm. The efficiency of Fe$_2$O$_3$ removal by bioleaching process; alone was 79.1 %, the Fe$_2$O$_3$ content was 0.0125 %. Whereas, combinations of magnetic separation and bioleaching have improved the removal efficiency to 85.8 %, the Fe$_2$O$_3$ obtained was 0.0085 % [11].

The removal of iron from silica sand using ultrasound and oxalic acid has been studied in [12]. The optimum conditions for the maximum removal of 75.4 % of iron with ultrasound were determined as follows:

- reaction temperature, 95 °C;
- stirring speed, 500 rpm;
- ultrasound power, 150 W;
- acid concentration, 4 g/l;
- reaction time 30 min.

Another study on treatment of relatively low silica grade deposits proved that gravity separation could not be enough and a combination of attrition scrubbing, gravity separators (like shaking table or spiral), flotation and finally HIMS must be employed.

As a result, with the mentioned combined processes, the shaking table with magnetic separation iron content was reduced to 0.65 % Fe$_2$O$_3$ and flotation with magnetic separation iron content was reduced to less than 0.1 % Fe$_2$O$_3$ [13].

This work aimed at studying the processing techniques for the purification of by-products rejected by kaolin treatment. The studies were conducted by treating physically and chemically such rejects to reduce the iron and clay impurities as well as, to obtain an optimal grade of silica concentrates to enable the use as a raw material for glass making.

2. Materials and Methods

2.1. Geographical location and geology. The El-Milia deposit has been known since 1925. It is located in the wilaya of Jijel in the North-East of Algeria, 15 km north of the Daïna of El-Milia whose reserves of the deposit amount to more than 14 million tons. The El-Milia kaolin processing plant subject of this study is located 4 km northeast of the town of El-Milia and is located 11 km from the deposit. It was put into production on 1st January 1994 with a processing capacity of 50000 T per year.

Tamazert kaolin is a primary deposit where kaolinite represents the direct result of weathering without subsequent transport. Evidenced the presence of abundant quartz, muscovite and relics of feldspar. The kaolinitized zone corresponds to the alteration of feldspathic gneisses intercalated by micaceous schists. Two main facies constitute the kaolinitized zone and are characterized by their clay mineral content. These are sandy kaolin richer in kaolin, in the form of a superficial layer 30 meters thick on average and kaolin gneiss located at depth. These two facies are crossed by ferruginous past located along faults and fissures. The Kaolin Tamazert deposit has the shape of a soft-sided anticline; it is subdivided into four bodies (Central, North, Oriental, and Sidi Kader). Kaolin is bound to an alteration zone, where it forms an arenized and kaolinitized layer (Fig. 1).

2.2. Characterization of the samples. A sample of about 60 kg was collected from the dump siliceous by-products of the kaolin-processing outcome. The sample was collected from different points with maximum diameter of 2 mm. The sample ore was well mixed, and quartered to small samples of about 300 g each. Representative samples were prepared for chemical analysis by X-ray fluorescence (XRF) and mineralogical studies by X-ray diffraction (XRD).

The mineralogical analysis was carried out using powder diffractometer branded «X’ Pert Prof Type P analytical MPD/vertical system θ/θ PDS pass 4x Accelerator (detector) platforms (Bracket) (sample-stage)+ with Cu radiation with a wavelength $\lambda = 1.5405980$ Å at 20 values between 10° and 100°. However, the XRF analysis was used in this study to determined chemical composition.

2.3. Sample classification by sieving. A representative sample was subjected to sieve analysis using sieve device type RETSCH to reject +500 μm and –100 μm fractions from the bulk sample. The particles <106 μm are removed because they represent iron and clay impurity [8]. The classified fractions were subjected in two processing procedures, the first consisting of only a physical treatment and the second one consisting of a chemical treatment.
2.4. Procedures. The silica sand processing is based on the nature of the accompanying minerals and gangue, the acceptable cost, and taking into consideration the limiting environment conditions. In this study, to improve silica recovery from siliceous by-products, pre-concentration was performed, followed by two separation processes, namely, magnetic separation and leaching for comparing their effects on the reduction of impurities.

2.4.1. Attrition scrubbing of the classified sample. The attrition scrubbing process was carried out on the fraction (–500)–(+100) µm to remove the coating of impurities (iron oxides and clay) from the surfaces of silica sand particles. The attrition process was executed at optimum conditions with solids percentage of 60 % and 500-rpm impeller speed for 5, 10, 20 and 40 min. The fraction (–500)–(+100) µm were filtered thoroughly and dried in an oven at 100±5 °C for 24 h. This experiment was designed to determine the effects of the duration of attrition on a raw siliceous by-products sample.

2.4.2. Magnetic separation. Dry magnetic separation tests were carried out on particle size fractions –0.5+0.1 mm obtained from attrition scrubbing. A fluted rotor separator with electromagnet bobbins was used to remove the ferriferous inclusions contained in the siliceous by-products. The magnetic particles adhere to the rotor under the influence of the magnetic force and are carried by the rotation in a low magnetic field area, which is detached with a brush. The magnetic field intensity was varied between 3 to 9 Amperes, and the drum rotating speed is constant 60 rpm. The variation of the intensity of the electric current allows to know what is the most adequate electric intensity for the realization of a good separation. Magnetic separation is among the best environment friendly method to remove iron from silica sand, because it is a physical method without using any chemical acids [15].

2.4.3. Leaching tests. After attrition scrubbing, five samples of the size fraction (–500)–(+100) µm was treated by leaching process. In the leaching tests, 50 g was placed in a 250 ml beaker containing different concentrations of 10 %, 20 %, 30 %, 40 % and 50 % of sulfuric acid (98 % H₂SO₄) prepared in an amount of 100 ml deionized water. The suspension was mixed by electrical mixer for different periods and then left stand for 24 hours in an ambient temperature with occasional stirring. Then the treated sand was washed and filtered thoroughly and finally dried in oven at 100 °C.

3. Results and Discussion

3.1. Characterization of raw samples. Chemical analysis was done on the bulk sample by XRF technique. The result of the chemical composition of bulk sample was given in Table 1. It shows that silica is the most abundant oxide in the studied samples at 82.83 %, alumina (Al₂O₃) content is high up to 10 %, the main impurities are Fe₂O₃ (0.86 %) and TiO₂ (0.33 %). Despite, some high impurities, but it is possible to remove or decrease.

Table 1

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>FeO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>82.83</td>
<td>10.78</td>
<td>0.86</td>
<td>0.33</td>
<td>0.15</td>
<td>0.27</td>
<td>2.44</td>
<td>0.02</td>
<td>2.25</td>
<td></td>
</tr>
</tbody>
</table>

Mineralogical results of sand sample revealed that the sample predominantly consists of quartz as the principal valuable mineral. The other minerals present in minor amounts are muscovite and orthoclase. The other associated minerals present in minor amounts (magnetite, rutile).

The results related to the diffraction X-ray spectra of the initial sample are shown in Fig. 2. Fig. 2. X-ray diffraction spectrum of the raw sample

3.2. Concentration of siliceous by-products

3.2.1. Classified sample. The dry sieving improves the silica content for the bulk sample from 82.83 % to 85.5 %, the content of Fe₂O₃ is decreased from 0.86 % to 0.73 %, and the Al₂O₃ content is tremendously reduced from 10.7 % to 7.14 %. The results of the fraction (–500)–(+100) µm classified by dry sieving are given in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>LOI</th>
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<tbody>
<tr>
<td>Content (%)</td>
<td>85.5</td>
<td>7.14</td>
<td>0.73</td>
<td>0.21</td>
<td>0.02</td>
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3.2.2. Effect of attrition time. Fig. 3 illustrates the effect of attrition time on the efficiency of the attrition scrubbing of the classified siliceous by-products. It was shown that gradual improvement in sand quality with increasing attrition time. After 10-minutes attrition, SiO₂ content increased from 85.5 % to 90.25 %, a difference of 4.75 %, the Al₂O₃ content was reduced from 7.14 % to 4.21 %, a change of 2.93 %, and the Fe₂O₃ content was reduced from 0.73 % to 0.49 %, a change of 0.24 %. The attrition at 20 min, gave a gradual increase in silica content, and a remarkable decrease of alumina and iron oxide, the SiO₂ content is 91.44 %, with an increase of 5.94 % compared to starting content (SiO₂ content in classified sample is 85.5 %). In addition, the Fe₂O₃ and Al₂O₃ contents decreased from 0.73 % and 7.14 % to 0.46 % and 2.39 %. A maximum reduction of iron and alumina impurities was noticed after 40 minutes of attrition scrubbing. During this period, the SiO₂ content increased from 85.5 to 92.17 %, a difference of 6.67 %, the Al₂O₃ content was reduced from 7.14 to 1.81 %, a change of 5.33 %, and the Fe₂O₃ content was reduced from 0.73 to 0.44 %, a change of 0.40 %.
Contents (%)

<table>
<thead>
<tr>
<th>Constituent content, %</th>
<th>Al₂O₃ content, %</th>
<th>Fe₂O₃ content, %</th>
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<tr>
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Fig. 4. Effect of intensity on the magnetic separation efficiency

Test results obtained from attrition alone is insufficient. For production of proper quality concentrate, the attrition scrubbing should be accompanied by other processes (physical, physiochemical or chemical) for higher efficiency [16]. The most frequently used method for beneficiation of low-grade silica is the attrition cleaning in combination with gravity and magnetic separation to improve the quality of silica to meet requirements industrial [17].

3.2.3. Effect of magnetic field intensity. The high quality product of attrition tests was treated with high intensity magnetic separator after drying and various tests were carried out with changing of field intensity. The influence of the variation of the intensity of the electric current is clear. Most of traditional magnetic separators are incompetent on provide for high-purity silica, due to their insufficient magnetic force for the attraction of weakly magnetism particles [18].

From Fig. 4, it can be seen that the percentage of the impurities gradually decreases with increasing the magnetic field intensity.

Fig. 3. Effect of attrition time on the attrition efficiency

At low field intensity only the high magnetically susceptible particles are attracted up by the rotating drum, which produces a grade concentrate relatively high impurities. The results show that there is considerable decreasing of the iron oxide and the clay with increasing the magnetic field intensity. The best result with 97.98 % of SiO₂, 0.05 % of Fe₂O₃, and 0.44 % of Al₂O₃ was obtained at a current intensity of 9 Amperes. Respectively, from the aforementioned results, it is possible to conclude that removal of impurities increase directly with the increasing of intensity the electric current.

3.2.4. Effect of sulfuric acid concentration. The influence of H₂SO₄ concentration on the iron and alumina removal was carried out in solutions containing H₂SO₄ concentrations vary from 10 to 50 % with an interval of 10 % between each assay. According to Fig. 5, the leaching rate increases with increasing concentration of sulfuric acid until 40 %, but increasing in acid concentration to 50 %, did not improve the results. Also, note that the alumina only slightly decreased with further increase in acid concentration. Therefore, 40 % H₂SO₄ can be chosen as an optimal concentration to obtain the optimum leaching results. Based on this, the Fe₂O₃ content decreased from 0.44 % to less than 0.04 %, Al₂O₃ reduced from 1.81 % to 0.66 % and SiO₂ content was increased from 92.17 % to 98.07 % under optimum leaching conditions.

Fig. 5. Effect of sulfuric acid concentration on the leaching efficiency

3.2.5. Flowsheet of the methods applied. Based on the tests that were carried out, a technological scheme was developed to valorization of siliceous by-products rejected by kaolin treatment to obtain of quality sand. The technological scheme is given in Fig. 6.

The laboratory scale processing tests consist of developing a purification process relating to silica sands in order to prepare industrial-grade sand that meets the requirements of glass. In this work, we have applied the following mineralogical processes on samples coming from siliceous by-products rejected by kaolin treatment. The first is based on the grain size classification before and after attrition. The attrition allows to decrease dyes oxides and to eliminate by washing the crust of silica grains. The second integrates magnetic separation under high intensity and leaching after attrition. The non-magnetic attritional fraction concentrates less than 0.05 % of Fe₂O₃ and attrition with leaching lowers the iron content to 0.04 %.

The subject is topical, not only for glass production but also can be developed to reveal a dual scientific and economic interest. The problem posed revolves around the difficulties encountered during the development of glasses following the natural characteristics of the raw material (mineralogical composition, granulo-chemical composition). To meet the requirements of glass manufacturers, work has
been carried out on the characterization with a view to enhancing the raw material while proceeding by separating harmful inclusions such as alumina and iron oxides. When the applicability of physical or chemical alone methods is less effective for the removal of impurities combinations of mineral processing techniques were investigated to were needed to make an efficient recovery process or further study is necessary to establish the process’s optimal parameters for getting better quality of products. Other expected prospects are the valorization of fractions smaller than 100 µm by reverse flotation or in a Hallimond tube.

![Flowsheet of the proposed preparation for the enrichment of siliceous by-products](image)

3.3 Limitations and directions of research development. The environmental impact generated by the increase in mining discharges is a topical subject. In order to minimize, valorized or eliminate these impacts, a proposed treatment model for the valorization of siliceous by-products aims to obtain a high purity of silica to meet glass-manufacturing standards. The treatment of silica by-products plays an important role in the socio-economic life of the entire region, the results obtained by this research allow balanced management to support economic development and that of protecting the environment in the medium and long term, and this is done by exploiting the results obtained by physical and chemical tests in the manufacture of glass. The installation of silica by-product enrichment equipment allows, on the one hand, the products resulting from the treatment processes can be used for the manufacture of glasses (economic interest) and, on the other hand, the discharges can be used directly in the manufacture of construction materials, it will also contribute to the rehabilitation of the mining site and the protection of the environment. The use of attrition for the preliminary treatment of impurities of clay and iron oxide which covers the surface of commonly used sand particles, but the silica content still remains below the required level and the impurity value is higher than the specified value for glass making. The results obtained by the two treatment methods (magnetic separation and leaching) can meet glass manufacturing specifications, but magnetic separation is convenient, simple and at minimal cost.

The development of this research endeavors to demonstrate the mastery of the preservation of the environment associated with the exploitation of silica by-products, it is essentially based on the analysis of the processes, and it specifies all the measures implemented to reduce the impact inside and outside the establishment. The management of the action plan aims to minimize the direct and/or indirect effects of discharges so as to keep them within acceptable limits and to integrate the environment as a component of the daily management of the company.

4. Conclusions

The present work reveals that it is possible to purify siliceous by-products that were rejected by kaolin treatment from Tama-zert (Eastern of Algeria). The beneficiation used to do so consist of two stages, one physical and one chemical. This study, allowed to draw the following conclusions:

- Results revealed that by screening to remove +0.5 and -0.1 mm fractions upgraded the silica content to 85.5 % against a feed content of 82.83 %. Furthermore, the alumina and iron contents have decreased by 3.56 % and 0.13 % respectively.
- The attrition treatment stage is capable of remove for the highest amount of clay with slight decrease in other impurities. So, this stage alone is incapable of remove all impurity presents in siliceous by-products. Any one of the subsequent beneficiation methods such as magnetic separation or leaching does upgrade the siliceous by-products to satisfy the requirements of the glass industry.
- The beneficiation tests performed on siliceous by-products using attrition scrubbing and magnetic sepa-
ration improvement the silica content to 97.98 % and reduced the iron content to 0.05 % of Fe₂O₃.

- For the chemical treatment stage, it was shown that the presence of H₂SO₄ was necessary for maximum removal of iron oxide; the increase in the acid concentration does not have a great effect on clay removal efficiency. Leaching in combination with attrition scrubbing produced a concentrate of 98.06 % SiO₂, 0.04 % Fe₂O₃ and 0.66 % Al₂O₃ with assay of 40 % H₂SO₄. The silica content in the concentrate recovered by this method is a little higher than that obtained by magnetic separation. In both cases, the resulting product is suitable for glass manufacture.

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Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

The manuscript has associated data in a data repository.

References


Soufiane Bouabdallah, PhD, Lecturer, Abderrahmane Mira University, Bejaia, Algeria, ORCID: https://orcid.org/0000-0002-9540-093X

Abdeslam Chaib, PhD, Head of Department of Mining, Badji Mokhtar University, Annaba, Algeria, ORCID: https://orcid.org/0000-0002-9778-013X

Mohamed Bounouala, Professor, Head of Laboratory of Valorization of Mining Resources and Environment, Department of Mining, Badji Mokhtar University, Annaba, Algeria, ORCID: https://orcid.org/0000-0001-5612-2152

Nadia Doebash, Researcher, National Scientific Centre «Institute of Agriculture of the National Academy of Agricultural Sciences», Chabua, Ukraine, ORCID: https://orcid.org/0000-0002-4741-2675

Aissa Benselhoub, Associate Researcher, Environment, Modeling and Climate Change Division, Environmental Research Center (C.R.E.), Annaba, Algeria, e-mail: aissabenselhoub@dcre.ee, ORCID: https://orcid.org/0000-0001-3891-2860

Stefano Bellucci, Senior Researcher, INFN Frascati National Laboratories, Rome, Italy, ORCID: https://orcid.org/0000-0003-0226-6368

Corresponding author