Book of Abstracts
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Enhancement of Solid Dissolution by Ultrasound

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Summary

The ultrasonic enhancement of the, industrially important, solid-liquid reaction between sphalerite concentrate (zinc sulphide) and dissolved ferric iron (Fe^{3+}) in sulphuric acid was investigated. The sphalerite is dissolved, simultaneously reducing the ferric iron to ferrous iron. Elemental sulphur is formed as a by-product. The rate of dissolution was determined by measuring the concentration of ferrous iron in the liquid phase by sequential injection analysis (SIA). Eleven different models for the dissolution of the solid particles, applied previously in silent conditions, were tested in the modelling. The experimental results could be explained in the best way by simple first order kinetics with respect to the solid phase. The activation energy was determined to be 52.3 kJ/mol. The induced ultrasonic power was varied between 0-210 W. Ultrasound was concluded to enhance the reaction rate in conditions where the mechanical agitation was not sufficient to overcome the mass transfer limitations. The rate enhancing effect increased with the introduced power. The rate of reaction achieved by vigorous agitation could, however, not be superseded with sonification.

Key words: Dissolution, Sphalerite concentrate, Ultrasound, Variable effect, Kinetic modelling

Extended Abstract

Acoustic cavitation is an emerging option for enhancing physical and chemical processes. The effects of ultrasound include cleaning, degassing, emulsification and enhancement of reaction rate as well as yield [1].

The ultrasonic enhancement of the reduction of dissolved ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}) with sphalerite (zinc sulphide) concentrate in a sulphuric acid solution, which is an industrially important reaction in zinc production, was investigated.

$$Fe_2(SO_4)_3(aq) + ZnS(s) \leftrightarrow 2FeSO_4(aq) + ZnSO_4(aq) + S(s)$$

The experiments were performed in a 1000 ml stirred glass reactor, which was placed in a water bath made of stainless steel. To this bath, six 30 kHz ultrasound transmitters with a variable maximum effect of 50W were coupled. An edged heating plate with silicon oil was used for temperature control. The reactor was equipped with a pitched-blade turbine, an oil lock, baffles and a reflux condenser.

The temperature of the experiments varied between 75-95°C. The initial concentration of ferric iron was 0.179 mol/l and a 1.2:2 reducing agent-to-ferric iron molar ratio was used in a 0.40 M sulphuric acid solution. The total amount of the liquid was 750 ml. The stirring rate was varied between 200 and 700 rpm. The induced ultrasonic power was varied between 0 and 210 W. Moreover, the influence of duration of ultrasound cycles and the time between the cycles was investigated. The concentration of ferric iron was determined by sequential injection analysis (SIA). The concentration of dissolved sphalerite can be calculated from the concentration of ferric iron (Figure 1).

The apparent effect of ultrasound varied depending on the conditions used, but it clearly enhanced the rate of the reaction especially when the impact of mass transfer was essential (Figure 2).

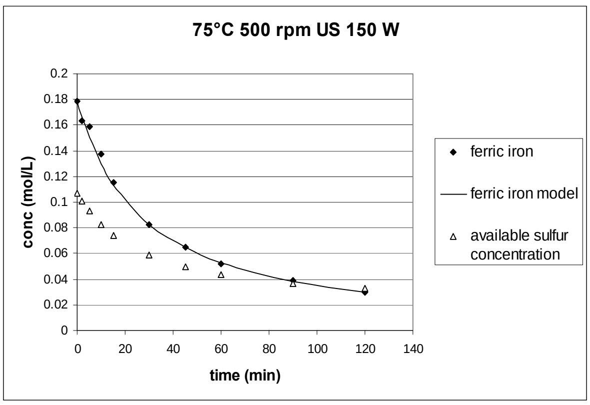

Figure 1. The measured concentration of ferric iron as a function of time (the filled symbols). The line represents the modelling result and the open symbols are the calculated values for sphalerite.

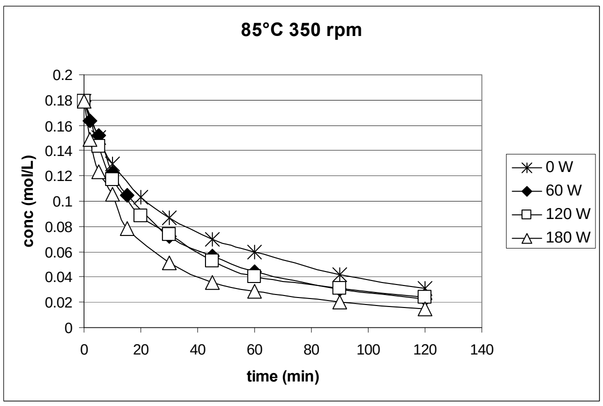

Figure 2. The concentration of ferric iron as a function of time for experiments performed with different ultrasonic power. Experiments were performed at 85°C with an agitation rate of 350 rpm.

Eleven different models were tested for silent systems [2]. These models are utilized in the present kinetic study for explaining the reductive dissolution reaction of spherical particles when ultrasound is employed. The experimental data could best be explained with a first order model for the sphalerite concentration. The effectiveness factor η is calculated based on the calculated rate coefficients as: $\eta = \frac{k_{observed}}{k_{\text{int}\, rinsic}}$.

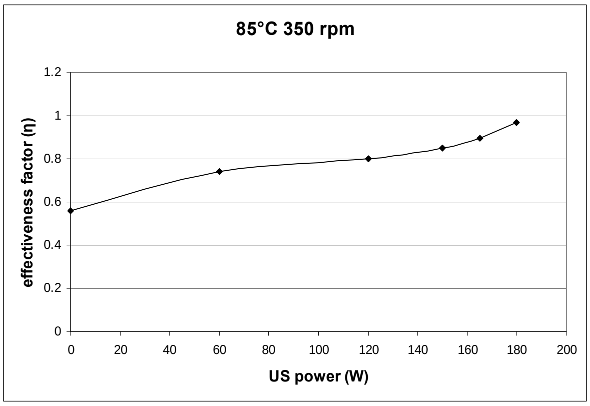

Figure 3. The effectiveness factor as a function of the induced ultrasonic power. Experiments were performed at 85°C with an agitation rate of 350 rpm.

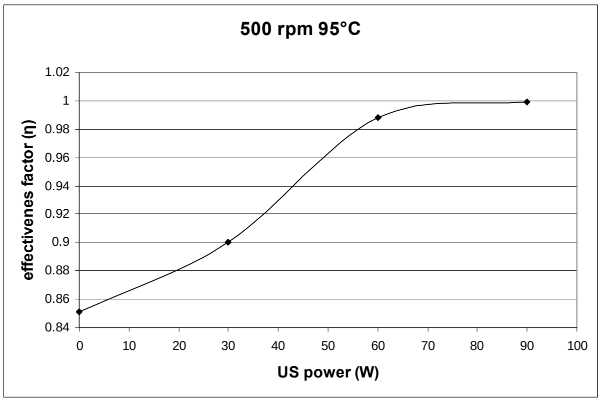

Figure 4. The effectiveness factor as a function of the induced ultrasonic power. Experiments were performed at 95°C with an agitation rate of 500 rpm.

As can be seen from Figures 3 and 4, the effectiveness factor increases with acoustic power approaching unity, i.e. conditions where external mass transfer does not limit the reaction.

The periodic cycling of ultrasound was applied in order to investigate, if it has an effect on the reaction rate. The effect of mass transfer limitation is noticeable in silent systems and the effectiveness factor increases with the percentage of time ultrasound is on, i.e. the total amount of induced power per unit time. A maximum in the effectiveness factor depending on the used periodic cycle was observed in some experiments. The reason for this interesting observation is unclear, requiring further detailed investigation.

Sonification was concluded to enhance the mass transfer of the system, but it could not increase the rate of reaction beyond the one achieved in silent systems with rigorous agitation. It can thus be concluded, that the influence of the acoustic power is purely limited to physical effects.

References

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[2] Markus H., Fugleberg S., Valtakari D., Salmi T., Murzin D. Yu., Lahtinen M, (2004) *Hydrometallurgy*, 73, 269-282.