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# The effect of surface area on the modelling of quartz dissolution under conditions relevant to the Bayer process

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ABSTRACT

The dissolution kinetics of natural quartz powders in strong caustic-carbonate solutions and synthetic Bayer liquor was investigated using a gas-fired digestion apparatus at 250 °C for up to 20 min. In caustic-carbonate solutions, a large number of etch pits formed with reaction time and contributed to the dramatic increase in B.E.T specific surface area. The surface roughness (ratio of B.E.T. area to geometric surface area) increased from ~280 to over 2000. In synthetic liquor, fewer etch pits formed because of the coating effect of sodalite formed on the surface. The dissolution rate in both caustic-carbonate solutions and liquor is proportional to the geometric surface area and not the B.E.T. area. The geometric area normalised rate in liquor is about one-fourth the rate in the caustic-carbonate solutions due to the coating of sodalite. The dissolution process in both cases, including the dissolution of fine quartz (<3 μm) in liquor, is better described by a shrinking sphere model than the phenomenological model used previously in the literature.

## 1. Introduction

The Bayer process is the principal method for producing alumina from bauxite. In this process, alumina-rich minerals in bauxite are digested into hot caustic solution. Insoluble components are separated from the liquor and gibbsite ($Al(OH)_3$) is precipitated and then calcined to alumina ($Al_2O_3$).

For ores containing boehmite and diaspore, digestion temperatures are often over 250 °C (Hudson, 1987). Under such harsh conditions, quartz, if present in the ore, reacts with aluminate in the liquor to form a sodalite "desilication product" (commonly known as DSP):

$$6SiO_2 + 6NaAl(OH)_4 + Na_2X \rightarrow Na_6[Al_6Si_6O_{24}]Na_2X \cdot 6H_2O + 6H_2O \quad (1)$$

where *X* represents inorganic impurity ions in the liquor, including carbonate, sulphate and chloride. DSP also forms from silicate clays like kaolin and the reactive silica of a bauxite is the total silica content of all minerals that react under given processing conditions. Since DSP is discarded with the residue, this loss of caustic and alumina from the liquor represents a significant and ongoing process cost.

With increasing demand for alumina and diminishing reserves of high-grade bauxite, processing of low-grade bauxite with high reactive silica becomes inevitable. The study of quartz dissolution kinetics (and consequent soda loss) during high temperature bauxite digestion is important in the evaluation of new and existing bauxites, especially for the accurate prediction of soda losses for proposed digestion conditions.

Numerous geologically based studies of quartz dissolution have been conducted because of its significance to mineralisation and weathering (Dove, 1994; Dove and Nix, 1997; Dove, 1999; Blake and Walter, 1999; Broekmans, 2004; Bickmore et al., 2006) and a mechanistic study in more concentrated basic solutions by Deleuze et al. (1995).

The kinetics of quartz dissolution directly relevant to the Bayer process was studied by Oku and Yamada (1971), who investigated the dissolution rate of quartz in Australian and Southeast Asian boehmitic bauxites at temperatures from 180 to 240 °C for liquors with a range of caustic and alumina concentrations. They found that the dissolution was a chemically controlled process. They developed a first-order equation which has been widely used in the alumina industry for estimation of quartz attack. However, in the authors' experience, it is now regularly used in the industry to predict quartz dissolutions under conditions outside of those used to formulate it.

Recently, Xu et al. (2008) investigated the applicability of Oku–Yamada equation in a wider temperature range and with different quartz particle size distributions. They found that although the equation can be extended to temperatures ~260–270 °C, it overestimates the dissolution rate with larger quartz particles and significantly underestimates the rate with fine particles. The authors believed this is due to an intrinsic shortcoming of the equation, which bases the dissolution rate on the amount of quartz present rather than on its surface area.

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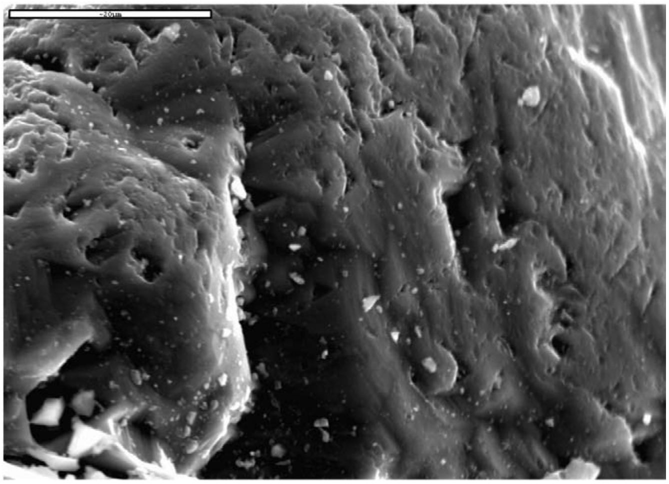

**Fig. 1.** Typical morphology of a starting quartz particle (size fraction: 231 μm) as examined by SEM.

Other authors investigated the influence of surface areas on quartz dissolution, but in deionised water (Gautier et al., 2001; Tester et al., 1994). Their results showed that the dissolution rate was better estimated using the geometric surface area (defined later in this paper) rather than the B.E.T. surface area. They observed the change of morphology of quartz particles and found that the increase of B.E.T. specific surface area was attributable to the large number of small etch pits developed during dissolution. Although these pits contributed substantially to the total surface area, they did not cause a proportionately enhanced dissolution. The explanation given was that the material originally in the pits was thought to be disordered and therefore more susceptible to initial attack than other more crystalline surfaces. Once this material was removed and more crystalline surfaces exposed, the extra area generated by this removal was less reactive to further leaching.

In this paper, we report a study of the effect of surface area on natural quartz dissolution in strong caustic solutions and synthetic Bayer liquor under extreme conditions typical of the Bayer process. The particle size distributions that have been chosen are representative of liberated quartz particles from bauxite (which range from 10s to several hundred microns) and to a fine fraction that may occur naturally or through the action of bauxite milling prior to digestion.

## 2. Experimental

Natural quartz used for this work was supplied by Cook Industrial Minerals of Western Australia. It was wet screened to different size fractions. Most experiments used a mean sieve size 231 μm quartz (standard quartz, D(0.5) = 220 μm as measured by Malvern), but a sub-sample of this fraction was ring milled and then decanted to produce a fine fraction (<3 μm, D(0.5) = 1.86 μm) which was used in some tests.

Specific surface areas of the quartz were measured by nitrogen adsorption via the B.E.T. method (TriStar Surface area and porosity analyser, Micromeritics). The size distributions of the quartz were determined using a Malvern Mastersizer (model 2000) with sodium hexametaphosphate as dispersant. All the fractions showed a normal distribution.

The true density of the quartz (2.696 ± 0.044 g/cm$^3$) was measured by Helium pycnometry (ASTM D4892-89).

The morphology of the quartz before (and after) dissolution was examined using a scanning electron microscope (SEM) (JEOL, JSM-5800LV). Apart from some small pits and cracks, a reasonably smooth surface was observed for all starting particles. A typical microphotograph of the quartz is shown in Fig. 1.

The purity of the quartz within each fraction was analysed by XRF (Art Philips PW2404) and was higher than 99.5%. XRD (Phillips X'PERT) examination found that quartz was the only phase detected.

Two types of solutions relevant to the Bayer process were used for this study: caustic-carbonate solutions and synthetic Bayer liquor. Caustic-carbonate solutions were prepared from AR grade chemicals. Synthetic Bayer liquor (hereafter called Bayer liquor) was prepared from a commercial caustic aluminate concentrate (Coogee Chemicals, WA). The concentrate was adjusted to the appropriate aluminium, caustic and silica concentrations using gibbsite (C31, Alcoa Chemicals), AR grade silicic acid, sodium hydroxide and carbonate. All supplemental materials were directly added to, and dissolved in, the reactor according to pre-determined amounts.

The quartz was charged at 30 g/L and dissolved in an Inconel bomb (250 mL in volume) using a gas-fired reactor system. The sealed bomb was rotated at ~70 rpm on its axis over a gas flame. The reactor was equipped with a water shower cooling compartment, and a Eurotherm temperature controlling unit linked to a computer. This system allows rapid heat-up (max linear heating rate ~40 °C/min) and cool-down (cooling rate ~70 °C/min). The system does not allow sampling in the course of a digestion and thus each kinetic data point for the dissolution was obtained through a separate test.

Two dissolution temperatures (250 °C and 175 °C) were investigated. These temperatures were chosen because they are representative (respectively) of high temperature bauxite (boehmitic) processing and a low temperature bauxite (gibbsitic) process used by a particular refinery where quartz attack may be significant.

As the reactor is not isothermal, the amount of quartz dissolved during heating to the thermostatic temperatures (either 250 °C or 175 °C) was pre-determined and subtracted from the total mass dissolved. Reported dissolutions are thus only those measured during the holding period (up to 20 min, typical in the industry) at the stated temperature.

All exit slurries were pressure filtered using a 0.45 μm membrane filter. The residue cakes were washed three times using aliquots of deionised water to ~pH 10.6. It has been determined (unpublished work) that at this pH value caustic entrained in the residue is negligible and sodalite will not dissolve. The washed residues were dried at 110 °C overnight and weighed. Starting and exit liquors were analysed for alumina, caustic and carbonate content by a standard gluconate titration (Connop, 1996).

The amount of quartz dissolved in caustic-carbonate solutions was determined gravimetrically from the residue. However, this was not possible in synthetic liquor because part of the dissolved quartz forms a sodalite precipitate leading to a mixed phase residue. To determine the amount of quartz dissolved in this case, the residues were first analysed by XRF to obtain the total silica in the residues. An accurately weighed ~0.2 g of dry residue was reacted in 0.05 M sulphuric acid (1 L) at room temperature for 1 h. The filtrate from this leaching was analysed for dissolved silica by ICP-OES (Varian Vista Pro Simultaneous). Total un-reacted quartz was found by the difference of the total silica and the sodalite silica in the residue. The results obtained in this way were found to be more accurate (±2.3% in error) than by

**Table 1**
Properties of starting quartz powders.

| Quartz size (μm) | BET area (m$^2$/g) | Calculated $A_{geo}$ using D(0.5) and Eq. (2) (m$^2$/g) | Calculated $A_{geo}$ using D(3,2) and Eq. (2) (m$^2$/g) | Roughness |
|---|---|---|---|---|
| <3 | 6.175 | 1.22 | 1.50 | 4.13 |
| 90 | 0.510 | 0.0198 | 0.0203 | 25.1 |
| 116 | 0.243 | 0.0164 | 0.0170 | 14.3 |
| 231 | 0.050 | 0.0101 | 0.0106 | 4.71 |
| 318 | 0.033 | 0.0081 | 0.0084 | 3.94 |