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Leaching gold by reactive flow of ammonium thiosulfate solution in high aspect ratio channels: Rate, passivation, and profile

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ABSTRACT

Dissolution of interfacial materials in spatially confined flow is an important physicochemical process. Here, we present a study of gold leaching, where the gold layer is removed from a microchannel wall within a high aspect ratio channel (8 μm × 4 mm cross-section; 1:500). The etchant is an aqueous solution of sodium thiosulfate, ammonium hydroxide, and copper sulfate. Optical transmission of the gold layer was used for quantitative, in situ, and real-time measurement of the layer thickness and its spatial uniformity along and across the channel. The onset of etching is not immediate, indicating that a passivation layer exists (even on 'bare' gold layers, where etching was delayed by approx. 2 min). Pre-treatment of the gold surface with an incomplete alkane thiol self-assembled monolayer (11-mercapto-1-undecanol) led to a later onset of etching and slower etching rate (5.5 nm/min) compared with that on 'bare' gold (6.2 nm/min). Flow profiles are reflected in the observed etch profiles. Upstream and downstream differences in etch rate are magnified for intermediate copper sulfate concentrations. This novel technique offers quantitative, in situ and real time monitoring of etching under controlled conditions in continuous laminar flow through microchannels, providing a valuable tool to understand various reactive processes in spatial confinement, such as heap or in-situ leaching in mineral processing.

1. Introduction

Lab-on-a-chip devices have been widely used to study a wide range of chemical, physical, and biological phenomena; however, their potential impact in a few non-traditional fields has yet to be realised, such as in mining and metallurgy (Becker and Locascio, 2002; Andersson and van den Berg, 2003; Priest et al., 2011). Many industrial processes are complex, involving reactions at the internal surfaces of micro/nano-scale porosity and confinements, with key examples including etching, leaching, cleaning, and corrosion protection (McNab and Consultants, 2006; Crundwell, 2013; Chomat et al., 2012; Sangeeta, 1997). Fractured materials, whether by design or failure, are inherently porous and often chemically reactive. For example, in mineral processing (whether above ground or in-situ) mined ore is deliberately fractured to create new surfaces that are reactive to leach reagents that recover valuable metals into solution for downstream refining. However, reactive micro- or nano-fluidic flow in a crack or fracture is difficult to quantitatively study. In this paper, we present a quantitative analysis of microchannel wall-etching of gold under the confinement of a high aspect ratio channel (8 μm × 4 mm). The effects of flow profile and etchant depletion are tracked in real-time, and the influence of adsorbed self-assembled (alkane thiol) monolayers is considered as a model passivation layer.

Most experimental studies to date have used quasi-two-dimensional confinement – parallel plates – to mimic a large planar crack in a material, often a mineral. The two plates may be rough or smooth (Berkowitz, 2002). Chomat et al. (2012) conducted leaching between two parallel borosilicate glass slides representing a simulated ideal crack (SIC) of different apertures (from a few to hundreds of micrometres). The SIC was immersed in NaOH solution with a vertical or horizontal orientation. The series of experiments showed direct correspondence between chemistry and transport in modelled glass cracks and proved that position in the reactor vessel has direct impact on the shape of SIC alteration profiles providing evidence of the prevailing transport mechanisms. Similarly, Fourar and Bories (1995) studied simulated horizontal 'cracks' between glass or baked clay plates with well-defined separation (ranging from 0.18 to 1 mm). The two-phase (air-water) flow was examined by varying the liquid flow rate and observing the pressure drop. A few studies have investigated more complex crack morphologies (Nazridoust et al., 2006; Singurindy and Berkowitz, 2005). Nazridoust et al. (2006) studied single-phase flows of air and water through fractures in sandstone taking into account tortuosity, and introducing a friction factor for this type of flow. Singurindy and Berkowitz (2005) experimentally investigated various types of fractures

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in carbonate rocks, which allowed the effects of fracture orientation, fracture surface roughness, and fluid flow rate to be determined.

Studies focused on mathematical modelling and numerical simulations were aimed at describing the fluid flow within the spatial variations of aperture, including microscale confinements (Brown et al., 1998). A numerical model introduced by Brown (1987) was based on simulation of flow between two parallel plates with rough surfaces, which was suitable to mimic fluid flow through rock joints. Bear et al. (2012) presented basic models of transport in fractured real rocks considering various rock matrixes. Hellström and Lundström used Computational Fluid Dynamics (CFD) for modelling of a flow through porous media to investigate the effects of *Re* number on flow (Hellström and Lundström, 2006).

Although literature related to simulated cracks can be found, the existing studies are focused on simulating flow between parallel plates with various apertures from several micrometres up to several centimetres rather than within channels or complex pore geometries (Chomat et al., 2012; Brown et al., 1998; Brown, 1995). We are unaware of publications that use a microfluidic device to investigate etching of mineral or metal surfaces in micro-scale confinement. Laminar flow etching has been used for channel formation (Kenis et al., 1999) and patterning (Abgrall and Gue, 2007; Brister and Weston, 2005), but a quantitative, in situ, and real-time study of etching from a channel wall is still lacking. Our approach permits systematic (and direct) variation of etch conditions including channel dimensions, flow rates, deposited materials, roughness of channel walls. Measurement of local etch rates is also possible where samples are spatially heterogeneous at the microscale or the downstream chemical conditions differ due to reagent depletion or reaction products.

In this paper, we use a high aspect ratio (8 μm × 4 mm; 1:500) microchannel partly coated with gold to mimic a crack in a mineral sample. A mixture of thiosulfate, ammonium hydroxide, and copper sulfate – considered a desirable alternative to cyanide for gold leaching - was introduced into a gold-coated microchannel under steady flow and the etch rate, its time-dependent thickness profile along two axes, and the effluent were analysed. The method proved to be very powerful for studying dissolution in micro-scale confinement, including complex phenomena such as the very significant effect of surface passivation on the initial rate of dissolution.

2. Experimental section

2.1. Chip design

The microfluidic chip design required the following features: a) optical transparency of the chip materials, excluding the thin gold film which is initially opaque; b) good chemical stability to thiosulfate, ammonium hydroxide, and copper sulfate solution; c) sufficient dimensional stability to maintain the desired channel geometry under pressure-driven fluid flow; d) an inlet and outlet that allows continuous flow of the etch solution; and (e) the ability to deposit a thin metal film on one (bottom) wall of the microchannel before chip bonding.

To meet all of the above design criteria, a glass-polydimethylsiloxane (glass-PDMS) hybrid microchip was used. The chip fabrication method is summarised in Fig. 1A. A flat plate of borosilicate glass (BOROFLOAT® 33, Praezisions Glass & Optik GmbH; Iserlohn, Germany) was used to seal a microchannel moulded in PDMS, with punctured inlets. The selection of BOROFLOAT® glass meets the requirements of chemical stability and optical transparency (Lin et al., 2001). PDMS is also transparent, chemically resistant to thiosulfate, ammonium hydroxide, and copper sulfate and, as is widely known, can be easily moulded to form microchannels, punctured for inlets, and bonded to glass by activation using oxygen plasma. Each microfluidic chip contained four identical channels to allow running multiple experiments simultaneously

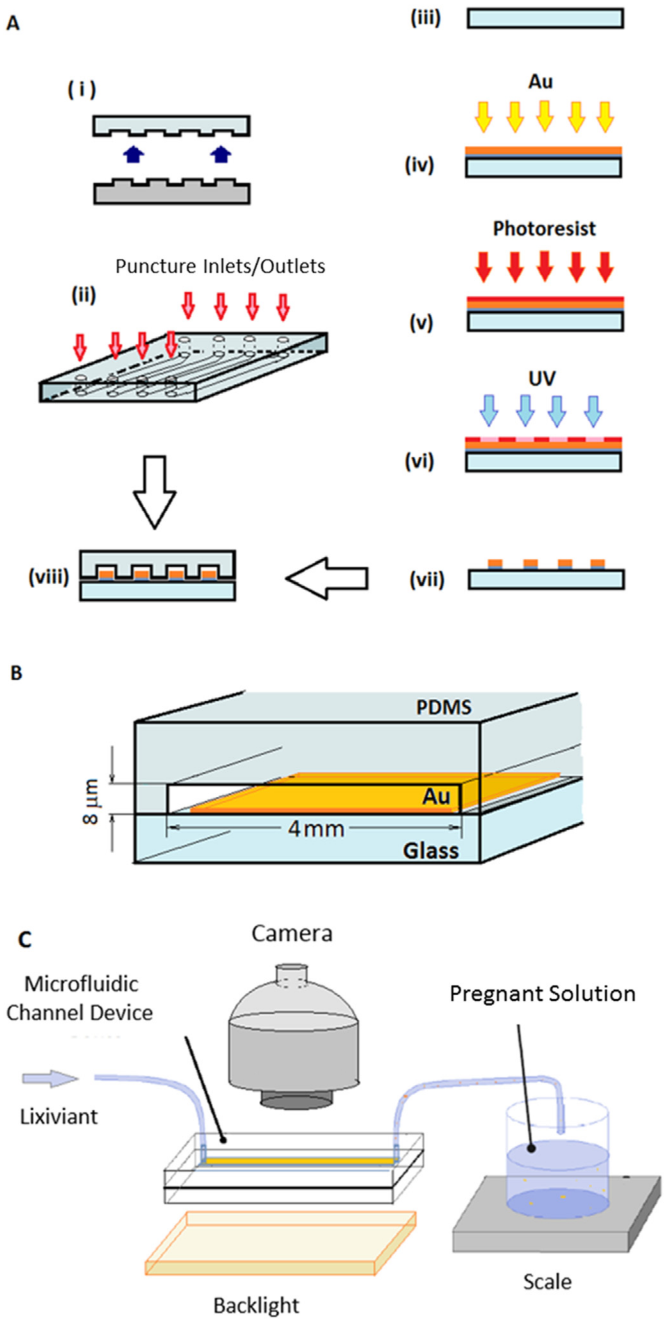

Fig. 1. Microfluidic device - processes of microfluidic device fabrication and gold layer leaching: (A) Schematic description of processing steps of microfluidic channels device fabrication, (B) schematic representation of single high aspect ratio channel of fabricated microfluidic device with deposited Au thin layer, (C) Microfluidic flow experiment set-up.

2.2. Chip fabrication

Fig. 1A shows the process flow for fabrication of the microfluidic chips used in this study. The PDMS (i–ii) and glass (iii–vii) halves of the chip were prepared in parallel, then plasma bonded (viii). The fabrication of the PDMS microchannels was carried out according to a widely reported method (Becker and Locascio, 2002): a mass ratio of 10:1 of Sylgard 184 silicone elastomer base and curing agent was mixed thoroughly and poured onto a hydrophobized hexamethyldisilazane (HMDS) master, i.e. a patterned SU8 photoresist on a silicon wafer. The PDMS was cured at 80 °C for 1 h, then peeled off from the master (i). Afterwhich, inlet and outlet fluid ports were punctured using a