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PRODUCTION OF HIGH-PURITY QUARTZ FOR OPTICAL APPLICATIONS

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ABSTRACT – The paper investigated the production of high-grade quartz for optical devices, starting with mined quartz. This material contained 668 mg/kg of Fe_2O_3, and the aim was to reduce the content to below 100 mg/kg through an environmentally and economically sustainable process. It was found that the sequential leaching water-oxalic-sulphuric acid is very efficient using two sequential stages; both acids can be used two times. The best conditions were: water leaching S/L 100%, temperature 90°C, time 45 min; oxalic acid stage: OA concentration 17 g/L, leaching time 2.5 h, temperature 90°C, S/L 20% wt/vol; sulphuric acid stage: SA concentration 2 mol/L, leaching time 1.5 h, S/L 20% wt/vol. OA can be recovered from the spent solution and recycled. SA recycling was tested using an NF membrane module: the rejection of iron sulfate and silica (silicic acid) was greater than 85%. The permeate can then be used for a further leaching stage. NF removes most of the significant elements, which avoids further iron leaching from quartz. The final high-grade product contained less than 100 ppm of Fe_2O_3, with a Whiteness Index (D65/10°) greater than 88, the minimum threshold required for optical applications.

Keywords: Iron Removal, Quartz, Acid Recycling, Process Optimization.

INTRODUCTION

Nowadays, the production of high-purity quartz for applications like semiconductors, optical fibers, photovoltaic panels, and other optical devices is highly strategic. Silica glass must have properties like chemical purity, optical transparency, and radiation resistance. Iron is the most harmful impurity in quartz sands and ores because it impairs light transmission and the glasses' transparency [1]. Manufacturing processes are relatively expensive in terms of energy and reagents. For this reason, the optimization becomes strategic to make this sector more competitive. Although many researchers investigated iron removal from quartz at a laboratory scale, such processes were not optimized to reduce the overall operating costs. High temperature (80-90°C) [2] and time (3-5 h) is required to achieve good iron extraction yields [3,4].

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Moreover, magnetic separation is also helpful in reducing the amount of iron undergoing the leaching stage [4]. Ubaldini *et al.* [3] tested continuous leaching through a fixed-bed column filled with quartz sand, recycling the oxalic acid solution and testing several operating factors. The highest iron reduction was 46 %, bringing Fe_2O_3 to 0.0163 %wt from 0.0302 %wt. The mechanism of that organic acid may be that of complexing and/or reducing Fe(III) to Fe(II) [4]. Oxalic acid was also used synergistically with sulphuric acid in a rotary drum reactor [4]. Oxalic acid demonstrated a high iron extraction yield even with red clay, decreasing Fe_2O_3 from 17.1 % to 3.64 %wt (-78.7 %) and making it suitable for ceramic manufacture [5]. The kinetics of iron dissolution in quartziferous ores by oxalic acid was also studied, and the activation energy resulted in 45.4 kJ/mol [6]. Besides oxalic acid, other reducing agents were used, such as citric acid and glucose mixed with sulphuric acid. Despite that, oxalic acid demonstrated the best performance (99% iron removal), keeping all the other process parameters constant. The yields were always higher than 70% with the other two reducing agents [1]. Roasting is another effective pre-treatment for natural quartz powder in the presence of ammonium sulphate that reduces Fe(III) into Fe(II) at 400-500°C in airflow: the following leaching with 5%wt H_2SO_4 + 10%wt HF can reduce Fe_2O_3 below 0.3 mg/kg from the original concentration of 145 mg/kg [7]. High-temperature roasting (from 600°C to 1200°C) can transform quartz's crystalline structure, enhancing the acid's effect in removing iron and other impurities. Iron extraction was nearly 99% in quartz pre-treated with magnetic separation [8]. The drawback of such a method is the high energy cost relevant to the thermal and leaching stages, which last 10 hours overall. Iron reduction is also required when high-silicon tailings are used as feedstock to recover 99.99 %wt of high-purity quartz. High-intensity magnetic separation, followed by a two-stage leaching with H_3PO_4/HCl/HF mixture reduced the iron oxide content by nearly 91% [9].

Zhang *et al.* [2] compared the results of using several acids, namely H_2SO_4, $H_2C_2O_4$, H_3PO_4, HCl, and HF, at a time to whiten quartz ores and sands under ultrasounds. Iron removal achieved a 77 % yield. Nonetheless, this result was achieved with a solid-to-liquid (S/L) ratio of 5 % wt/vol, almost low: when the S/L ratio was increased to 20%, the iron oxide extraction decreased to 46%. Bioleaching is another technique that can be applied to iron removal from quartz sand. The kinetic is much lower than standard chemicals like mineral and organic acids. However, Styriakova *et al.* [10] achieved a 50% Fe_2O_3 reduction after 83 days of treatment with heterotrophic bacteria in an in-situ pilot plant. This experimental campaign confirmed lab-scale results obtained with three quartz samples from different Slovak locations [11]. HF enhances the removal because it can dissolve the surface of quartz particles and penetrate through small channels, making contact with iron and other metal particles embedded inside possible. Nevertheless, HF use poses severe corrosion problems in industrial plants that treat several thousand tons of quartz annually.

There is a gap in the literature regarding improving environmental sustainability and economic viability of high-grade quartz production. In this paper, we optimized a process to reduce the iron oxide content below 100 mg/kg without grinding the samples supplied from a Turkish mine, as requested by the mining company, maximizing acid and water recycling to reduce operating costs.

EXPERIMENTAL

All trials were carried out using a particle size of -1200 µm, as provided by the Turkish company that mines quartz. It was ground with a ball mill to -150 µm for digestion in aqua regia and some drops of concentrated HF. Iron was measured by Atomic Absorption Spectrometry (AAS, spectrometer SpectrAA 200, Varian). The sample was also characterized by X-ray fluorescence (XRF, Spectro Xepos) and X-ray diffraction (XRD, Philips X-Pert). Leaching tests were performed in 250 mL flasks and placed in a Dubnoff water bath (BSD/D, ISCO) with a mechanical stirring rate of 200 rpm, unless otherwise indicated.

The following experimental plans were tested: 1) Direct leaching in a 2^5 full factorial design, studying S/L ratio, H_2SO_4 concentration, reaction time, volume of wash water and temperature; 2) Cross-current configuration, in which the leach liquor was reused to leach other two fresh quartz sample (3-stages), with a make-up of fresh H_2SO_4 to bring back the solution volume to the initial one; 3) Counter-current leaching configuration (3-stages); 4) Direct leaching with water-$H_2C_2O_4$-H_2SO_4 and partial reuse of the leach liquors for further leaching stages.

RESULTS AND DISCUSSION

Characterization of quartziferous ore

The Fe_2O_3 concentration of the quartz sample was 668±54 mg/kg. XRD analysis showed no further crystalline phase than quartz because of the low iron concentration. Nevertheless, the company communicated that iron was in the form of hematite. The XRF analysis is shown in Table 1.

Table 1 Main elements contained in the quartz sample

	Concentration (%wt)								
Element	Si	Al	K	P	S	Ca	Ti	Cr	Zr
	44.4	0.64	0.11	0.03	0.02	0.03	0.05	0.02	0.45

Leaching tests

If 100 ppm is the final target concentration, the leaching process was effective whether the iron extraction yield was at least 85%. The leaching mechanism can be expressed as follows [3,4]:

$$Fe_2O_3 + 6\ H_2C_2O_4 \rightarrow\ 2\ Fe(C_2O_4)_3^{3-} + 6\ H^+ + 3\ H_2O \quad (1)$$

$$2Fe(C_2O_4)_3^{3-} + 6\ H^+ + 4\ H_2O \rightarrow\ 2\ FeC_2O_4 \cdot 2H_2O + 3\ H_2C_2O_4 + 6\ CO_2 \quad (2)$$

$$Fe_2O_3 + 3\ H_2C_2O_4 + H_2O \rightarrow\ 2\ FeC_2O_4 \cdot 2H_2O + 2\ CO_2 \quad (3)$$

There are two main mechanisms: complexing and/or reduction of Fe(III) into Fe(II). The latter prevails at low pH values, i.e., <1.5, whereas at pH 2-3, the complexing action of OA is predominant [4]. Furthermore, the presence of light may increase the process kinetics of Fe(III) reduction.

Direct leaching

The best iron extraction yield (EY) was only 80.5%, namely insufficient, and was achieved with a 10% wt/vol S/L ratio, 2 mol/L H_2SO_4 in 3 h at 90°C by using 50% of wash water volume with respect to the leaching solution, to wash the quartz cake recovered by filtration. This single test was repeated in the same experimental conditions but using a hot plate with a magnetic stirrer; after 90 min, the EY was 91%, confirming that the grinding effect of the anchor allows a faster and more efficient iron reduction. The problems with this configuration are the high acid consumption, the additional cost associated with the alkaline reagent required to neutralize the spent solution, and the huge amount of salts generated (Na_2SO_4, $CaSO_4$, etc.), because the reuse of leach liquor for a second stage did not achieve the minimum iron extraction.

Cross-current configuration

A three-stage configuration, using the same experimental conditions of the best direct leaching trial but with magnetic stirring, led to the following iron EYs: 89.9% in the 1st stage, 62.1% in the 2nd, and 26.7% in the 3rd one, respectively. Only the first stage could reduce iron below 100 ppm, despite the leach liquor having sufficient residual H_2SO_4 (173 g/L) to leach the second sample of fresh quartz. It is difficult to understand why the solution's leaching strength decreased dramatically just after the first stage when the consumed acid is rather low; one possible explanation is the presence of dissolved silica that forms some sort of protective layer around quartz grains, preventing the acid from accessing the particles in an effective way. We also decreased the percentage of the leach liquors reused in the following stages, i.e., in the 2nd and 3rd, while increasing the amount of make-up acid, but the results did not improve.

Counter-current configuration

The experimental conditions of the 3-stage counter-current leaching were the following: 2M H_2SO_4, S/L 30% wt/vol, 90°C, time 1.5 h, Temperature 90°C, wash water volume 50%, make-up each stage with 2M H_2SO_4 solution. The total iron EY was 90.6%. This configuration allowed the reduction of Fe_2O_3 in quartz below the threshold for optical applications, but the consumption of acid was not reduced so much.

Water-$H_2C_2O_4$-H_2SO_4 configuration

Tests were carried out on magnetic stirred and heated plates. Pre-treatment with hot water was carried out by using 20 mL of water with 20 g of fresh quartz and heating it at the leaching temperature, i.e., 90°C; the overall scheme is reported in Figure 1. At the end of each sequence, iron content in the final quartz was 88 and 121 ppm, respectively, measured by AAS after acid digestion of the solid samples. The second sample exceeded the target concentration. However, it is possible that the leaching power of the pregnant solution will increase after filtration to remove iron and silica. Pre-treatment with hot water is very important since it weakens the grain surface, and acid can diffuse better, removing the iron trapped inside each quartz particle. Figure 2 shows the original quartz and the sample after the highest iron EY, i.e., 92%. A full factorial design with 3 factors

and 2 levels was investigated to optimize the experimental conditions of the water heating step and the oxalic acid leaching. The optimized parameters were: 1-Water stage: S/L 100% wt/v, 45 min, 90°C; 2-OA stage: OA 17 g/L, S/L 20% wt/v, 2.5 h, 90°C; 3-SA stage: SA 2 mol/L, S/L 20% wt/v, 1.5 h, 90°C. The iron EY was 92%. Despite the configuration, what was inferred from the experimental tests was: firstly, dissolved and colloidal silica, i.e. metasilicic (H_2SiO_3) and ortho-silicic acid (H_4SiO_4) that can polymerize when the solution is cooled down, impairs the reuse of sulphuric acid solution in a second stage and secondly, the same colloidal silica makes filtration hard, because it clogs the filter channels. Hence, a regeneration treatment is required to save acid and ensure the viability of the plant.

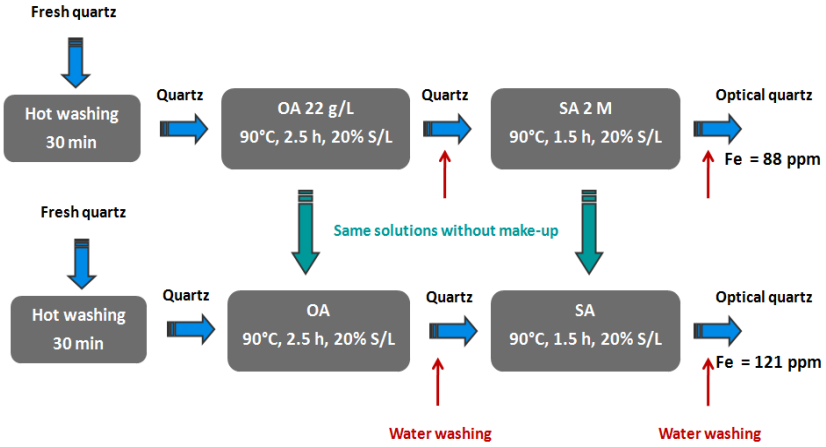

Figure 1 Scheme of the sequential leaching water → OA → SA

Figure 2 Original quartz (left) and treated sample with 53 ppm of Fe_2O_3 (right)

Treatment of H_2SO_4 spent solution

Several methods were tested to reduce the concentration of iron and silica in leach liquors in order to reuse them in further leaching stages. This stage is crucial to lower operating costs. Polyelectrolytes and hydrated lime gave Si and Fe precipitation yields up to 40%. Around 52% of silica was removed by an anionic resin. The best regeneration treatment was nanofiltration (NF), carried out by the German group Osmo Membrane. The result of the membrane filtration was the following: Feed solution, 4500 mL: H_2SO_4 203 g/L, Fe 183 mg/L, Si 59.1 mg/L; Permeate, 3987 mL: H_2SO_4 181 g/L, Fe 3.1 mg/L, Si

6.7 mg/L; Retentate, 513 mL: H_2SO_4 234 g/L, Fe 555 mg/L, Si 366 mg/L. The permeate, nearly 89% of the feed volume, was reused for another quartz leaching in the water/OA/SA configuration, and the iron removal was 90%.

Figure 3 Retentate and permeate after titration with NaOH

CONCLUSIONS

The following conclusions can be inferred from the experimental campaign:

- A three-stage leaching with water, oxalic, and sulphuric acid was the most efficient way to obtain high-grade quartz for optical applications, with a final Fe_2O_3 concentration of 53 ppm.

- Recycling of OA and SA is crucial to reduce operating costs. OA solution can be recycled one time. Instead, the SA must be purified to remove the dissolved iron and colloidal silica. The best treatment is NF: permeate can be recycled, whereas retentate shall be neutralized, and the resulting sludge shall be disposed of.

- The water pre-treatment stage has a positive effect, but a mild grinding of quartz could replace it, and a -500 µm fraction could be used to improve iron extraction. Furthermore, a high-intensity magnetic separation can remove iron particles before the hydrometallurgical treatment, enhancing the overall reduction. A techno-economic analysis shall be carried out to figure out the most convenient route.

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