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# Iron Removal Process for High-Purity Silica Sands Production by Oxalic Acid Leaching

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In this article, a leaching study, carried out on a quartz sample to obtain high-purity silica sands, has been presented. A leaching process by using oxalic acid to remove low iron content from the ore under study and to obtain a material suitable for fiber optic production has been evaluated. A characterization study has been carried out to establish the location of the iron impurities on the ore: 77 g/t was the maximum iron contamination, whereas, a final iron content <10 g/t (as Fe) has to be achieved for the application considered. The effect of the grinding process on the iron extraction yield has been established; the maximum iron extraction yield obtained with the ore as-is was about 45−50%, whereas extraction yields greater than 80−90% can be obtained after grinding the ore in different experimental conditions. An empirical model was evaluated to correlate the iron extraction yield obtained after 3 h of leaching at 80 °C, with 3 g/L of oxalic acid and 10% (w/v) of ore concentration, as a function of the average particle diameter of the ore after grinding. An iron extraction yield of about 98−100% can be obtained with an average particle diameter of about 20 $\mu$m. A schematic flowsheet of the process has been proposed considering the obtained experimental results and the results obtained in the literature for the waste treatment aspects. The experimental results have shown the technical feasibility of this process for the production of high-purity silica sands.

## 1. Introduction

Processes for the purification of industrial minerals, such as quartz sand, feldspars, and kaolins, contaminated by iron are essential to render these raw materials used both for traditional industrial applications (ceramics, papermaking, etc.) and for more advanced applications that ensure a higher value-added component, such as optical fibers and the production of pure silicon.[1]

Several techniques are available for upgrading quartz by partial removal of iron, e.g., flotation, heavy-media separation, or magnetic separation, but these seldom reduce the iron to an acceptable level.[2,3] Other techniques available are based on the use of $H_2SO_4$ or HCl. These are generally costly and have a considerable impact on the environment.[1] In this scenario the use of oxalic acid as leachant agent in the iron removal process from industrial minerals holds potential interest.[2,4−6] The chemical reactions can be summarized as follows:

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

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

$$Fe_2O_3 + 3H_2C_2O_4 + H_2O = 2FeC_2O_4{\cdot}2H_2O + 2CO_2 \quad (c)$$

The interest in this kind of process is indicated by several industrial projects financed by EU (contracts MA2M-CT90−0014, BRE2-CT92−0215, BRPR−CT96−0156) in which important industrial partners have been involved.[1,7]

Oxalic acid reacts with surface Fe(III) ions to form complexes.[8,9] Once the surface complex has formed, the dissolution mechanism differs depending on the iron mineral concerned. In magnetite,[8] where both ferric and ferrous species are present on the surface, the mechanism involves the reductive dissolution of surface Fe(III) ions, and an autocatalytic process, involving the formation of ferrous oxalate, has been observed. This catalytic effect has also been studied on the hematite,[10,11] coupling the study with a systematic thermodynamic analysis[12]; a positive influence on the iron extraction kinetics was then observed in leaching tests by using quartz sands in the presence of ferrous ion.[13]

In this research a final stage of study is necessary (which is not the object of this article) on a pilot-scale organic, acid−leaching plant, which also includes a wastewater treatment unit [7,14] to ascertain the marketability of such a system and to assess plant and process scale-up problems. For these reasons, this aspect forms the subject of an EU Contract (BRPR-CT96-0156) of which the design and construction of a pilot unit for the removal of iron from quartz sands already upgraded to some extent by flotation is the main objective. The iron-removal process is necessary to obtain a raw material of greater value added, for the manufacture of optical fibers and the production of silicon, markets of considerable interest for the EU.

In this ambit, the purpose of the work reported here is the removal of iron from a floated mineral (noted as FL) originating from the Santa Florinas mines (Sardinia, Italy) and the performance of some experimental tests in lab-scale reactors to reduce the iron content of

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**Table 1. Chemical Composition of the Florinas Sample FL for Different Granulometric Classes**

| sample ($\mu$m) | as-is ore | +500 | +250−500 | +180−250 | +125−180 | +90−125 | +53−90 | −53 |
|---|---|---|---|---|---|---|---|---|
| abundance (%) | 100 | 3.7 | 37.8 | 36.3 | 15.2 | 5.3 | 1.4 | 0.3 |
| $SiO_2$ | 99.10 | 98.0 | 98.3 | 99.2 | 99.0 | 98.5 | 97.5 | 94.2 |
| $Al_2O_3$ | 0.40 | 0.76 | 0.57 | 0.14 | 0.21 | 0.35 | 0.77 | 2.27 |
| $Fe_2O_3$[a] | 110 | 130 | 90 | 81 | 107 | 186 | 341 | – |
| $K_2O$ | 0.33 | 0.63 | 0.47 | 0.13 | 0.19 | 0.40 | 0.81 | 1.87 |
| $Na_2O$ | 0.13 | 0.085 | 0.11 | 0.105 | 0.08 | 0.067 | 0.12 | 0.21 |
| CaO | 0.18 | 0.27 | 0.15 | 0.39 | 0.34 | 0.26 | 0.26 | 0.34 |
| MgO | 0.0042 | <0.0002 | <0.0002 | <0.0002 | 0.0012 | 0.0056 | 0.0028 | 0.043 |
| sum | 100.14 | 99.75 | 99.60 | 99.97 | 99.82 | 99.58 | 99.46 | 98.93 |

[a] Composition in g/t.

this quartz ore from an initial $Fe_2O_3$ value of 110 g/t to a final iron content of <10 g/t for optical fiber applications. A further target value is <1 g/t for silicon production.

The leaching operation, performed with oxalic acid as the leaching agent, has been carried out in a lab-scale slurry reactors. With this objective various preliminary experiments were conducted to ascertain the main operating conditions that must be adopted in the leaching treatment. For these reasons, chemical and mineralogical characterization of FL, preliminary tests to ascertain the reproducibility of the leaching conditions, and leaching tests to assess the effect of the grinding process (ore size distribution) on the iron extraction yield (IEY) and on the aluminum extraction yield (AlEY), have been performed. Very low levels of iron must be reached in the ore after leaching to permit its use for fiber optic applications.

## 2. Materials and Methods

**2.1. Ore.** The silica sand (noted as FL) comes from the Florinas quarry located in the north of Sardinia, Italy. Table 1 shows the chemical analysis of the ore in the different size fractions.

*2.1.1. Grinding Process and Particle-Size Analysis.* The FL material was adopting various particle-size distributions. The FL was ground under different experimental conditions; dry grinding in an agate laboratory mill was carried out for different periods of treatment to obtain different size fractions for the lab-scale leaching studies. Particle size analysis was performed using Tyler sieves and a Helas laser granulometer.

*2.1.2. X-ray Diffraction and Scanning Electron Microscopy Analysis.* The apparatus used was a Siemens D-500 Diffractometer. Operating conditions were: 40 kV, 40 mA, slit 1, monochromator with curved graphite crystal. Scanning electron microscopy (SEM) analyses have been performed by a Philips model 505 coupled with microanalysis (energy dispersive system, EDS).

**2.2. Leaching Tests.** The leaching tests were carried out in a column and a stirred reactor. Column leaching tests were conducted percolating the leaching agent through a packed-bed column by using FL as-is ore. Further leaching tests were conducted in a 2-L reactor with thermostat. Various amounts of mineral (FL as-is or FL ground to various sizes) were treated with 500 mL of oxalic acid solutions at a temperature of 80 °C. In both cases 0.5-mL samples were taken every so often and diluted to 2 mL to monitor iron extraction during the course of the process. These experimental conditions were adopted according to previously reported tests.[2,4,5]

**2.3. Analytical Measurements.** A Perkin-Elmer 6500 ICP (Inductively Coupled Plasma) instrument was used to determine iron, aluminum, etc., in the liquid samples taken during the leaching and the mineral characterization studies.

Solid samples, after filtration and washing, were brought into solution by treating 0.5 g with HF and $HClO_4$ at high temperature. The process was taken to dryness and the residue was then redissolved in 20 mL 1:1 HCl, warmed, and brought to volume. A comparison between the iron extraction yield calculated from the measures in solution + material balance, and the metal extraction yield calculated from the leach residues demonstrates a substantial accord of the experimental results in terms of iron extraction yield. When the iron extraction yield is approximately 100%, the measures in the solid residues can be given as <5 g/t for the iron content in the quartz sand.

## 3. Results

The main objective of the characterization study was to ascertain the iron-bearing minerals in the Santa Florinas ore tested by flotation (referred to as FL as-is). On the other hand, the main objective of the leaching study was to ascertain the main operating conditions in lab-scale tests, for iron removal, with particular reference to the particle-size factor, which is of fundamental importance regarding the type of reactor to be adopted in the design and construction of the pilot leaching unit. (This task is in progress and it is not considered in this phase of the experiment.)

**3.1. Characterization of the FL Ore.** The results of particle-size distribution of Florinas FL are reported in Table 1. The sample exhibits a modal distribution, with maximum abundance of particle-size classes between 500 and 125 $\mu$m.

The results of quantitative analysis of the Florinas FL sample, for different size classes, are reported in Table 1. The diffractometric spectra (data not shown) of the Florinas FL sample shows that quartz is the main component with small quantities of plagioclase and k-feldspar. Figure 1 shows a particle of quartz covered by small feldspar particles as an example. The microanalysis carried out by SEM showed that the main iron impurities are located on the feldspar particles (white small particles in Figure 1).

**3.2. Leaching Tests.** *3.2.1. Column Leaching Tests.* Column leaching tests were performed to verify the possible application of this kind of reactor to reach the targets required for fiber optic production, in terms of iron extracted, by using FL as-is ore. Figure 2 shows the iron extraction yield that can be extracted in the tested experimental conditions. The maximum yield was obtained after 4 h of operation and is about 50%.

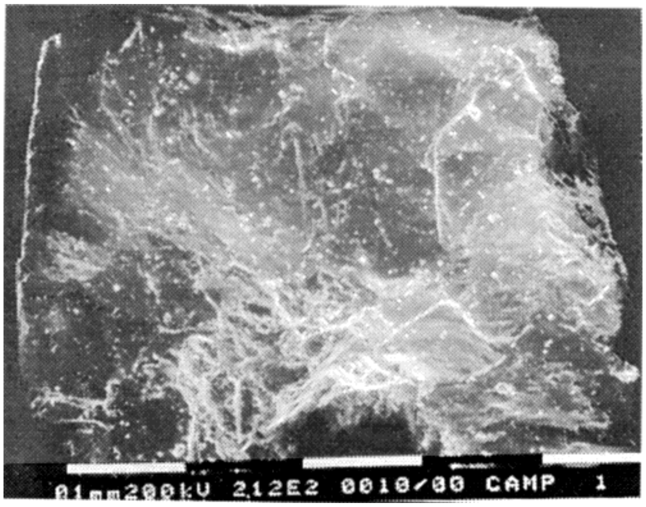


**Figure 1.** Photo by SEM of the FL sample as-is: particle of quartz covered with small particle of feldspar (marker, 100 $\mu$m).

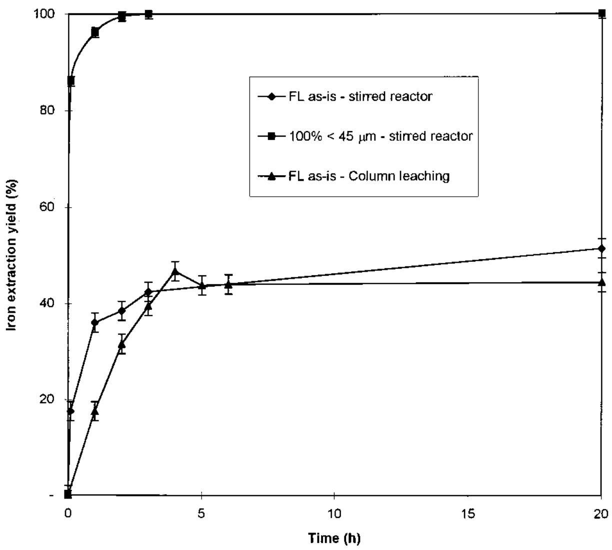


**Figure 2.** Iron extraction yield vs time of the FL as-is and ground in the preliminary leaching tests. Leaching in stirred reactor: Ore concentration 10% (w/v); temperature, 80 °C; oxalic acid concentration, 3 g/L; 400 rpm. Column leaching tests: solid/liquid ratio, 0.77 kg/L; temperature 70 °C; oxalic acid concentration, 6 g/L; specific flowrate, 0.90 kg/m$^2$ s.

The results of these experiments show the capacity of the packed-bed reactor to be used as an iron-extraction system, but the iron-extraction yield does not agree with the required target conditions (Fe < 10 ppm). This limit could be caused by the hindered contact of the oxalic acid with the iron present in the crystal lattices of the ore. For this reason, a grinding process has been considered to verify if the target values imposed in this work for the FL sample can be obtained in these conditions.

*3.2.2. Preliminary Leaching Tests in Stirred Reactor.* Preliminary leaching tests in stirred reactor were run on small quantities of the FL as-is material to assess the main conditions required for this process and to determine the relevant degree of reproducibility. The main experimental conditions involved were (tests carried out twice): Mineral concentrations, 10 wt % (50 g + 500 mL of leaching solution); temperature, 80 °C; oxalic acid (OA), 3 g/L; pH, value corresponding to the OA concentration, 1.8; mixing, 300 rpm; leaching time, from 15 min to 20 h.

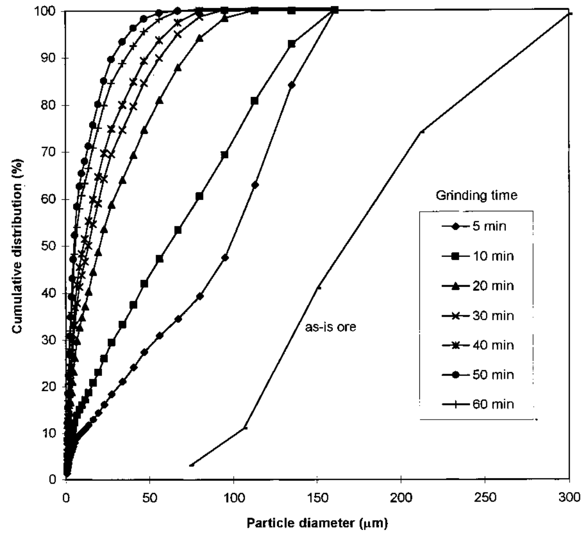


**Figure 3.** Cumulative size distribution of the FL ground ore obtained at different grinding times.

The same experimental conditions were also held constant in the preliminary leaching tests with the ground FL material, namely 100% < 45 $\mu$m. The results of these tests indicate the following: (1) The iron extraction rate in the first few minutes is very high; as indicated in Figure 2, yields larger than 40% are obtained in just 5 min leaching by using FL as-is; with ground FL the yields exceed 80% for the same leaching time.

(2) Yields of 45–50% are obtained after 20 h under the above conditions and approximately 40% after 3 h by using FL as-is. In any case, despite the excess of oxalic acid used in the iron complexing–reducing process with the FL as-is, yields of better than 50% cannot be achieved. In this case the iron content of the material after careful washing should be about 30–35 g/t, which does not meet the target level required for optical fiber manufacture (<10 g/t as Fe). Higher extraction yields are obtained with the ground FL, and Yields of about 100% are achieved after 3 h treatment (see Figure 2).

(3) Reproducibility is good, considering the quantity of material used in relation to the volume of leaching solution.

*3.2.3. Effect of Grinding on the Leaching.* Tests on various particle sizes were necessary to establish the maximum degree of liberation of iron from the silica matrix and to choose the reactor types that could be used for the pilot plant design: fixed-bed or percolation reactor or mechanically stirred reactor. Hence, because the preliminary tests showed that the leaching process rate is high under the tested conditions, the extraction limit is about 45–50% on the FL as-is, and the grinding process has a markedly positive effect on extraction, the influence of mineral particle size on the iron-extraction process has been assessed in wider and more controlled experimental conditions. Various FL fractions were produced for this purpose under diverse operating conditions by varying the grinding time (5, 10, 20, 30, 40, 50, and 60 min). The leaching conditions were selected as reported above.

The particle-size classes were analyzed by means of a laser granulometer to determine the size distribution of each class. Figure 3 illustrates the cumulative particle-size distributions of the FL classes thus obtained, compared with the FL as-is material. Figure 4

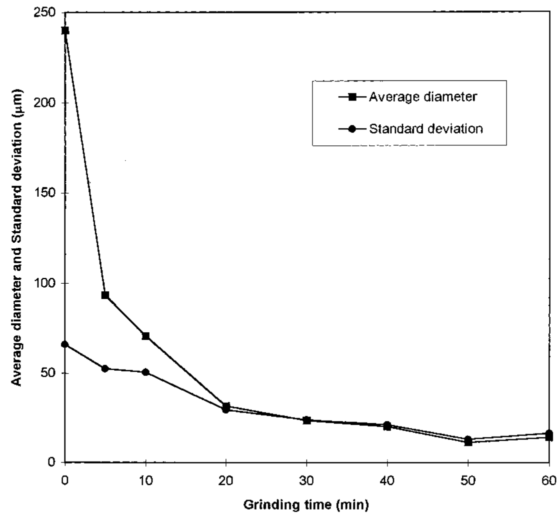


**Figure 4.** Average ore particle diameters and related standard deviations of the size distributions shown in Figure 3 for different grinding times.

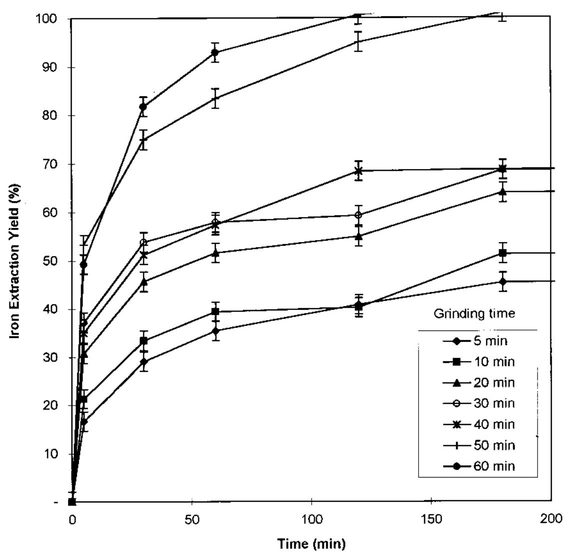


**Figure 5.** Iron extraction yield vs time in the leaching tests: effect of the grinding time. Ore concentration 10% (w/v); temperature 80 °C; oxalic acid concentration 3 g/L; 400 rpm.

indicates the average diameter and the standard deviation of the relevant distributions, as a function of grinding time. The results of the leaching tests on these particle-size classes are shown in Figures 5 and 6. (In terms of IEY and AlEY, respectively). The following points emerge from examination of the experimental results.

1. As expected, as the grinding time increases, the mineral-particle diameter decreases. Grinding also results in the monomodal distribution of the FL as-is becoming bimodal (Figure 3). The average diameter and the standard deviation of the distributions tend to decrease with grinding time (Figure 4).

2. In the FL fractions subjected to the longest grinding time there is an increase in the final process yield from 42 to 43% to about 100% (Figure 5). Furthermore, the maximum iron extraction yields, obtained with the various particle-size fractions, always occur after at least 2−3 h treatment. The initial iron extraction rate does not seem to be markedly influenced by the grinding process (Figure 5). Similar results have been obtained considering the AlEY (Figure 6).

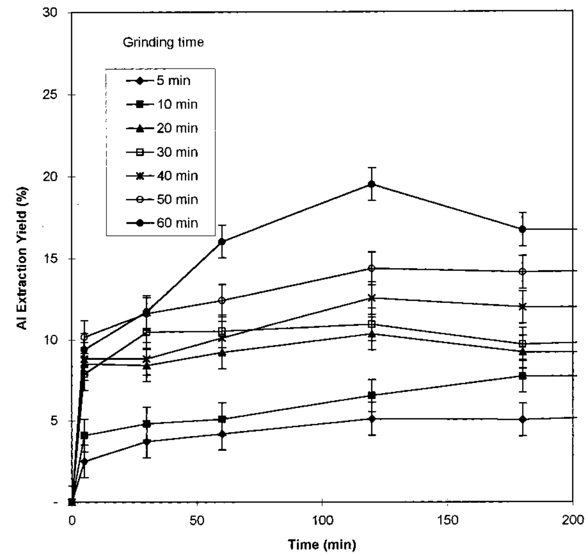


**Figure 6.** Aluminum extraction yield vs time in the leaching tests: effect of the grinding time. Ore concentration, 10% (w/v); temperature, 80 °C; oxalic acid concentration, 3 g/L; 400 rpm.

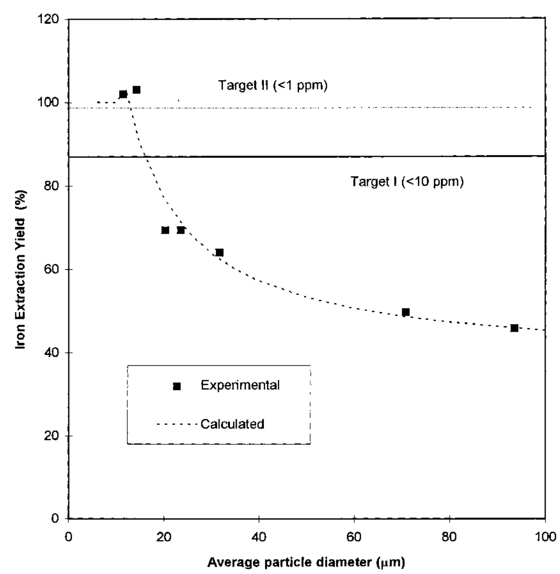


**Figure 7.** Iron extraction yield after 3 h of leaching vs average ore particle diameter: dotted line represents the empirical model (1).

Figures 7 and 8 illustrate the maximum IEY and AlEY trends, respectively, for each particle-size fraction as a function of the ore particle average diameter. In both cases, the experimental results have been fitted by means of an optimization program, with the following empirical models:[15]

$$\mathrm{IEY} = A + \frac{B}{d_\mathrm{p}} \tag{1}$$

$$\mathrm{AlEY} = C + \frac{D}{d_\mathrm{p}} \tag{2}$$

where IEY and AlEY are the iron and aluminum extraction yields, respectively, after 3 h treatment, and $d_\mathrm{p}$ is the average particle diameter. $A$, $B$ and $C$, $D$ are the model parameters obtained by fitting the experimental data shown in Figures 7 and 8, respectively, with eqs 1 and 2.

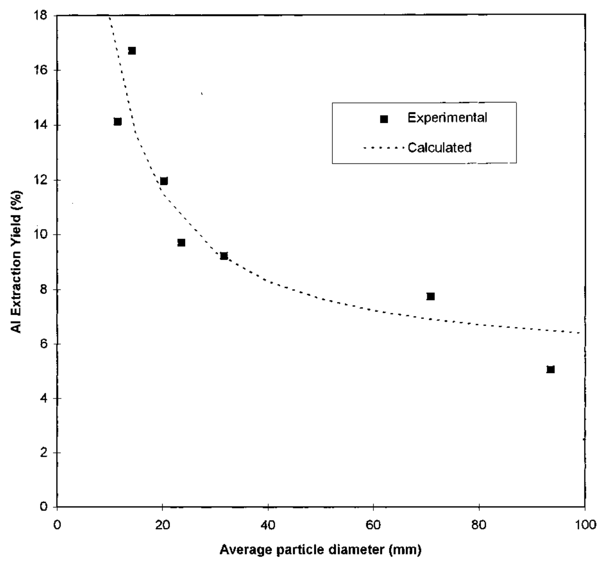


**Figure 8.** Aluminum extraction yield after 3 h of leaching vs average ore particle diameter: dotted line represents the empirical model (2).

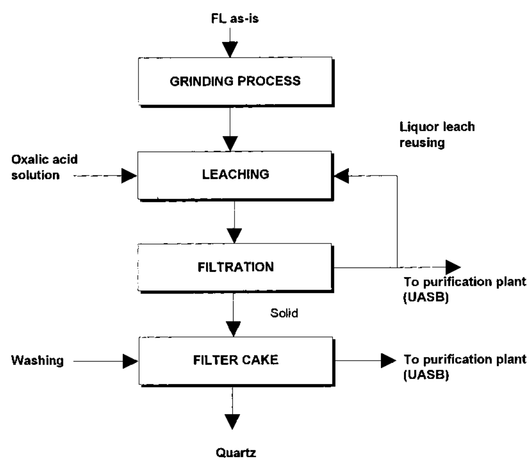


**Figure 9.** Schematic flowsheet of the iron removal process.

The parameters of models 1 and 2 obtained by regression analysis are: $A = 38 \pm 4$; $B = 790 \pm 90$; $C = 3.4 \pm 0.9$; $D = 85 \pm 17$.

According to the results given in Figure 7, to attain the an average FL particle size of about 20 $\mu$m is necessary iron-extraction target values, although average diameters and standard deviations of distributions alone do not appear sufficient to describe and characterize unequivocally a particle-size distribution.

The maximum AlEY obtained after 3−4 h of treatment ranges from 10 to 11%. From this analysis it is possible to observe that in these experimental conditions no large AlEY can be obtained, although its dissolution is related to the IEY (data not shown).

Considering the results obtained in this work and elsewhere by Dudeney et al.[14] regarding the waste treatment aspects of this process (biodegradation of oxalic acid and precipitation of iron by upflow anaerobic sludge blanket, UASB), a schematic flowsheet of the process has been proposed (Figure 9). The main steps of the iron removal process are grinding, leaching, and filtration. After the filtration and the washing of the filter cake (by using water), necessary to remove the liquor leach entrapped in the filter cake, the liquor leach and the wash water can be treated in the wastewater treatment plant as reported by Dudeney et al.[14] Potentially, a part of the liquor leach could be recycled to the leaching section because the oxalic acid used in the leaching tests is in great excess. For these reasons, further tests on the filtration, washing, and possible reuse of the liquor leach are in progress to obtain a complete material balance of the process and to design the main equipment of the pilot plant.

## 4. Conclusions

The FL quartziferous sand has been characterized from the chemical and physical aspects. The parameters determined in each case were particle-size distribution, chemical and mineral forms present, and iron content. The iron content of the FL floated sample is about 77 g/t (as Fe).

Leaching tests with oxalic acid were also run to assess the extraction rate and maximum yields obtainable both with the FL as-is fraction and with this material ground under various experimental conditions. The results indicate good reproducibility of the experimental conditions (considering the low iron content of the FL). In the case of no grinding, the maximum yields attainable are 40−45% after about 3 h treatment with 3 g/L oxalic acid, $T = 80$ °C and an S/L ratio of 0.1 (10 wt %). Yields greater than 85−98% are needed to attain the target values for fiber optic application. Hence, the study has been tailored to assess the effect of grinding on liberation of the iron and on the possibility of its removal by the leaching agent. The experimental results permit an initial rough indication that a particle-size distribution with an average diameter of about 20 $\mu$m would be needed to obtain the target values. This ore size excludes the possibility of using column leaching for this process. With this size distribution the yields obtained in such cases varied from 80 to 100% after 3 h treatment under the conditions indicated earlier. A schematic flowsheet of the process has been proposed considering the experimental results obtained and the results obtained in the literature for the waste treatment aspects.[7,14] The experimental tests were able to find the main process conditions for the pilot plant design, which is the main goal of the project under study.

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