Powder Technology 224 (2012) 209–216

Contents lists available at SciVerse ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Electrical fragmentation as a novel route for the refinement of quartz raw materials for trace mineral impurities

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ARTICLE INFO

Article history:
Received 4 October 2011
Received in revised form 31 January 2012
Accepted 25 February 2012
Available online 3 March 2012

Keywords:
Comminution
Crushing
Electric fragmentation
Liberation
Magnetic separation
Industrial minerals

ABSTRACT

The availability of a selective liberation method to eliminate contaminating minerals in quartz is crucial to achieve high purity silicon feedstock for solar cell Si-production. In this study we evaluate and compare the effects of electrical fragmentation to conventional mechanical crushing; particularly to remove fine-grained trace-minerals that often jeopardize otherwise promising high purity quartz commodities. The possibility to combine both comminution techniques upstream in the solar silicon value chain is also discussed. A bulk hydrothermal vein quartz sample containing trace impurities of muscovite and orthoclase is fragmented. After fragmentation the particles are sieved in two fraction sizes [0.3–0.5 mm] and [0.5–4 mm] and are magnetically separated. The morphology of the particles, the crack distribution, and the degree of mineral liberation are studied by optical microscopy, electron probe micro-analyzer (EPMA), and X-ray diffraction (XRD).

Electrical fragmentation generates particles with spherical geometries and deep cracks that selectively are pointing towards contaminant mineral inclusions, and produce a higher percentage of liberated minerals. Mechanical crushing, on the contrary, produces elongated fragments with fewer cracks that predominantly run parallel to the fragment surfaces.

Muscovite fractures both along its cleavage planes and along its grain boundaries whereas orthoclase fractures along its grain boundaries, only. Muscovite containing 5.8 wt.% Fe was easily removed by magnetic separation.

1. Introduction

The concentration of impurities strongly inhibits the performance of solar grade silicon (SoG-Si) for photovoltaic applications [1]. Industrially, silicon is extracted from quartz via carbothermic reduction in an electric arc furnace. Thermodynamic and experimental studies of the distribution of trace elements in silicon show the influence of the impurities in raw material to the final purity of silicon [2]. Metallurgical quartz 99.95% pure (less than 500 ppmw impurities) is currently used to produce solar silicon. This quartz is geologically classified as “intermediate-purity quartz” [3]. Most of the hydrothermal deposits are intermediate-purity quartz and will in the future be one of the most important raw feedstock sources to satisfy the explosive growth of the photovoltaic industry. Lumps of hydrothermal quartz conventionally crushed are currently the main feedstock in commercial production of metallurgical silicon and SoG-Si. However most of the contaminant, embedded in quartz as minute trace minerals, cannot be removed with conventional crushing techniques, and contaminates the silicon.

Evonik is scaling up the innovative Solsilc route by Fesil [4] which uses pellets of high purity metallurgical quartz to produce SoG-Si. The advantage of using quartz pellets is that it is possible to refine the quartz prior to the furnace process. However fine grained quartz need to be micronized and agglomerated to cm-sized pellets in order to be charged into the electric arc furnace.

Our study aims at investigating the potential of electric fragmentation for the refinement of hydrothermal quartz. This is the first documentation of the efficiency of electrical fragmentation upon the removal of trace minerals comprising <1% of a mono-mineralogical rock type that does not benefit from the contrasting conductive properties that characterizes a mineralogically complex rock type such as, for example, a granite. In this work we investigate a novel route for the refinement of hydrothermal quartz under the removal of trace minerals. We performed electrical and mechanical fragmentation tests on the same quartz batch. After fragmentation, the particles are sieved and magnetically separated. Fraction sizes of [0.3–0.5 mm] and [0.5–4 mm] were studied. We analyzed the degree of liberation, the fragment morphology, the crack distribution, and interpret our

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doi:10.1016/j.powtec.2012.02.055

observations. Muscovite and orthoclase are the only contaminant inclusions present in the quartz batch; a discussion of their properties is also included in this paper.

1.1. Previous work

Quartz purification involves the removal of structural impurities, fluid inclusions, and solid inclusions [5]. While structural impurities are not easily removed [6], fluid inclusions can be removed upon heating [7,8].

Solid undesired inclusions may be partially or fully embedded in the quartz grains or occur at the interface between two grains.

Before removal the inclusion must be exposed for either acid leach [9], flotation techniques, magnetic separation or various other physical techniques [10]. Crushing to various grain sizes (typically 150 μm or larger) of the quartz commodity is required before removal of foreign minerals may be accomplished. Aulich [6] suggested an acid leach route on low purity quartzite to upgrade the quartz commodity to solar grade quartz. Some studied the mechanical and electrical fragmentation on multi-mineral aggregates [11]. Other authors [12–16] studied the dynamics and effects of electrical fragmentation on different ore types where the goal was to liberate the ore-minerals from the host rock (including hydrothermal quartz [10]). But neither of these studies documented the mechanisms of electric fragmentation upon minute foreign minerals in hydrothermal quartz as we do in the present study.

2. Materials, analytical methods, and experimental procedure

2.1. Materials

The company, Nordic Mining provided the hydrothermal quartz, from the Nesodden deposit, which is located in the Hardanger fjord (Norway). The promising low trace element content, and the availability of min. 2.7 million ton provides an interesting raw feedstock for SoG-Si production with a purity of more than 99.95% [17,18]. Two lumps (around 8 kg each) were collected from the sample locality of the deposit at a place where future mining is thought to commence.

2.2. HV pulse pulsed power equipment

Electrical fragmentation was done with a Selfrag Lab utility [19]. The batch equipment handles samples from 1 to 10 kg, and consists of a HV power supply, HV pulse generator, portable process vessels and a lifting table. Samples are loaded into a portable water loaded processing vessel which subsequently is placed onto the lifting table in the loading section. Subsequently, short pulses (pulse rise time less than 500 ns) of high-voltage electrical fields are applied.

Once the predetermined voltage is reached, the energy of the pulse generator is discharged from the electrode through the solid sample to the bottom of the processing vessel. Electrical fragmentation is the result when a shock wave propagates spherically throughout the material. A sieve is inserted in the bottom of the process vessel to collect the fragmented particles.

2.3. Analytical methods

Standard polished petrographic 30 μm sections were prepared and investigated by reflected and transmitted cross-polarized light (xpl) microscopy using a Nikon Eclipse E600 microscope with LUP at maximum 50× total magnification. A 2 megapixel SPOT Insight IN320 digital camera in combination with a SPOT software by Diagnostic Instruments Inc (Sterling Heights, MI, USA) allowed the recording of images in real time.

A JEOL JXA-8500F was used to collect primarily chemical maps of the samples. This instrument is a thermal field electron probe microanalyzer (EPMA) with submicron SEM capability integrated with X-ray analysis.

Standard microanalysis reference materials Astimex 53 Minerals Mount MINM25-53 were used for the standardization and calibration of the instrument [20].

D8 Advance XRD, BRUKER-EVA qualitative, and X-ray fluorescence (XRF) BRUKER S8 Tiger 4 kW X-ray spectrometer (Bruker AXS Nordic AB, Solna, Sweden) were used to confirm mineral identification and to determine silica phases present after fragmentation.

ICP-MS analyses were carried out to identify the purity of the original and the fragmented quartz. About 20–40 mg of quartz was dissolved in 0.5 ml conc. HNO3 + 0.5 ml conc. HF and digested in autoclave at 255 °C for 1 h. Standard silica DIABASE W-2 and BCS-CRM 313/1 have been used as reference material.

2.4. Experimental procedure

The experiments were designed to perform electrical fragmentation and conventional mechanical jaw crushing followed by sieving and magnetic separation. The experimental flowchart is shown in Fig. 1.

The two 8 kg bulk samples were crushed to 5 cm lump sizes and split in three batches of 1 kg each. The first kg was mechanically crushed in a laboratory Retsch steel jaw crusher. The remaining 2 kg (Test 1 and Test 2) were fragmented by SELFRAG AG (Kerzers, Switzerland) in a laboratory electrical fragmentation chamber. Process parameters used for the electrical fragmentation are provided in Table 1. Low voltage was applied. Under these conditions, the shock wave strength is low and the streamlets selectively direct the fragmentation towards the inclusions.

Subsequently, two size ranges were sampled for detailed studies: [0.3–0.5 mm] and [0.5–4 mm]. The 4 mm upper boundary represents the largest grains produced during fragmentation. The fraction [0.5–4 mm] was chosen with the aim of studying fracture distribution associated with partially liberated contaminant trace minerals. Trace minerals are <0.3 mm hence the [0.3–0.5 mm] fraction was chosen for the study of successfully liberated foreign minerals.

The sieved fractions were analyzed by quantitative petrographic microscopy. Approximately 1500 mineral fragments were studied in each size fraction. The structure of the fragments, in terms of size, shape, texture, structure, fracture distribution, and the degree of liberation/separation were studied by point counting. The degree of liberation is defined as the fraction of minerals still locked in the quartz fragments, while the degree of separation as the fraction of free minerals separated by sieving and magnetic separation. It was not the purpose of this work to study the fines generated with the two techniques. Polished thin sections of mineral fragments were also studied by SEM and optical microscopy. Fragmented particles in the [0.3–0.5 mm] range were additionally studied by XRD for qualitative identification of the phases.

3. Results

3.1. Quartz before fragmentation

Fig. 2 is a representative micrograph of the un-processed quartz. Both intra- and trans-granular cracks are present. Trails of intergranular fluid inclusions often intersect several grains. The shape of the grain is seriate interlobate. It is not possible to define an average grain size, rather the grain size distribution is bi-modal the most coarse-grained population falling around 4 mm in diameter and the other population clustering around 1 mm. The quartz rock experienced deformation and recrystallization. Bulging (BLG) recrystallization, subgrain rotation (SGR) recrystallization and grain boundary migration (GBM) recrystallization are common features.

Two types of foreign trace-mineral inclusions are identified. These are orthoclase KAl_3SiO_8, and Fe-rich muscovite, $(Fe,Mg)KAlSi_4O_{10}(OH)_2$,