A Flow-Through Reaction Cell for Studying Minerals Leaching by In-Situ Synchrotron Powder X-ray Diffraction

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Abstract: A flow-through reaction cell has been developed for studying minerals leaching by in-situ time-resolved powder X-ray diffraction, allowing for a better understanding of the leaching mechanisms and kinetics. The cell has the capability of independent control of temperature (up to 95 °C) and flow rate (>0.5 mL min⁻¹) for atmospheric pressure leaching. It was successfully tested at the powder diffraction beamline at the Australian Synchrotron. Galena powder was leached in a citrate solution under flow-through condition at a flow rate of 0.5 mL min⁻¹, while diffraction patterns were collected during the entire leaching process, showing rapid galena dissolution without the formation of secondary mineral phases. The flow-through cell can be used to study leaching processes of other ore minerals.

Keywords: flow-through cell; in-situ PXRD; galena leaching

1. Introduction

A clear understanding of the mechanism and kinetics of mineral leaching is important for further optimization of leaching parameters [1–4]. Leaching is commonly studied by ex-situ techniques, which involve the recovery of leached products by cooling and filtration and subsequent characterization [3–7]. Ex-situ techniques provide valuable information, but the results may not reflect the true mechanism of leaching because samples may have changed during recovery. On the other hand, in-situ techniques characterize reaction products under leaching conditions [8–11], avoiding the problems experienced by ex-situ techniques. Hence, in-situ techniques are important complementary tools to ex-situ techniques for a complete understanding of the leaching reactions.

There are a number of in-situ techniques, capable of studying the solution phase by X-ray absorption spectroscopy [12] and Raman spectroscopy [13], and solid phase by transmission electron microscopy [14], atomic force microscopy [15], neutron diffraction [16–18], and powder X-ray diffraction (PXRD) [19–22]. In-situ PXRD in the presence of an aqueous solution can reveal the phase evolution of the crystalline materials and has been applied extensively in materials chemistry for elucidating crystallization mechanisms of hydrothermal materials syntheses [23–28]. This technique has also been applied in studying mineral leaching, but mostly under static conditions using glass capillary tubes [8–11].

For in-situ PXRD studies of mineral leaching, flow-through reaction cells are particularly useful for achieving a wider range of solid/solution ratios to mimic various types of leaching conditions. For this
purpose, a number of flow-through cells have been reported [8,29–31]. Some of them were specifically designed for electrochemical reactions at room temperatures [32,33], and have been demonstrated in studying electrochemical reaction in ion-selective electrodes [29,34], and electrochemical oxidation of copper [32]. Some cells were designed to flow the solution through a flat substrate [8,35], and have been used for studying scale formation on a steel substrate mimicking Bayer processing condition at 70 °C [8], and the evolution of PbO2/PbSO4 surface layers during copper electrowinning on a Pb anode substrate at 45 °C [35]. For higher temperatures, a reflux flow-through cell using polytetrafluoroethylene (PTFE) membrane as the sample holder was developed and demonstrated by crystallization of titanium phosphate at up to 175 °C [30]; however, the cell was not designed to control flow rate or to hold pressure, so the solid materials may react with vapor instead of aqueous solution above the boiling point of the solvent. Compared with reflection mode flow-through cells, transmission mode cells can avoid signals from the substrate. For this, a flow-through cell using a glass capillary tube has been developed [31], and has been used to study Cu isotope fractionation during bornite dissolution [36], Cs exchange into hexagonal H-birnessite [37], chalcopyrite dissolution [10], and oxidative dissolution of chalcocite and covellite [31], but all at room temperatures.

Many minerals leaching processes are conducted at non-ambient temperatures and controllable flow rates. To meet these conditions, we have designed a flow-through cell setup and demonstrated its in-situ PXRD capability for minerals leaching at the Australian Synchrotron, Melbourne, Australia.

2. The Flow-Through Cell Setup

The design of the flow-through cell setup is shown in Figure 1 and a photograph of the set-up is shown in Figure 2. The leaching solution is pre-heated in a solution reservoir by a hot plate under stirring and pumped by a peristaltic pump through flexible tubing and flow through the mineral sample in the sample cell. The temperature of the sample cell is maintained by a hot air blower underneath the sample section. After reacting with the mineral sample and flowing out of the sample cell, the leaching solution returns to the solution reservoir, completing a closed loop. PXRD patterns are continuously collected during solution-mineral reactions in the sample cell, achieving in-situ monitoring of dissolution/crystallization processes. The specifications of the sample cell, the solution reservoir, and the pump are described in the following paragraphs.

![Figure 1. Schematic diagram of the flow-through cell experimental apparatus. Blue arrows show the flow direction.](image-url)
The design of the sample cell is shown in Figure 3. It consists of an open-end capillary tube (Figure 3b), two 316 stainless steel fittings (one T-piece and one straight piece), and an aluminum frame to hold the two fittings. The capillary tube is made of either silica glass or sapphire and is 50 mm long, 1.0–1.3 mm in internal diameter, and 0.1 mm in wall thickness. Silica glass is stable under acidic to mild alkaline conditions (e.g., pH < 9), while sapphire is inert under higher pH conditions. On each end of the tube, a PTFE ferrule is glued onto the tube using superglue. The powder sample (~3 mm long) is loaded into the middle section of the tube, and the sample position is fixed by adding a silica glass wool plug on both sides of the sample. The capillary tube is fixed to the two 316 stainless-steel fittings. The sealing on each side is by cone/cone seal between the cone surface of the ferrule and the cone surface of the ports of the fittings. Both fittings are fixed to an aluminum frame. The T-piece fitting is for solution inlet and the straight fitting is for solution outlet. The assembled sample cell can be fixed horizontally to the goniometer head spinner of the X-ray diffractometer (Figure 2 inset).

A second set of T-piece and straight piece fittings were made by Hastelloy for more corrosive leaching conditions that are not manageable by 316 stainless steel.

The solution reservoir is a 500 mL borosilicate glass bottle with four ports on the lid, one for solution delivering tubing inlet, one for solution delivering tubing outlet, one for a K-type thermocouple, and one for pressure equalization using a 0.2 µm membrane filter. The reservoir was insulated using a silver foil air bubble wrap, in which a small window (20 × 80 mm) was cut to allow flow observation during in-situ PXRD experiments. The solution in the reservoir was pre-heated under magnetic stirring using a hotplate stirrer (IKA RCT basic).
Minerals 2020, 10, x 4 of 9

polypropylene-based tubing that is appropriate for the acidic solution and has a temperature rating between $-59 \, ^\circ C$ to $135 \, ^\circ C$. Viton tubing can also be used for higher temperature applications up to $230 \, ^\circ C$.

3. In-Situ PXRD of Galena Leaching

The flow-through-cell was tested at the powder X-ray diffraction beamline at the Australian Synchrotron using an X-ray beam energy of 21 keV ($\lambda = 0.5904 \, \text{Å}$). An in-situ PXRD experiment on galena leaching was carried out under the condition summarized in Table 1. A high-purity galena specimen from Quiruvilca Mine, Santiago de Chuco Province, La Libertad, Peru, was used [6,38]. The galena was ground to less than 38 $\mu m$, controlled by a 38 $\mu m$ sieve. To reduce X-ray micro-absorption by Pb, galena was diluted by mixing with inert silica glass powder (also $< 38 \, \mu m$). The solid packing ratio is 20% (determined using a 10 mL bottle) in the mineral sample position of the capillary (Figure 3b), and the volume ratio between galena and silica powder is 1:9. This means only 2% volume of the sample position of the capillary was occupied by galena, resulting in a low total X-ray microabsorption ($m\mu R = 0.91$).
As an example, the first dataset is shown in Figure 5. Rietveld-based analysis was conducted on this standard (NIST SRM 660b). The background was modeled using a 5th order polynomial function, and the peak shape was modeled using a Pseudo-Voigt function. The broad peak centered at about 8° is similar to the reported value, 

\[ a = b = c = 5.9362 \text{ Å} \] [39]. Preferred orientation was observed as the preferred orientation effect, and improving particle statistics. During the in-situ PXRD experiment, temperature of the solution reservoir, solution level in the reservoir, and flow rate (Video S2 in Supplementary Materials) were monitored using a web camera, while temperature of the hot air blower (e.g., the sample section) was recorded in the diffraction files.

The lixiviant was prepared using Milli-Q water and reagent-grade chemicals, including H₂O₂ (30%, Rowe Scientific), citric acid anhydrous (≥99.5%, Sigma-Aldrich), and trisodium citrate dihydrate (≥98%, Sigma-Aldrich).

Before the in-situ PXRD experiment, the temperature of the hot air blower was calibrated based on the polymorphic phase transition from orthorhombic to trigonal KNO₃ at 128 °C. For the in-situ PXRD experiment, as soon as the solution was pumped through the sample at 35 °C, data acquisition started. Each PXRD pattern was collected for 2 min, using a Mythen position-sensitive detector in the 2θ range of 1–81°, under the Debye-Scherrer geometry. The sample cell was set to oscillate over 45° with a frequency of 0.07 Hz (Video S1 in Supplementary Materials), for uniform heating, minimizing the preferred orientation effect, and improving particle statistics. During the in-situ PXRD experiment, temperature of the solution reservoir, solution level in the reservoir, and flow rate (Video S2 in Supplementary Materials) were monitored using a web camera, while temperature of the hot air blower (e.g., the sample section) was recorded in the diffraction files.

Figure 4 shows the PXRD patterns during the in-situ leaching of galena. A systematic reduction in galena peak intensity with time suggests progressive dissolution of galena. Galena peaks disappeared after 14 min, suggesting rapid leaching under the studied condition. This agrees with rapid leaching of galena reported in an ex-situ study under similar conditions [38].

The data quality was good, suggesting effective minimization of microabsorption by dilution. As an example, the first dataset is shown in Figure 5. Rietveld-based analysis was conducted on this dataset using Topas Academic v6.0. The detector zero shift was determined by refining a Lab₆ standard (NIST SRM 660b). The background was modeled using a 5th order polynomial function, and the peak shape was modeled using a Pseudo-Voigt function. The broad peak centered at about 8° is from the amorphous silica tube, silica powder, and leaching solution, and was treated as background. The unit

| Parameter          | Value                                                                 |
|--------------------|----------------------------------------------------------------------|
| Mineral            | Galena (PbS)                                                        |
| Particle size      | <38 µm                                                              |
| Lixiviant          | 0.08 M citric acid + 0.92 M trisodium citrate + 0.75 M H₂O₂         |
| Solution pH        | 6                                                                   |
| Flow rate          | 0.5 mL min⁻¹                                                         |
| Temperature        | 35 °C                                                               |
| Leaching time      | 48 min                                                              |

Table 1. Summary of leaching condition.

Figure 4. In-situ PXRD patterns showing rapid galena leaching at 35 °C in a pH 6 solution.
cell parameters of galena were refined, starting from the crystal structure of galena, #9008694, obtained from the Crystallography Open Database (COD) [39]. The value $a = b = c = 5.9372$ Å is similar to the reported value, $a = b = c = 5.9362$ Å [39]. Preferred orientation was observed as the intensity of the (200) peak at $11.4^\circ$ is higher than expected (Figure 5). This is due to the perfect cleavage of galena on [100] lattice planes.

![Figure 5. Rietveld refinement of the first dataset from the in-situ PXRD experiment.](image)

4. Conclusions

In this study, a flow-through cell was designed for in-situ PXRD studies of minerals leaching. The cell was successfully tested at the Australian Synchrotron using galena leaching at $35^\circ$C by 0.75 M H$_2$O$_2$ in a pH 6 citrate buffer solution, under a flow rate of 0.5 mL min$^{-1}$. The results showed rapid galena dissolution. The test demonstrated the ability of the flow-through cell for performing leaching experiments in which the solid is kept in the sample cell as the stationary phase, and the desired amount of solution circulates through the sample. The flow-through cell can be used to study leaching of other ore minerals by in-situ PXRD.
Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/10/11/990/s1, Video S1: cell oscillation, Video S2: flow monitoring.

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