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IRON REMOVAL PROCESS FOR HIGH-PURITY SILICA PRODUCTION BY LEACHING AND MAGNETIC SEPARATION TECHNIQUE

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ПРОЦЕС ВИДАЛЕННЯ ЗАЛІЗА ДЛЯ ВИРОБНИЦТВА ВИСОКОЧИСТОГО КВАРЦУ ШЛЯХОМ ВИЛУГОВУВАННЯ ТА ТЕХНІКИ МАГНІТНОГО ПОДІЛУ

Purpose. The preliminary study of El-Aouana (Algeria) sandstone quality improvement aimed to obtain high-purity silica sands without iron oxides to meet the standards of glass manufacturing.

Methodology. The sandstone from El-Aouana deposit was crushed and sieved. The mineral was characterized by X-ray diffraction and chemically analyzed by X-ray fluorescence, and atomic absorption spectrophotometry. The material (-250+125 μm) was leached with hydrochloric acid. The study of main parameters of the leaching process in different ranges was realized. Thus, magnetic separation by means of the dry high-intensity magnetic separator was employed.

Findings. The leaching allows us to reduce the iron content in quartz sand significantly, while wet sieving removes only the fraction of these contaminating minerals (<125 μm). The applicability of magnetic separation requires further study and substantiation.

Originality. The originality consists in the utilization of hydrochloric acid as the leaching agent. Various preliminary experiments were conducted to determine the conditions of the main experiment.

Practical value. The results obtained by leaching method can satisfy the specifications for glass manufacturing. The sandstone enrichment by magnetic separation is practical and simple at minimum cost, but it is not effective for impurities removal.

Keywords: *leaching, magnetic separation, sandstone, mineral processing*

Introduction. Silica is a major component used in various applications such as glass, ceramics and foundry manufacturing [1] and in high technology sectors such as photovoltaic solar cells. Despite its importance, the use of silica sand in Algeria remains limited due to the quality of the material containing harmful mineral inclusions, including the case of El Aouana deposit, where the presence of impurities, mainly iron oxide, restricts the use of sandstone for the production of high-quality glass.

The sand with iron content lower than 0.03% is suitable for float glass manufacturing [2]. In addition, the particles size influences the release of siliceous minerals compared to the gangue. The average size of quartz grains used in glass furnaces varies between 100 and 250 μm.

A number of physical, physicochemical or chemical methods can reduce the iron, being the most detrimental impurity, namely: attrition processes, aiming at removing iron-bearing minerals from the surface of the particles [3]; separation processes (magnetic separation or flotation) for the separation of iron-rich minerals [4, 5]. When the applicability of physical methods is not effective for the removal of chemical or physical impurities which are not sufficiently liberated in mineral structure, other methods are then used at dissolving iron oxide: chemical [6] or biological [7] treatment, however they have a rather restricted use in industrial scale due to their high operation costs and environmental hazards.

The method of froth flotation was applied to improve the quality of silica sand by using the cyclojet cell, this method removes about 80.49% iron oxide in silica sand, and Fe_2O_3 content in silica sand was decreased from 0.41% to 0.08% [5].

Various combinations of mineral processing techniques were investigated to purify silica sands from Jeddah deposit and removing iron impurities. The beneficiation tests performed including shaking table with magnetic separation reduced the iron content to 0.05% Fe_2O_3 and flotation with magnetic separation reduced the iron content to 0.1% Fe_2O_3 [8]

Zhang et al. [6] have recently presented the method of sand treatment by phosphoric acid. The results obtained show that H_3PO_4 is a good agent for the removal of impurities contained in sand, up to 77.1% efficiency compared with the other comparable methods that use industrial strong acids such as sulphuric (H_2SO_4), hydrochloric (HCl), and even hydrofluoric (HF) acids.

Recently, experimental studies examining the leaching by different acids have demonstrated a high degree of iron removal [9]. The highest Fe_2O_3 removal was 86.6% in the conditions of temperature 90°C, 1M H_2SO_4 and 10% S/L ratio of solid to liquid for 120 min. Accordingly, the results obtained show that the HCl is an effective acid for removal of iron impurities in raw material reach 86.5% under the same conditions with a 20% S/L ratio

Bioleaching methods use microorganisms, different bacteria capable of dissolving iron in 63 days at 24°C [8].

In this article, the leaching and magnetic separation study that was carried out on a sandstone sample to obtain high-purity silica sands has been presented. The leaching process by using hydrochloric acid to remove iron impurity from the ore under study and to obtain a material suitable for flat glass production has been evaluated.

Materials and Methods. ***Characterisation studies.*** The raw sandstone sample of 50 Kg obtained from El-Aouana deposit (located on the coast, in northeastern Algeria).The rock was subjected to crushing, mixing, quartering and dividing to obtain representative samples of 500 g. The samples from the prepared sandstone were used for chemical and mineralogical analysis.

A representative sample from the quarry site and then ground to µm is subjected to chemical analysis by calorimeter and spectrophotometric and, the chemical composition of the sandstone is determined in the laboratory analyzes Ferphos (Iron Company and Phosphate) of Tebessa.

Other samples had been prepared the same way and became the subject of an X-ray diffraction analysis in the Laboratory of Material Technologies and Process Engineering (LTMGP) at the University of Bejaia (Algeria). We used the powder diffractometer branded "X' Pert Prof Type Panalytical MPD/ vertical system θ/θ PDS pass 4 x Accelerator (detector) platforms (Bracket) (sample-stage)" with Cu radiation with a wavelength $\lambda = 1.5405980$ Å at 2θ values between 10 and 100°.

A 500 g representative sample was subjected to sieve analysis using sieve device type RETSCH with a diameter of 200 x 50 mm, the particle size measurement range is from 0.045 to 4 mm on a vibratory sieve for 15 min at the amplitude of 60 mm.

Samples preparation. For the purposes of the study, the El-Aouana sandstone was crushed to a size smaller than 5 mm and then it was classified by sieving to 250 µm before the milling stage for the recovery of the particles less than 250 µm.

A 200 g Sample of silica sand was ground under different experimental conditions (room temperature, stainless balls); dry grinding in a ball mill was carried out for different times of treatment (5, 10, 15 and 20 min) with a rotation speed of 200 rpm.

Experimental procedure. In this work, we have applied physical and chemical processes on samples for the iron oxides content reduction. During this study, the parameters of current intensity effect were examined, as well as the effect of hydrochloric acid and the effect of temperatures reaction.

Samples of the size fraction (- 250 + 125 µm), of 100 gm each, were subjected to magnetic separation tests in order to remove the ferriferous inclusions contained in the siliceous material. The range of the current variation in the magnetic separator that was used is from 3 to 15 Amperes, and drum rotation rotor 60 rpm.

The performances of the magnetic separation strongly depend on the physical properties of particles to be separated (size and magnetic nature), the quality of the applied magnetic field and the difference in magnetic susceptibility between the separated particles. The high intensity magnetic separator of laboratory working dry way is composed of three bobbins surrounding the electromagnet provided with a fluted rotor turning between the pole pieces of a magnetic circuit (fig.1). The magnetic poles or pole pieces, between which turns the rotor are subjected to a magnetic induction. The main magnetic separator parameters are the magnetic flux density, which varies from 1.2 to 2 Tesla; the particle size should be less than 1 mm and the rotational speed 60 rpm.

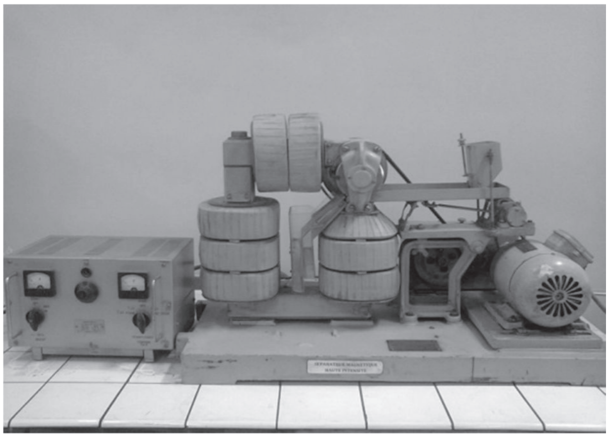

Fig. 1. Magnetic separator high intensity of laboratory (MSHI)

For the first part of the experiment, the leaching tests were carried out in a round-bottomed flask (500 mL). For each run, 200 mL of hydrochloric acid solution (prepare in water) at different concentrations (1, 2, 3, 4 and 5 mol/L) were added to the flask at room temperature. Then, 25 g of sand was added. The suspension was stirred for 1 hour and then was left to stand for 24 and 48 hours in an ambient temperature with occasional stirring.

In the second part, we tried to optimize the leaching parameters to achieve a high degree of removal of iron oxide from silica sand. The procedure used was the same (25 g of sample per 200 ml solution). The concentration of hydrochloric acid was fixed at 3 mol/l, the leaching time was used, respectively 30, 60, 90, 120 and 150 minutes with a temperature range (40 to 90°C). The tests were performed in the Laboratory of Valorization of Mining Resources and Environment, Mining Department, Badji Mokhtar University, Annaba.

The leaching reaction is based on the ability of the hydrochloric acid to dissolve iron oxides; the chemical reaction during the removal of iron oxide by an attack with HCl is as follows

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \qquad (1)$$

The contents were washed with distilled water several times for removing any unconsumed acid and dried at 105°C.

The environmental risk from liquid effluents is decisive. Therefore, the potential acid is important for the leaching of iron and titanium impurities with hydrochloric acid. To overcome this phenomenon affecting the environment, neutralization with quicklime is recommended. In contact of water with the quicklime is obtained slaked lime $Ca(OH)_2$, which causes an increase in pH. At the industrial level, the neutralization process can be realized in settling washtubs.

Results and Discussion. ***Chemical analysis and X-ray Diffraction analysis.*** The results of the chemical analyzes and mineralogical are shown in (table 1) and (fig. 2), respectively.

Table 1

The Results of Chemical Analysis of Raw Sandstone

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3	PAF
Contents (%)	97.20	1.04	0.62	0.09	0.1	0.26	0.01	0.22	0.02	0.40

According to the study conducted on several samples, we found a dominance of SiO_2 content of 97.2%, the remaining oxides are divided into two categories, those that have a low weight percentage (Al_2O_3, Fe_2O_3, TiO_2, Na_2O) and those to trace (MgO, CaO, K_2O, SO_3).

The XRD spectrum confirms of quartz as the principal mineral and other minerals present in very minor to trace amount.

Particle size analysis. The results collected from the chemical analysis of size fractions reveal SiO_2 contents vary from 93 to 98% in the size fractions. As for the ferriferous inclusions contents are 0.28 to 1.20% Fe_2O_3 showing excess iron in the raw material that does not meet the required standard (Fe_2O_3<0.03%) and the TiO_2 content not exceeding 0.38%. We note that the distribution of irregular particles with a high yield included in fractions of 0.125 to 1 mm, and 2 to 4 mm. A low yield presented by fractions < 125 μm and by the fraction -2 + 1 mm.

Also, note that the iron oxide content increases as the particle reduction. The results of the chemical analysis of size fractions are given in Table 2.

Grinding process and particle-size analysis. After grinding, the sandstone sample were classified according to the sieve fractions. The particle size obtained from each sample was compared with the particle size obtained from the original sample (fig. 3).

According to the grinding of the sample to a particle size below 1 mm, it was found that the liberation of valuable mineral to the desired particle size is achieved at an optimum time of 15 minutes with a mass percentage of 55%. In passing 20 minutes of time grinding, we note that the performance of fine particles almost doubled and the recovery of the desired fraction does not exceed 45%.

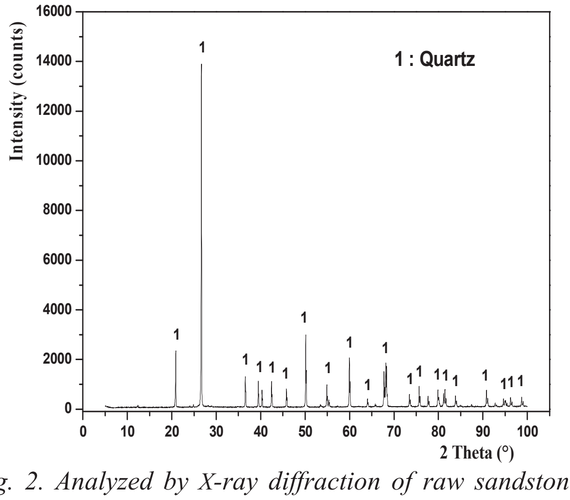

Fig. 2. Analyzed by X-ray diffraction of raw sandstone sample

Table 2

The Results of Chemical Analysis of Size Fractions of Sandstone Sample

Fraction (mm)	Yield (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO	PAF
> 4	15.4	93.4	2.09	0.534	0.14	0.110	0.03	0.364	0.012	0.24	0.01	2.92
-4 + 2	18.81	96.0	1.36	0.554	0.11	0.093	0.02	0.364	0.012	0.18	0.01	1.27
- 2 + 1	08.95	97.1	0.66	0.433	0.05	0.099	0.01	0.364	0.012	0.14	0.01	1.08
- 1 + 0,5	11.33	97.8	0.49	0.351	0.07	0.081	0.01	0.350	0.006	0.16	0.01	0.66
- 0,5 + 0,25	18.78	98.4	0.26	0.283	0.04	0.080	0.0	0.350	0.006	0.12	0.01	0.43
- 0,25 + 0,125	15.99	98.2	0.32	0.374	0.05	0.065	0.0	0.357	0.012	0,11	0.01	0.49
- 0,125 + 0,063	06.98	97.6	0.87	0.523	0.04	0.073	0.01	0.350	0.012	0.16	0.01	0.32
- 0,063 + 0,045	01.29	95.6	1.66	0.734	0.07	0.093	0.02	0.364	0.018	0.29	0.01	1.09
< 0,045	02.47	94.3	3.29	1.209	0.05	0.109	0.02	0.377	0.018	0.38	0.02	0.19

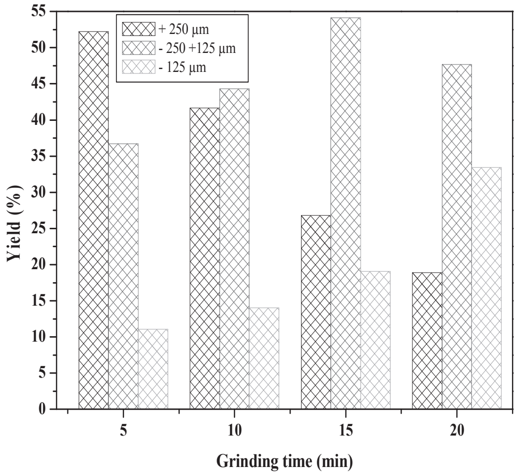

Fig. 3. Effect of the grinding time on the mass yield

A closed grinding system would further reduce particles > 250 µm, this possibility is economically feasible.

High impurities of iron and clay content was observed in the chemical analysis results from fraction < 125 µm, this fraction was rejected by washing with water on a 125 µm sieve. The chemical analysis results by FX, a significant decrease percentage of clay is noted and which is of the order of 0.12%. The Fe_2O_3 content of the sandstone sample were 0.6% against to 0.28%. The results show that washing by settling is required to remove the soft and clay minerals.

In the early experiments, the stage of desliming was carried out by quartz washing with water in a sieve of 38 µm to remove the required amount of clay impurities. The test results obtained by flotation of iron impurities while pressing silica show that the iron content is approximately 0.05 or 98.8% SiO_2 and the recovery of 68.35%. Another magnetic separation - flotation in an acid medium obtained 0.01% Fe_2O_3 and a high content of 99.3% SiO_2 with the optimal recovery of 84.75% [4].

Evaluation of the iron removal efficiency. The efficiency of iron removal can be calculated by the following equation

$$\mathrm{E}\ (\%) = \left[1 - \left(\frac{\mathrm{Fe_2O_3}\text{content in concentrate}}{\mathrm{Fe_2O_3}\text{ content in feed}}\right)\right] * 100, \qquad (2)$$

where E (%) – iron removal efficiency.

Effect of current intensity on the performance of the magnetic separation. The influence of the magnetic field intensity is an important factor in this process. The magnetic separation of the silica sand to a laboratory scale has been studied by several authors [10, 11]. The influence of the magnetic field strength and the grain size on reduction of the rate of iron oxide.

Table 3 shows the effect of current intensity of the coil on the efficiency of removal of the iron oxide from the sandstone. From the results that were obtained by high-intensity magnetic separation (MSHI), we have found that the significant improvement in silica content, and a remarkable reduction of impurities such as hematite and rutile was obtained in the range between 12 and 15 Amperes. We have determined that the iron impurity content decreases from 0.28 to 0.10% with the increase in the intensity of the electric current at 15 Ampere. The optimum efficiency of removal of iron oxide was obtained in the range of 64.3%. As for the content of TiO_2, regresses 0.13 to 0.07%, we noticed a low removal rate of 47%.

Table 3

Effect of Current Intensity
on the Iron and Rutile Removal

Intensity (A)	Fe2O3 (%)	Fe2O3 (%)	E (%)	TiO2 (%)	TiO2 (%)	E (%)
3	0.28	0.26	7.2	0.13	0.12	8
6		0.21	25		0.1	23.1
9		0.17	39.3		0.08	38.5
12		0.12	57.2		0.07	46.2
15		0.1	64.3		0.07	46.2

Effect of hydrochloric acid concentrations. During processing of the sandstone by different concentrations of HCl, there is an efficiency of the dissolution of the metal components mainly of iron with increasing HCl dose. Table 4 shows the results of the percentage of iron removed, with a dose of 1 mol/L a slight decrease of 0.22% the Fe_2O_3 is noticed and of HCl 2 mol/L, no remarkable improvement . However, with an HCl concentration of 3 mol/L almost get the same result of 0.12 and 0.1%. The removal efficiency of iron oxide was observed that it reached 67.9% in the first 24 h followed by a relatively maximum removal of 78.6% in 48 h with using of 4 mol/L; it was reduced iron content to about 0.09 and 0.06%.

A significant improvement is witnessed by increasing the concentration of HCl 5 mol/L; it was observed slower removal relatively of 0.08 in the first 24 h, the iron removal of 71.4%, after 48 h, we found a maximum elimination of iron oxide of 85.7% and the iron oxide content was decreased from 0.28 to 0.04%.

Table 4

Efficiency of Iron Removal
for Different Concentrations

		24H		48H	
HCl (mol/l)	Fe_2O_3 (%)	Fe_2O_3 (%)	E (%)	Fe_2O_3 (%)	E (%)
1	0.28	0.23	17.9	0.22	21.4
2		0.18	35.8	0.16	42.9
3		0.12	57.2	0.1	64.3
4		0.09	67.9	0.06	78.6
5		0.08	71.4	0.04	85.7

Effect of temperature. The influence of temperature on the iron removal was studied for temperatures of 40, 65, and 90°C in solutions containing 3mol/l of hydrochloric acid.

The results illustrated in table 5 show that, the highest temperature 90°C was improved the removal efficiency to 96.4% with iron content reduced to 0.01% after 150 min. At lower temperatures, varying between 40–65°C, the removal of iron oxide about 75%; decreasing Fe_2O_3 contents from

0.28%, in the raw sand to 0.07% with same retention time, since at 40°C and increase of the leaching time up to 150 minutes no significant effect on the iron extraction. It was found out that the higher is the temperature the more efficient is leaching to remove the iron from the sand.

Table 5

Efficiency of Iron Removal at Different Temperatures with Concentration of 3 mol/L

	3 mol/l						
Time (min)	Fe_2O_3 (%)	40°C	E (%)	65°C	E (%)	90°C	E (%)
		Fe_2O_3 (%)		Fe_2O_3 (%)		Fe_2O_3 (%)	
30	0.28	0.22	21.4	0.21	25	0.18	35.8
60		0.18	35.8	0.16	42.9	0.12	57.2
90		0.15	46.4	0.13	53.6	0.07	75
120		0.12	57.2	0.09	67.9	0.03	89.3
150		0.09	67.9	0.07	75	0.01	96.4

Conclusions. The study conducted on the sandstone quarry of El-Aouana (Jijel) allowed us to draw the following conclusions:

The obtained results show that after the granulometric separation by sieving of sandstone samples, the pondered yields are significant in the fractions (2 to 4 mm) (0.125 to 0.5 mm).

Information from a representative sample at the physicochemical characterization confirmed the dominance of proportions, silica-rich inclusions with the inclusion of iron oxides and titanium

A better release of silica minerals is located in the fraction (250 to 125 μm), which reduces the levels of iron from 0.6 to 0.28% of Fe_2O_3 while eliminating fine particles < 125 μm by wet sieving.

The non-magnetic final concentrate obtained by high intensity magnetic separation contained a Fe_2O_3 content of 0.1% does not respond the standards of high-quality glass manufacturing.

The leaching by hydrochloric acid for 3mol/L at temperature 90°C had eliminated almost all of the iron oxide impurity (0.01%). The results obtained significantly encourage the use of sandstone of El-Aouana for the production of flat glass.

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Мета. Попереднє дослідження піщаників El-Aouana (Алжир) з метою поліпшення їх якості для отримання кварцових пісків високої чистоти без домішок оксидів заліза у відповідності до прийнятих стандартів виробництва скла.

Методика. Піщаник родовища El-Aouana подрібнювали та просівали. Мінерал піддавали рентгенівській дифракції та хімічно аналізували за допомогою рентгенівської флуоресценції, атомно-абсорбційної спектрофотометрії. Матеріал (-250 + 125 мкм) вилуговували соляною кислотою. Проведено вивчення основних параметрів процесу вилуговування в різних діапазонах. Була використана магнітна сепарація з використанням сухого сепаратора високої магнітної інтенсивності.

Результати. Вилуговування дозволяє отримати зниження вмісту заліза у кварцовому піску, у той час як мокрий розсів видаляє лише частину цих забруднюючих мінералів (<125 мкм). Питання застосування магнітної сепарації потребує подальшого вивчення.

Наукова новизна. Оригінальністю цього дослідження є застосування процесу вилуговування соляною кислотою. Для з'ясування основних експериментальних умов були проведені різні попередні експерименти.

Практична значимість. Результати підтверджують, що метод вилуговування задовольняє технічні вимоги виробництва скла. Проте збагачення піщанику магнітною сепарацією може бути практичним і простим за мінімальних витратах, але не є ефективним для видалення домішок.

Ключові слова: *вилуговування, магнітна сепарація, піщаник, переробка мінеральної сировини*

Цель. Предварительное исследование песчаников El-Aouana (Алжир) с целью улучшения их качества для получения кварцевых песков высокой чистоты без примесей оксидов железа, согласно принятым стандар-там производства стекла.

Методика. Песчаник месторождения El-Aouana измельчали и просеивали. Минерал подвергали рентгеновской дифракции и химически анализировали с помощью рентгеновской флуоресценции, а также атомно-абсорбционной спектрофотометрии. Материал (-250 + 125 мкм) выщелачивали соляной кислотой. Проведено изучение основных параметров процесса выщелачивания в различных диапазонах. Была применена магнитная сепарация с использованием сухого сепаратора высокой магнитной интенсивности.

Результаты. Выщелачивание позволяет добиться снижения содержания железа в кварцевом песке, в то время как мокрый рассев удаляет лишь часть этих загрязняющих минералов (<125 мкм). Вопрос применения магнитной сепарации требует дальнейшего изучения.

Научная новизна. Оригинальностью этого исследования является применение операции выщелачивания соляной кислотой. Для выяснения основных экспериментальных условий были проведены различные предварительные эксперименты.

Практическая значимость. Результаты доказывают, что метод выщелачивания удовлетворяет техническим требованиям производства стекла. Однако обогащение песчаника магнитной сепарацией может быть практичным и простым при минимальных затратах, но не является эффективным для удаления примесей.

Ключевые слова: *выщелачивание, магнитная сепарация, песчаник, переработка минерального сырья*

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