SO$_2$/O$_2$ AS AN OXIDANT
IN HYDROMETALLURGY

By

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This thesis is presented
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I declare that this thesis is my own account of my research and
contains as its main content work
which has not previously been submitted for a degree
at any tertiary education institute.

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ABSTRACT

The oxidation of Fe(II), Mn(II) and As(III) by SO₂/O₂ has been studied in acid media, and various applications to hydrometallurgical processes investigated. The kinetics and mechanism of oxidation are reviewed and detailed mechanistic pathways are proposed and rationalised against observed experimental data.

The kinetics of iron catalysed SO₂/O₂ system has been studied at 80 °C as a means of generating Fe(III) and H₂SO₄ for subsequent leaching reactions. The rate of Fe(II) oxidation in the range of optimum SO₂/O₂ ratio can be expressed by equation:

\[ r = k_{\text{obs}} [\text{Fe(III)}] [\text{SO}_3^{2-}] / f_{\text{obs}}(\text{H}^+) \]

for 0-0.02 M Fe(III) where \( f_{\text{obs}}(\text{H}^+) \) is a function of pH. Both Fe(II) and SO₂ are oxidised with the ratio Fe(III)/H₂SO₄ about 2. Above 9% SO₂ in the gas mixture by volume and pH 1, dithionate was detected, and the proportion of dithionate to sulphate increased with higher SO₂/O₂ ratio. A radical chain reaction mechanism is proposed, involving the formation of a ferric sulphite complex and decomposition to produce the sulphite radical SO₃⁻. This is followed by a fast reaction with O₂ to form peroxo-monosulphate SO₅⁻, which is responsible for the autoxidation of Fe(II).

In order to examine the application of SO₂/O₂ to the leaching of copper sulphides with Fe(III) and regeneration of Fe(III), the oxidation of 0.1M and 0.5M iron(II) with O₂ and with SO₂/O₂ mixtures are compared in the presence of CuSO₄ at 80 °C. The Cu/SO₂/O₂ system oxidises Fe²⁺ at a faster rate than the Cu/O₂ system, particularly at low concentrations of Fe²⁺. With O₂, the rate is second order with respect to Fe²⁺ concentration; but with SO₂/O₂, the rate is independent of Fe²⁺. It is proposed that copper catalyses the oxidation of Fe²⁺ by O₂ through a mechanism that involves the formation of ionic CuO₂⁺ and H₂O₂ as the oxidant. In contrast, oxidation by SO₂/O₂ involves the peroxo-monosulphate radical that is inhibited by Cu²⁺. The free radical scavenger, hydroquinone, inhibits the oxidation of Fe²⁺ with SO₂/O₂, but has little effect on the oxidation with O₂. It is shown that when high concentrations of Fe²⁺ and Cu²⁺ are oxidised by SO₂/O₂, the reaction is initially dominated by the Cu/O₂ mechanism, but is overtaken by the Fe/SO₂/O₂ mechanism as Fe²⁺ is consumed. Leaching studies with pure Cu₂S and Cu₂S concentrate showed that whilst higher
levels of Fe(III) were attained using SO$_2$/O$_2$, no improvement in copper recovery was achieved at 80 °C due to slow leaching CuS or CuFeS$_2$. Addition of Cl$^-$ ion, however, benefited copper recovery and Fe(III) regeneration.

Oxidation of Mn(II) is similar to Fe(II), but the rate is dependent on pH up to pH 6. The mechanism involves Mn(III) rather than Fe(III). It has been found that selective precipitation of iron then manganese can be achieved from nickel-cobalt solutions using SO$_2$/O$_2$ at pH 3 but not at pH 5. Applications for Mn removal from typical nickel laterite leach solutions and cobalt ore leach solutions are examined.

The kinetics and mechanism of As(III) oxidation by SO$_2$/O$_2$ and by UV light/O$_2$ are also examined in conjunction with Fe(II), with the aim of precipitating insoluble ferric arsenate from leach solutions or waste water. The rate of oxidation with the Fe/SO$_2$/O$_2$ system is fast, and complete oxidation of 100 mM As(III) is achieved in about 2 hours between 25 °C and 60 °C. The following empirical rate expression was established over the range 0-100 mM As(III), 0-10 mM Fe(III), and pH 0.5-2.

$$-\frac{d[\text{As(III)}]}{dt} = k_1[\text{Fe(III)}][\text{As(III)}]^{0.5}[\text{H}^+]^{-0.2}$$

*where* $k_1 = (5.76 \pm 0.7) \times 10^{-3}$ ([mM]$^{0.5}$/min) at 25°C and $E_a = 20$ kJ/mol. With the UV/Fe/O$_2$ system, the rate of oxidation of trace As(III) (0.1 mM) was similar, but the rate was much slower with 6.5 mM As(III). Fundamentally the Fe/SO$_2$/O$_2$ system is more suitable for oxidising more concentrated As(III) solutions found in hydrometallurgical processes. The combination of both SO$_2$/O$_2$ and UV light, offers faster kinetics for the oxidation of dilute As(III) solutions than either of the individual systems in the presence of low concentrations of Fe(III).

To demonstrate the application of SO$_2$/O$_2$ to the recovery of arsenic, leaching studies are reported on a nickel smelter fume containing low levels of arsenic, followed by precipitation of ferric arsenate using SO$_2$/O$_2$. It was found that only partial leaching of arsenic could be achieved with H$_2$SO$_4$ or NaOH at various concentrations and further studies with other high arsenic fumes are recommended. A dilute H$_2$SO$_4$ leach is proposed for optimum recovery, selectivity, and reagent use.
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PUBLICATIONS

The following papers have been published from the work described in this thesis.


Paper to be submitted for publication

"Oxidative precipitation of manganese with SO$_2$/O$_2$ from nickel and cobalt", to be submitted to *Hydrometallurgy*. 
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