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Dissolution of iron from quartz sands by basin bioleaching under static *in-situ* conditions

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Ultra-fine iron particles and clay minerals which coat quartz grains or are impregnated in silicate matrix are difficult to treat by conventional mineral processing methods. Treatment by basin water bioleaching in combination with electromagnetic separation can substantially improve the quality of quartz sands. The purpose of this *in-situ* study was to evaluate the feasibility of using a biological basin treatment process to improve the quality of quartz sands. The environmental conditions involved the changes of climate temperature, using fresh surface water without disinfection, inhibition of algae and fungi, and promoting bacteria. Analyses of the solution phase were used to monitor the dissolution of iron during the bioleaching of the quartz sands and to optimize the *in-situ* conditions for the bacterial activity. The rate of iron dissolution varied with environmental conditions, with the addition of chelators and organic feedstock in the form of glucose. Bacterial removal of clay and iron minerals can be used to expose the white surfaces of quartz grains. The quartz sands from the Šaštín deposit (Slovakia) can be used in glass industry after decreasing the Fe content.

1. Introduction

The content of iron oxides in glass of various grades is strictly regulated. Thus the permissible Fe_2O_3 content in household glass is no more than 0.05%, in clear glass 0.012–0.02%, crystal glass 0.025–0.035%, light engineering and medical glass not more than 0.07%. The content of Fe_2O_3 in sheet glass is permitted within the limits of 0.09–0.20% [12].

Batch materials for glass production with a required content of iron-bearing impurities are produced using various concentration methods, including dry and wet separation. Depending on the content of Fe minerals, it is possible to vary the degree of sand concentration using a special adjustable gate, which separates pure (concentrated) material from magnetic impurities (tails) [4]. The effectiveness of magnetic separation decreases and the relative amount of waste increases when the sand contains iron impurities coating grain surfaces.

Bioleaching is a technology applicable to metal extraction from low-grade ores and ore beneficiation. The technology is environmentally sound it may lower operational cost and energy requirement. Heterotrophic bacteria have the potential for producing acidic metabolites that can solubilize oxide, silicate, carbonate and hydroxide minerals by reduction, acid attack, and complexation mechanisms [7]. The application of the bioleaching to the improvement of quality of non-metallic materials has yet to lead to commercial-scale processes. Research in this area could be of great commercial interest to ceramic and glass industries.

Several experiments have now confirmed that *Bacillus* spp. enhance the bioleaching of quartz sands by dissolution of clays and Fe minerals from quartz surface. Sugars and molasses can be used as the bulk carbon source to enhance biomass growth and production of organic acids as leaching agents [16].

Shelobolina [14] stimulated iron-reducing bacteria by addition of the chelator, nitriloacetic acid (NTA) which was used to increase the bioavailability of Fe in clay and to intensify natural processes.

The purpose of the present study was to investigate the feasibility of using *Bacillus* spp. in the *in-situ* improvement of quartz sands. A part of pilot experiment was designed to determine the effect of bioleaching natural conditions on the extent of Fe removal from quartz sands. The effect of media composition with chelators (Na_2EDTA, EDTA p.a., Na_4EDTA, NTA) on the extent of bacterial dissolution of iron impurities from quartz sands was studied under laboratory condition.

2. Materials and methods

2.1. Material

The quartz sands from the locality Šaštín (Slovakia) of Aeolian origin were formed in the catchment area of the Morava River (Vienna Basin) during the Würm glacial stage of the Quaternary Period [8].

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The mineralogical composition of natural quartz sands of size distribution from 0.063 mm to 2 mm were determined for:

- natural (untreated) sands (denoted as Q)
- washing treated sands (denoted as QW)
- sands after bioleaching pretreatment (denoted as QB)

Partial elemental composition of Q and QW is listed in Table 1. The characterization of fresh surface water sample is included in Table 2.

2.2. XRD analysis

X-ray diffraction method was the basic method used for qualitative and quantitative determination of clay and non-clay minerals present in the quartz sands. Qualitative XRD analyses of oriented and random specimens were carried out using a Phillips PW 1710 diffractometer (35 kV, 20 mA) with CuKα radiation and a graphite monochromator. The quantitative XRD analysis was performed by Rock Jock computer program [3].

2.3. Laboratory bioleaching

The laboratory bioleaching experiments were carried out in conical flasks containing 50 g powdered samples Q and 100 ml liquid medium. Fe (III) reduction in samples Q was tested in media with and without 2 mM NTA and 2 mM EDTA p.a., 2 mM Na_2EDTA, 2 mM Na_4EDTA. Appropriate abiotic controls with chelators and biotic control without chelators were included in the experiments.

2.4. In-situ bioleaching experiments

13 tons of QW was treated in fixed-basin container (volume 16.3 m^3) filled with a leaching solution consisting of 7000 l fresh surface water W (Table 2) supplemented with (per liter) 0.5 g NaH_2PO_4, 1.0 g $(NH_4)_2SO_4$ and 0.2 g NaCl. Moreover 20 g of technical-grade glucose A60 per liter media was added into the container, respectively. The medium W was inoculated with 1 m^3 of mixture of *Bacillus cereus* and *Bacillus megaterium.* The isolates were identified with the BBL Crystal Identification System (Becton, Dickinson & Co., Franklin Lakes, NJ). Prior to the experimental use, these bacterial strains were grown in 4 l of Nutrient broth No.2 (Imuna, Šarišské Michaľany) at 28 °C for 18 h. A concentration of 10^7 cells per ml was added to 1 m^3 of liquid medium W for growth and subsequently used for inoculation of the container. Nutrient broth No. 2 (pH 7) contained 5 g/l of each meat extract, 5 g/l of peptone and 2.5 g/l of NaCl.

The *in-situ* stimulation of ferric iron dissolution by the two *Bacillus* isolates was tested in quartz sand suspension in the presence of 2 mM Na_2EDTA. The container was incubated under static ambient conditions for 3 months. The liquid phase was replaced four times with 7000 l of fresh medium. The spent media (leachates) were sampled for iron analysis.

Microbial counts of the total heterotrophic bacteria (THB) were carried out using the agar medium composed of 5 g/l of peptone, 2.5 g/l of yeast extract, 1 g/l of glucose and 14 g/l of agar. The redox potential and pH was measured with platinum and silver chloride electrodes (GPRT 1400 A, Greisinger, Germany).

Table 1
Chemical composition of untreated samples of quartz sands.

Element (%)	Q	QW
SiO_2	94.3	94.6
Al_2O_3	2.93	2.91
Fe_2O_3	0.295	0.258
TiO_2	0.04	0.03
CaO	0.16	0.12
MgO	0.07	0.06
Na_2O	0.41	0.40
K_2O	1.22	1.27
MnO	<0.01	<0.01

Table 2
Characterization of the fresh surface water sample.

Elements (mg/l)	pH	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
W	6.6	<0.75	<0.29	20.39	10.03	9.58	1.93

2.5. Chemical leaching in laboratory

Chemical leaching of the washed quartz sand (QW) sample in laboratory conditions was carried out to serve as a comparison with the effectiveness of the *in-situ* bacterial leaching. Chemical leaching involved 0.5 M HCl [14] and citrate bicarbonate dithionite methods [11] for extraction of poorly crystalline and crystalline iron oxide phases present in the quartz sands.

2.6. Chemical analysis

For the qualitative and quantitative determination of clay and non-clay minerals quantitative changes in the solid phase were measured with a Model 30 Varian atomic absorption spectrometer. Dissolved Fe^{2+} and Fe^{3+} were measured spectrophotometrically using the *o*-phenanthroline method [6,15].

2.7. Magnetic separation

Dry electromagnetic separation (MB) was carried out using a laboratory high gradient magnetic separator with the induction of magnetic field at 1.3 T.

3. Results

3.1. Constituents of the quartz grains

The XRD analysis revealed no significant changes in the mineral composition between natural (untreated) quartz sands, washing treated and bacterially treated quartz sands. These results indicate that washing process as well as the bacterial leaching, do not affect the mineralogy of the quartz sands. It followed from the qualitative and quantitative determination that the quartz sands consist predominantly of quartz (86%), small amount of feldspars (7%), plagioclase (3%), mica (2%), kaolinite (1%) and chlorite (<1%).

These naturally brown quartz sands contain iron and clay minerals, which coat or are impregnated on quartz grain surfaces and are difficult to remove. These iron minerals have less distinct separation characteristics in terms of conductivity and magnetic susceptibility, combined with the increased surface clay coating problems. Magnetic susceptibility of the magnetic product was $271 \cdot 10^{-6}$ A/m before bioleaching and $853 \cdot 10^{-6}$ A/m after the bioleaching. The non-magnetic fraction of quartz sands contained 2.21% of Fe_2O_3 without the pretreatment by bioleaching.

As the magnetic fraction of quartz sand contains minerals which are not listed in the Rock Jock mineral database, it was impossible to determine its quantitative composition. Only the qualitative mineral composition of the magnetic fraction was found. The relative amounts of the individual minerals present in the magnetic fraction were estimated from the intensity of diffraction peaks of these minerals in XRD patterns (Fig. 1). We expected a higher amount of amphibole, garnet and chlorite in the magnetic fraction of washing (QW) and bioleaching (QB) treated sand than in the magnetic fraction of the untreated sand (Q).