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Low Temperature Separations in the Sulphuric Acid Decomposition Stage of the Sulphur Iodine and Hybrid Sulphur Thermochemical Water Splitting Cycles

Rachael H. Elder, Andrew Shaw, Moises Romero, Najwa Elbakhbaki, Geof H. Priestman, Ray W. K. Allen, University of Sheffield, UK

The Sulphur Iodine and Hybrid Sulphur thermochemical cycles are promising routes for large scale production of hydrogen from water [1-3]. The thermal decomposition of aqueous sulphuric acid to form SO_2 , O_2 and H_2O is common to both cycles and involves high temperatures and difficult separations. The energy requirement is large due to the excess of water present. This work investigates the separations involved with a view to improving efficiency.

1 SO_2 - O_2 - H_2O VLE

Oxygen is a by-product of the decomposition process and must be separated from the reaction products. This could be achieved via conventional low temperature processes, such as absorption. Before design of such a system can be carried out, thermodynamic data and reliable models are required for the multicomponent phase equilibrium relationships between SO_2 , O_2 and H_2O .

The binary mixture of sulphur dioxide and water has been modelled using the methodology derived by Zemaitis [5]. These initial simulations were extended, on the same mixture, using a similar methodology, but adding oxygen into the multicomponent VLE equations. The model of the mixture including Oxygen, was analysed extensively and compared with predictions from the salting out equation derived by Setschénow [4]. By observing and comparing the results with the existing literature, the mathematical simulation results were shown to lay a solid foundation for describing the PVT behaviour of both mixtures. The multicomponent equilibria calculations, rather than the salting out equation, were found to be more reliable when trying to estimate dissolved concentrations of oxygen in aqueous sulphur dioxide solutions. Although the methods used to predict solubility parameters are consistent with the literature, measurements are required to prove the actual behaviour of these species at operating conditions more relevant to the design process that is to follow. In order to verify the calculations, accurate and updated VLE data for the ternary system is required.

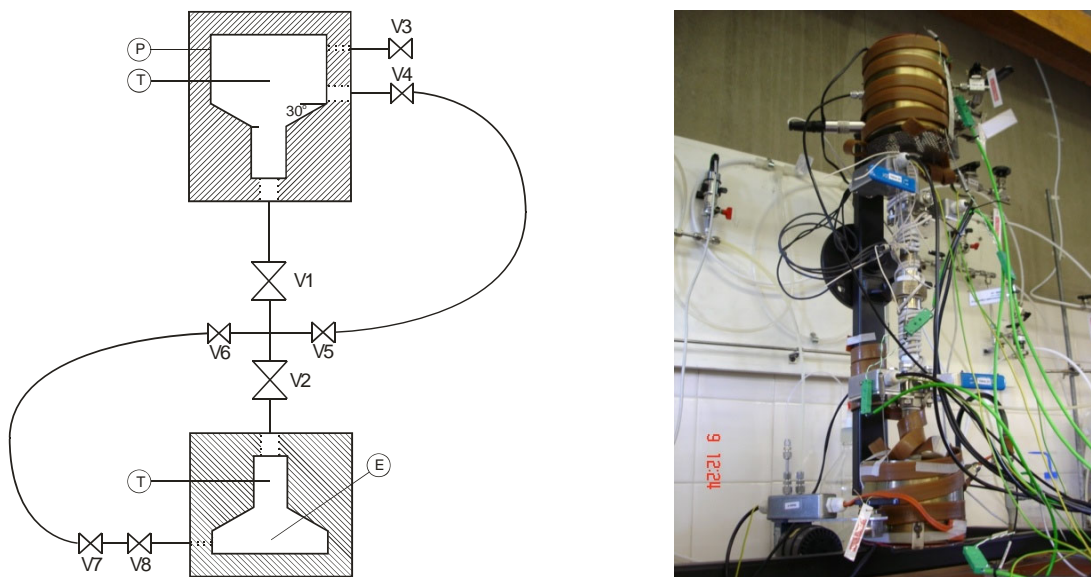


Figure 1: Schematic and Photo of the Equilibrium Still (insulation removed for clarity).

A novel experimental apparatus has been designed, constructed and commissioned as seen in Figure 1. Known amounts of each species are brought in contact in a vessel of known volume providing large interfacial areas for mass transfer and having a controllable uniform temperature distribution in the range of 20 to 120 °C. The pressure range is between atmospheric and 30 bara. The main apparatus consists of two chambers connected by a pipe through two valves, V1 and V2. Once equilibrium is established, the chambers are isolated and representative samples of the gas and liquid phases are removed for analysis without disturbing the equilibrium. The whole apparatus is PTFE lined as contact with metal ions can disrupt the equilibrium.

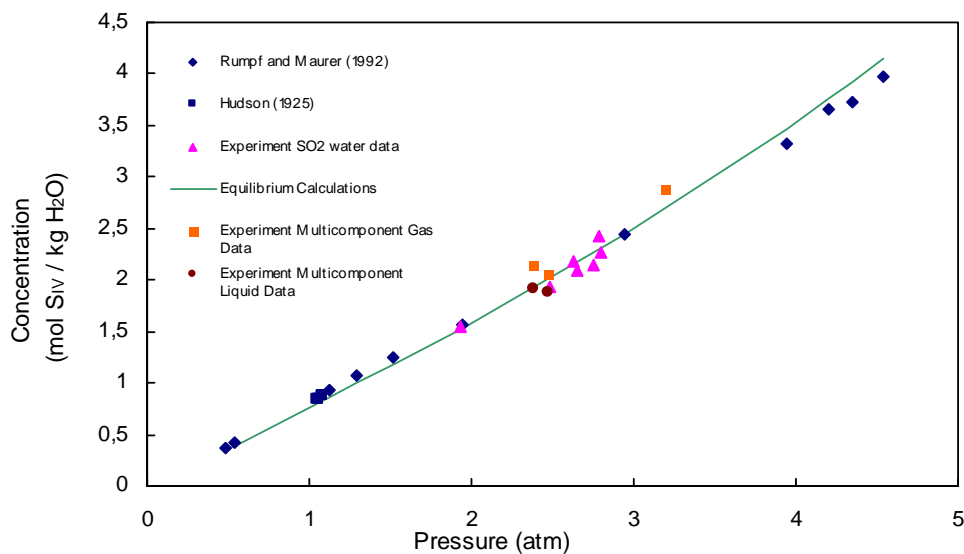


Figure 2: Comparison of experimental SO₂ solubility in water at 40 °C with calculations.

Data points have been collected for a number of binary and ternary solutions and further data collection is currently underway. These experimental results have been used to validate the calculations of the multi-component equilibria, as shown in Figure 2.

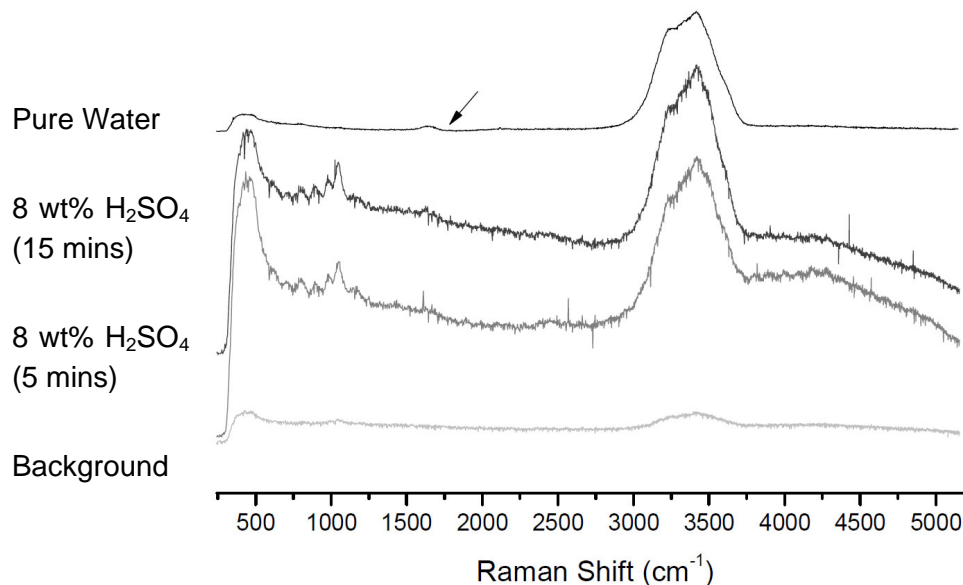


Figure 3: Raman Spectra of Aqueous Sulphur Species. The arrow shows an OH⁻ stretching, particular from water.

Improvements to the experimental rig to allow online analysis are being investigated. Raman spectroscopy has been identified as a suitable analysis technique. Figure 3 shows an exploratory Raman spectra for a sample of 8 wt% H₂SO₄ aqueous solution. The graph shows the different acquisition times for different samples, water being the darker spectrum on the top with parametric smoothing and the lightest the dark-room spectrum that was subtracted from the two samples in the middle.

2 Low Temperature Membrane Separations

The aqueous sulphuric acid stream entering the decomposition section is currently concentrated by a series of evaporators and distillation columns; however this is complex and energy intensive. Membrane separations are under investigation as a low energy alternative. Dewatering by pervaporation is investigated experimentally to find the fluxes and selectivities achievable through different membranes. Nafion membranes of varying thicknesses have been tested in the setup shown in Figure 4 and a sample of the results are shown in Figure 5. The permeate is almost pure water with only trace amounts of sulphuric acid which are below detection limits.

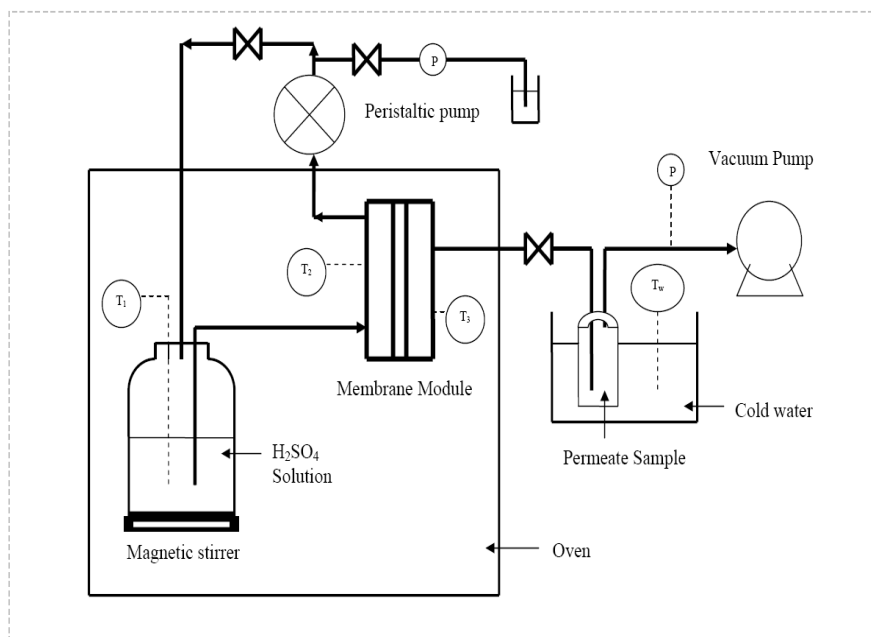


Figure 4: Experimental setup for membrane flow testing.

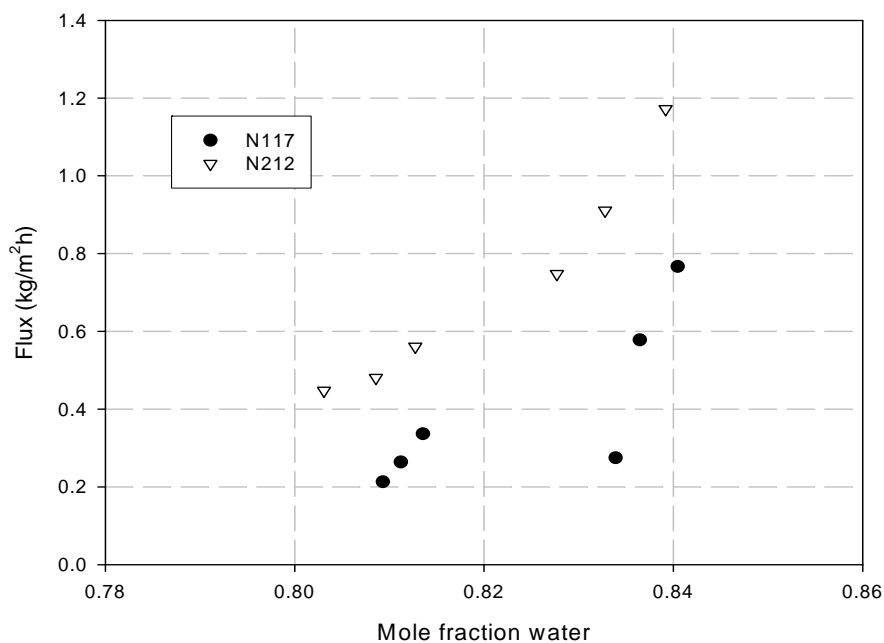


Figure 5: Flux through Nafion membranes for aqueous H₂SO₄ solutions.

An investigation into boundary layer formation has also been undertaken, using a different, semi-batch membrane testing apparatus shown in Figure 6. The aim of this series of

experiments is to find out what causes the flux decrease seen as each experiment progresses. An example results graph is shown in Figure 7.

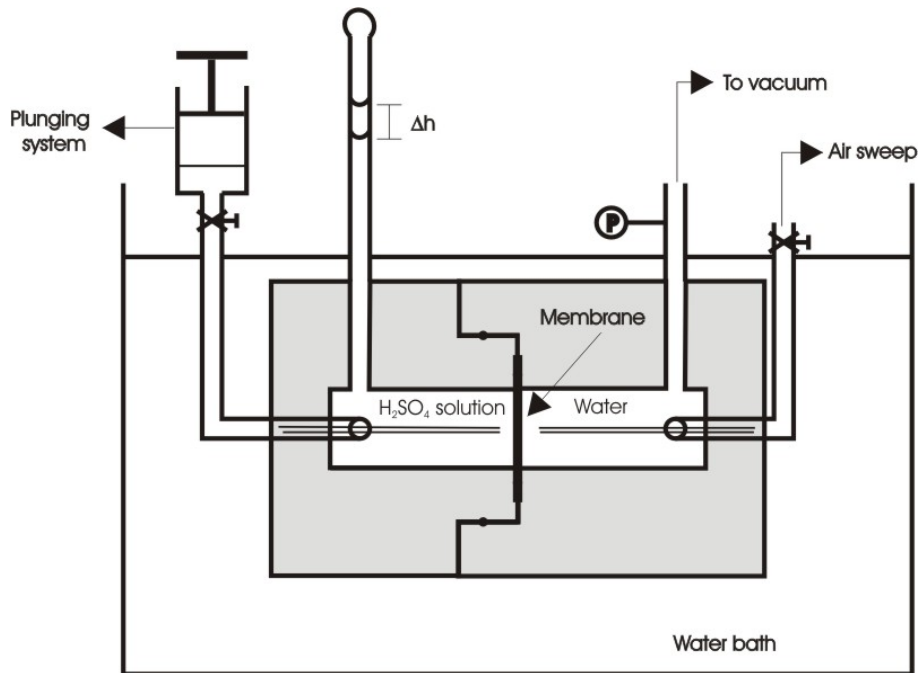


Figure 6: Experimental setup for membrane semi-batch testing.

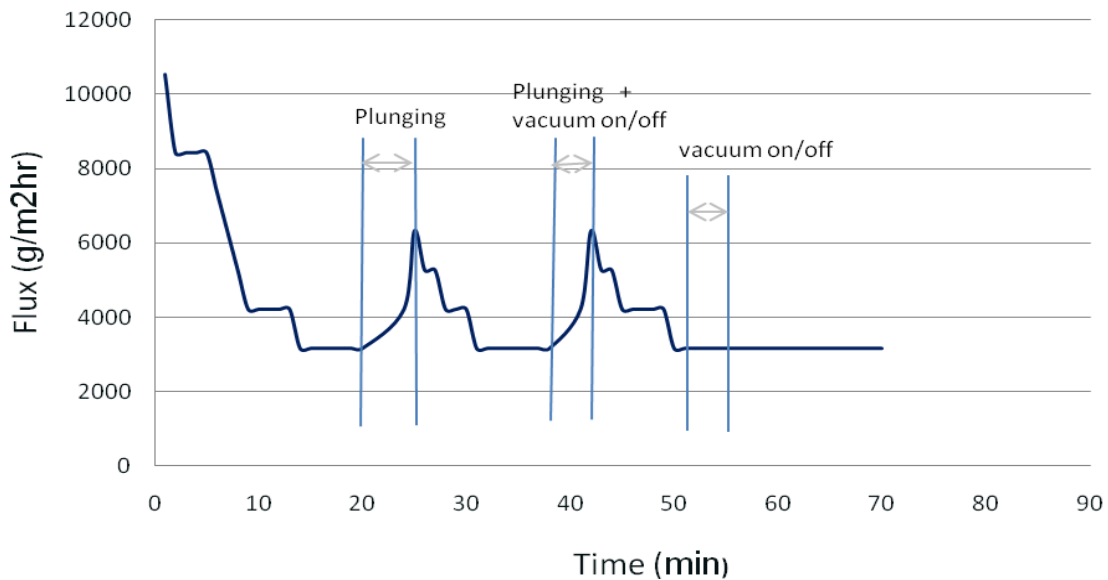


Figure 7: Example results graph for boundary layer formation investigations.

Plunging of the system, causing an abrupt change in the feed side flow rate and hence mixing, leads to an increase in flux. This suggests that a boundary layer is indeed the cause of the flux decrease. Further work will identify appropriate mixing techniques to allow the maintenance of high flux levels.

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