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Effects of grinding on the preg-robbing potential of quartz in an acidic chloride medium

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ABSTRACT

The effect of high-energy milling on the surface properties of quartz is examined with regard to its preg-robbing behavior towards gold. A standard ring mill is used to process dry quartz samples, and the changes in the morphology of the particles, structural deformations and surface chemistry are investigated to explain the increased preg-robbing ability of quartz in acidic chloride solutions. The transition from fine grinding to mechanochemical activation of quartz can be observed from changes in the morphology of the particles, as well as the types of structural deformations. The transition occurs between 1 and 5 min of grinding in the mill used, corresponding to particle sizes around 0.55 μm. Structural studies differentiate two stages of fine grinding: particle breakage with limited structural disruption, and structural disturbance by mechanochemical alteration, which occurs after particles reach their grinding limits. Quartz keeps its structural order to some degree even after 30 min of aggressive grinding. The surface chemistry of ground quartz demonstrates generation of point defects including low valence silicon and non-bridging oxygen centers. These defect sites play an important role in the surface reactivity of the quartz, and influence the extent of gold loss during preg-robbing.

1. Introduction

Grinding is an essential procedure used in almost every mineral processing operation to reduce particle size, and to liberate or expose the valuable minerals (Fuerstenau and Han, 2003). The size reduction of solids is an energy intensive and inherently inefficient process; less than 1% of energy consumed in comminution is used for actual size reduction (Rhodes, 2008). In addition to size reduction, the grinding process also alters the physicochemical characteristics of the particles (Kuo et al., 2008). In fine particles (less than 10 μm), these effects greatly exceed those caused by particle size reduction (Juhász, 1998). Mechanochemistry is the science dealing with these mechanically induced inter-conversions of mechanical and chemical energy in material bodies (Baláž, 2008; Simionescu and Oprea, 1988). Almost all critical particle properties which influence down-stream operations, including density, shape, color, bulk and surface chemistry, magnetism, conductivity, porosity, mineral liberation and association (Erdemoğlu and Baláž, 2011; Fuerstenau and Han, 2003) can also be changed via mechanochemical processes.

There are a number of reports in the literature describing utilization of the effects of mechanochemical activation in metallurgical processing of minerals (Baláž, 1996; Boldyrev and Tkáčová, 2000; Takacs and Šepelák, 2004). The consensus in the literature is that fine grinding generally favors the leaching process by exposing and activating the surface of valuable minerals, consequently increasing the leaching rate as well as recovery. However, a dramatic change in the structure and surface properties of all minerals during comminution is not always desirable (Beyer and Clausen-Schaumann, 2005; Fubini et al., 1987). One of the unwelcome effects of mechanochemical activation is enhanced preg-robbing of gold by silicates (Mohammadnejad et al., 2011, 2013). Mechanochemical alteration during fine grinding can activate other mineral surfaces, leading them to interact with dissolved gold complexes and to adsorb these back onto the solids, resulting in loss of gold from solution (Miller et al., 2005).

In nature, gold ores almost always contain large amounts of silicates, mainly quartz, and these are commonly regarded as chemically very inert mineral species (Iler, 1979). However, they can exhibit surprising reactivity in the freshly ground state (Baláž, 2000; Gaudin, 1955; Mohammadnejad et al., 2013). Therefore, the physicochemical effects of grinding of quartz as well as other common silicates with regard to gold processing can be significant.

Mechanochemical activation of silicates has been extensively studied for the last few decades (Baláž, 2008; Hlavay et al., 1977, 1978; Juhász, 1974; Kleiv and Thornhill, 2006; Lin and Somasundaran, 1972; Lomovsky and Golubkova, 2000; Palaniandy et al., 2007; Tertykh et al., 2008). Grinding leads to structural distortions in silicates through disordering of the crystal lattice

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(Lomovsky and Golubkova, 2000). The nature of structural alteration under mechanical action has been shown to be different for various types of silicates (Juhász, 1998).

Nagelschmidt et al. (1952) showed that both the density and crystallinity of quartz powder are reduced during grinding, and Lier et al. (1960) revealed that this takes place through the formation of a partially disordered surface layer, 300–1000 Å in thickness. Hochstrasser and Antonini (1972) investigated the role of dangling bonds produced during grinding of silica, and found that the dangling bond is usually localized in an Si–O vacancy of the quartz lattice, with a trapped electron associated with the nearest silicon atom. Petrovich (1981a,b) also reported that the number of paramagnetic centers in quartz related to broken Si–O bonds is increased by grinding. However, upon exposure to humid air or any other water-bearing medium, the surface of silicate is hydroxylated, and the hydroxyl ions complete most of the tetrahedra that had lost an oxygen atom (or the connection with a further silicon atom) during fine grinding (Gallei, 1973; Petrovich, 1981a,b).

This study compares the preg-robbing ability of quartz as a model framework silicate, through the investigation of freshly ground and aged surfaces. To gain further insight into the nature of mechanical activation and surface modification by fine grinding, the as-received and ground samples are characterized using nitrogen sorption with Brunauer–Emmett–Teller (BET) surface area calculation, dynamic light scattering (DLS), Fourier transform infrared (FTIR) spectrometry, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) with depth profiling. The results are compared with previous studies, and the implications regarding the role of the mechanically activated components are discussed in a mineral processing context.

2. Materials and methods

Quartz, initially in the size range 0.1–2.5 μm, was provided by Unimin Australia. The sample was dried at 50 °C overnight before grinding for adsorption tests and spectroscopic analysis. The sample was dry ground in a Labtechnics LM1 Standard series ring mill for surface activation; the ring mill was selected as it has been reported to be an efficient high energy milling technique (Pardo et al., 2009). Before grinding of any samples, the 400 cm^3 Labtechnics steel bowl including ring and puck was loaded with coarse quartz sand (0.3–2.5 mm in size) to remove any oxide scale or other contamination from the surface, and then washed with water and fully dried. Batches of 20 g of quartz were ground, for durations of 30 s, 1, 5, 15 and 30 min. During grinding, the temperature of the rings and bowl of the mill rose significantly.

Preg-robbing experiments were carried out at room temperature and pressure, using an acidic chloride solution with 50 g/L of as-received or ground quartz, and 10 ppm gold solution (supplied as 1000 ppm $HAuCl_4$ solution, Sigma–Aldrich Australia, and diluted with RO-grade purified water) immediately after grinding. The sorption testing was performed in glass beakers with 500 mL of chloroauric acid per test, under dynamic conditions using a magnetic stirrer. The initial pH of the solution with 10 ppm chloroauric acid was 2.2–2.5, and no adjustments were made after adding the silicates. Samples of 10 mL were taken every 30 min for the first 2 h, then every hour until 5 h, and finally at the end of the run. The Eh and pH of the solution were measured with every sample collection. The specimens were then centrifuged, filtered with 0.2 μm polycarbonate membrane filters, and finally diluted (5×) with distilled water for inductively coupled plasma optical emission spectroscopy (ICP-OES; Varian Instruments) analysis.

To investigate the nature of surface alteration by grinding, samples were characterized using a Malvern HTTP dynamic light scattering (DLS) instrument equipped with a He–Ne laser operating at a wavelength of 633 nm as well as N_2 sorption and the BET method using an ASAP2010 instrument (Micromeritics, USA) after degassing at 110 °C for 6 h. FTIR spectrometry (Bruker T27 instrument, using the KBr pellet technique) and XRD (Bruker D8 Advance) were used to characterize the crystallinity and surface chemistry. The original and milled quartz was also studied using sputter depth profiling XPS. Destructive depth profiling by Ar^+ sputtering was conducted on the original quartz sample, as well as freshly ground samples after 30 s, 5 and 30 min of grinding. The samples were ground, and analyzed within 24 h. Samples were mounted in a 1 mm powder sample holder and scanned using a Thermo K-alpha X-ray Photoelectron Spectrometer equipped with a micro-focused monochoromated source of Al Kα radiation (1486.6 eV) and a PHI-5500 spherical capacitor analyzer. The spectra were recorded under a vacuum of 10^{-9} Torr. After the collection of a spectrum from each as-milled surface, the samples were bombarded with a 3 keV ion beam with a current of 54 nA and 400 μm spot size, across an area of 2×2 mm^2. Argon ion sputtering was applied for 10 s per step in 14 steps (140 s in total), with an XPS measurement taken for each step. The thickness of the material removed in each step is estimated to be around 3.5–4 nm, based on the known performance of this specific sputtering system. All spectra collected were calibrated using the carbon 1s peak at a binding energy of 284.6 eV to correct for sample charging.

3. Results and discussion

3.1. Morphology of the ground quartz

Fig. 1 shows the DLS and BET results for the original quartz as well as ground products, where grinding time is shown on a logarithmic scale. The average size of the particles decreases at first, while surface area increases, but after approaching a certain particle size, it then remains almost constant while surface area decreases slightly. The average particle size from DLS measurements is based on the assumption that particles are approximately spherical and in a narrow size distribution. Beyond 5 min of grinding, which corresponds to a particle size of approximately 0.55 μm, particle breakage becomes much slower and fairly limited in extent. As an absolute value, this limit depends on both grinding mechanism and material characteristics (Stamboliadis et al., 2009).

The existence of a grinding limit is known to be inherent within the process of fine grinding (Boldyrev et al., 1996; Kotake et al., 2011; Smékal, 1942). Particles larger than this size experience brittle breakage, while smaller particles only undergo plastic deformation (Boldyrev et al., 1996). The mechanical impacts in a grinding mill are obviously limited by the energy intensity of the mill, which is determined by the grinding mechanism and the operating conditions (Boldyrev et al., 1996), and this determines the particle size which can be reached under a given set of conditions. Different

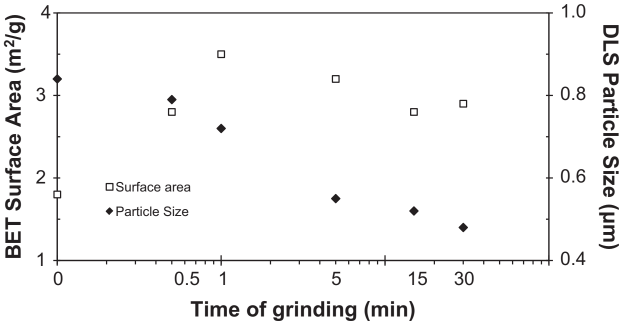

Fig. 1. Average particle sizes of silicates after fine grinding in a ring mill.

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