In-situ pH monitoring of high concentration acidified solutions at elevated temperatures

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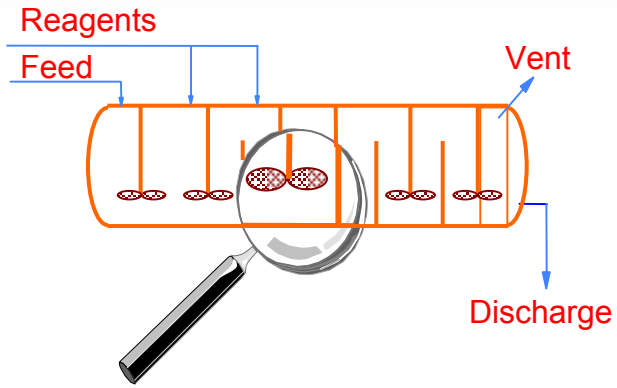

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Outline

- Experimental technique
- pH measurements
- pH calculations
- Validation and comparisons

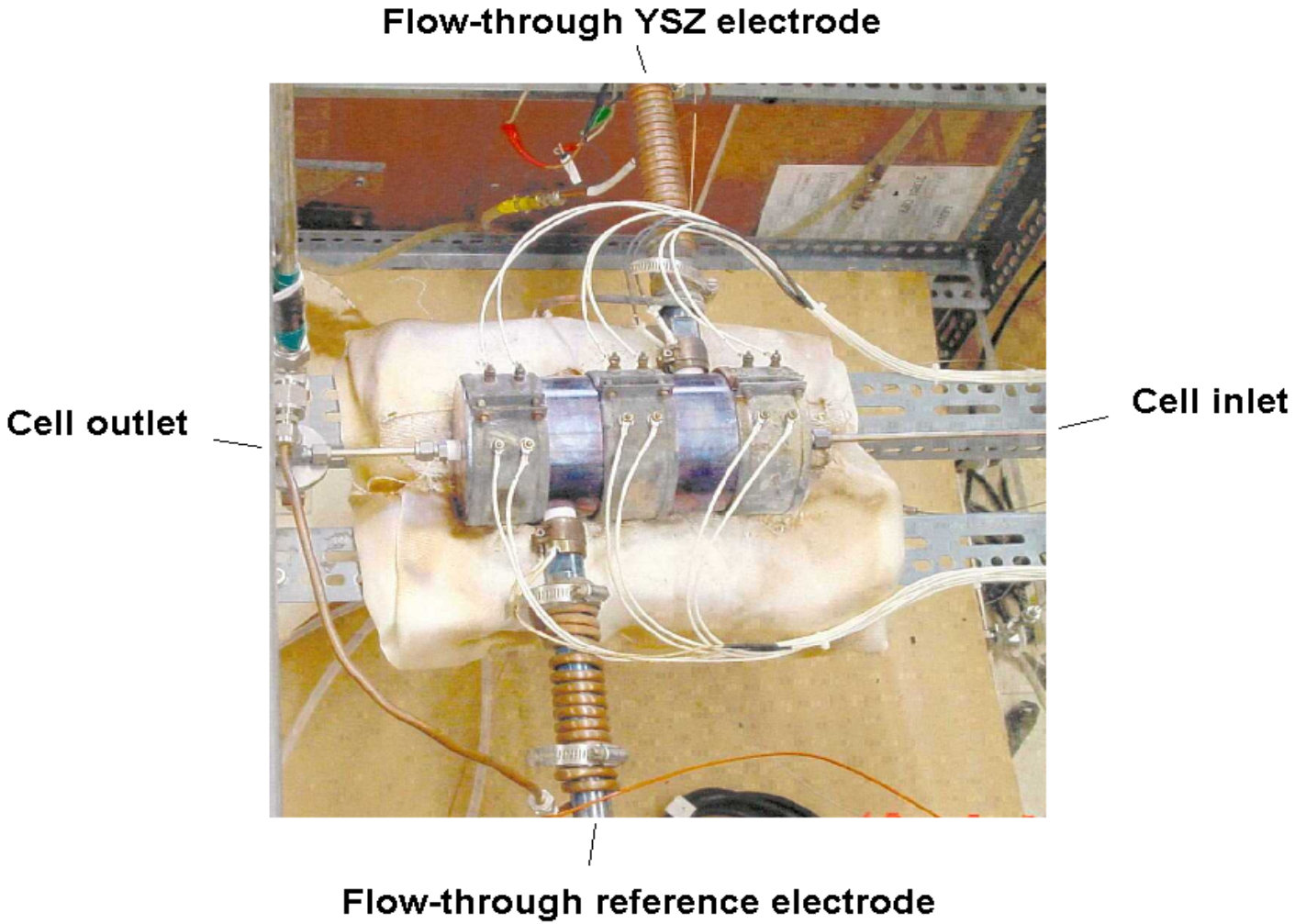
Introduction

- Measurement of pH at temperature is important for understanding the behavior of a variety of industrial and natural systems
- pH is a major variable in high temperature aqueous processes of minerals (hydrometallurgy), controlling reaction rates, metal extraction and scale deposition
- A flow-through electrochemical system (Penn State) is used for on-line monitoring of pH in high temperature process solutions

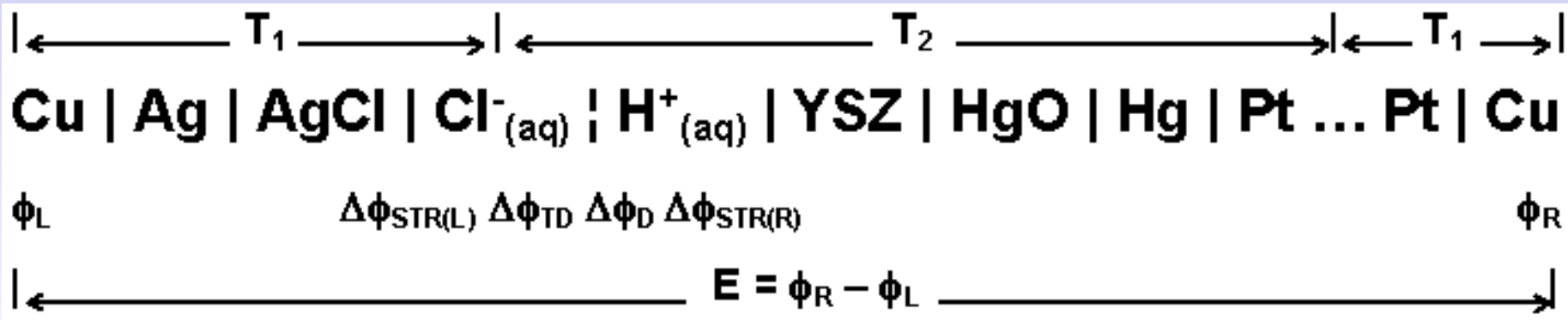
Introduction (cont'd)

- This system involves an yttria-stabilized zirconia pH sensor with a EPBRE Ag/AgCl
- Reliable high temperature pH measurements ($\pm$0.03 pH units) have been achieved only in dilute solutions ($I<0.5$ mol kg^{-1})
- This work demonstrates that pH measurements of high concentration solutions are possible with an accuracy of 0.1-0.3 pH units from 100 to 280^{o}C

Flow-through high-temperature electrochemical cell



Theory of the flow-through electrochemical cell



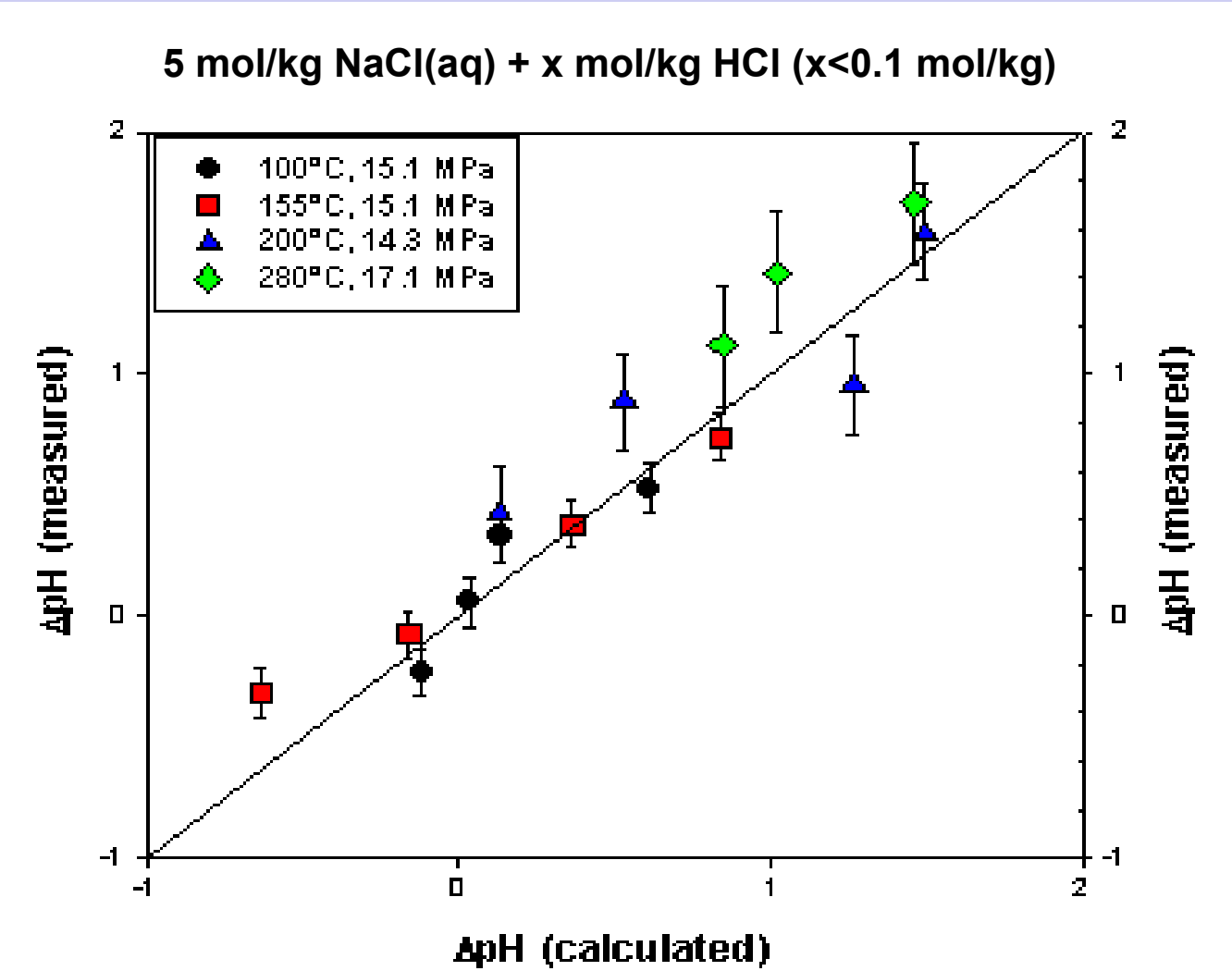
$$E_{in} = \frac{1}{F}\left[\frac{1}{2}\mu_{HgO}(T_2) + \mu_{H^+}(T_2) + \mu_{Ag}(T_1) + \mu_{Cl^-}(T_1) - \frac{1}{2}\mu_{Hg}(T_2) - \frac{1}{2}\mu_{H_2O}(T_2) - \mu_{AgCl}(T_1)\right] + \Delta\phi_{TE} + \Delta\phi_{TD} + \Delta\phi_{D} + \Delta\phi_{STR(L)} + \Delta\phi_{STR(R)}$$

pH calculations

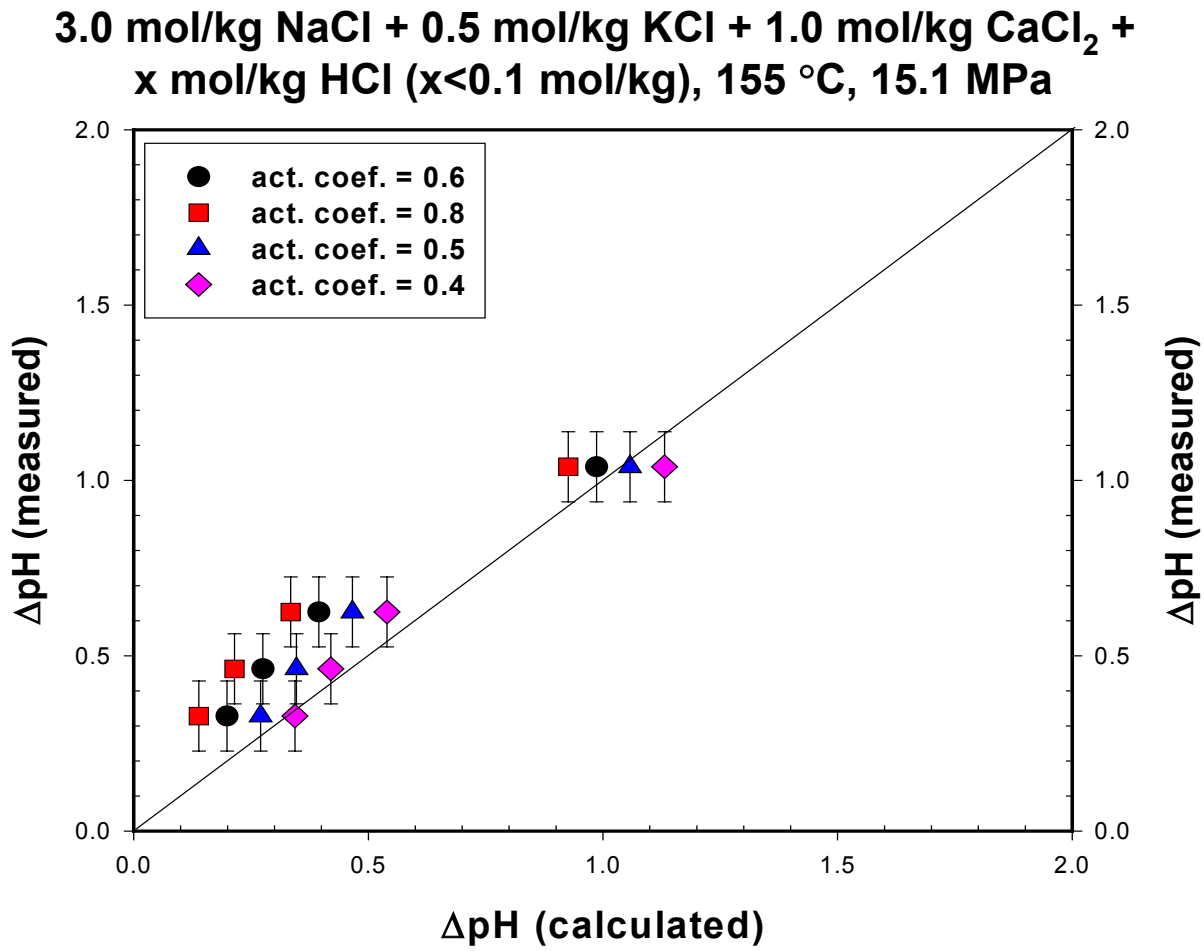
$$pH_1 - pH_2 = -\alpha \frac{(E_1 - E_2)}{\frac{2.303\ RT}{F}} - \frac{1}{2}\log\left[\frac{a_{H_2O}^{(1)}}{a_{H_2O}^{(2)}}\right] + \frac{(\Delta\phi_{d,1} - \Delta\phi_{d,2})}{\frac{2.303\ RT}{F}}$$

$$pH(X) - pH(S) = -\alpha \frac{(E_X - E_S)}{\frac{2.303\,RT}{F}} - \frac{1}{2}\log\left[\frac{a_{H_2O}^{(X)}}{a_{H_2O}^{(S)}}\right] + \frac{(\Delta\phi_{d,X} - \Delta\phi_{d,S})}{\frac{2.303\,RT}{F}}$$

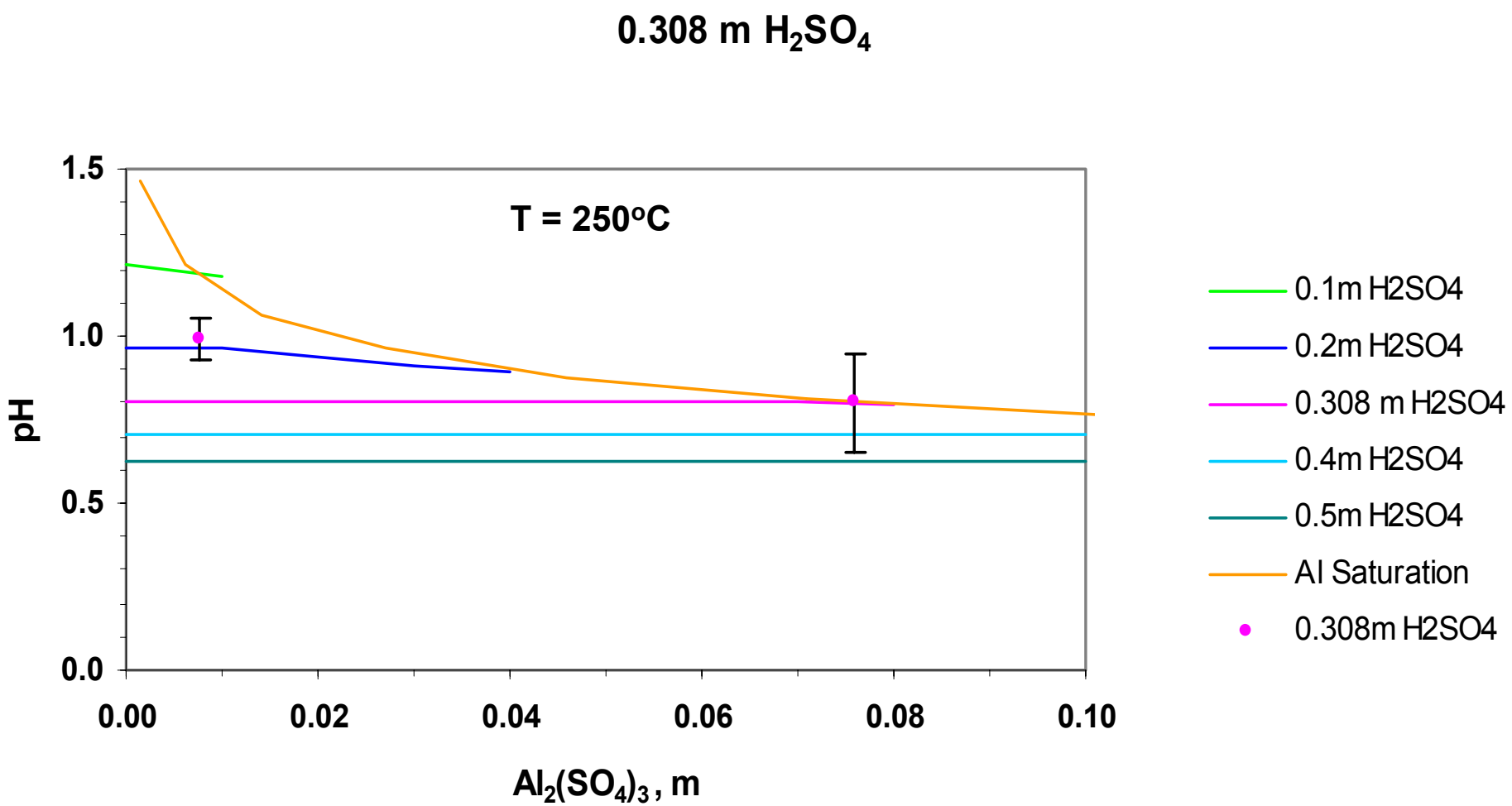
Concentrated NaCl solution



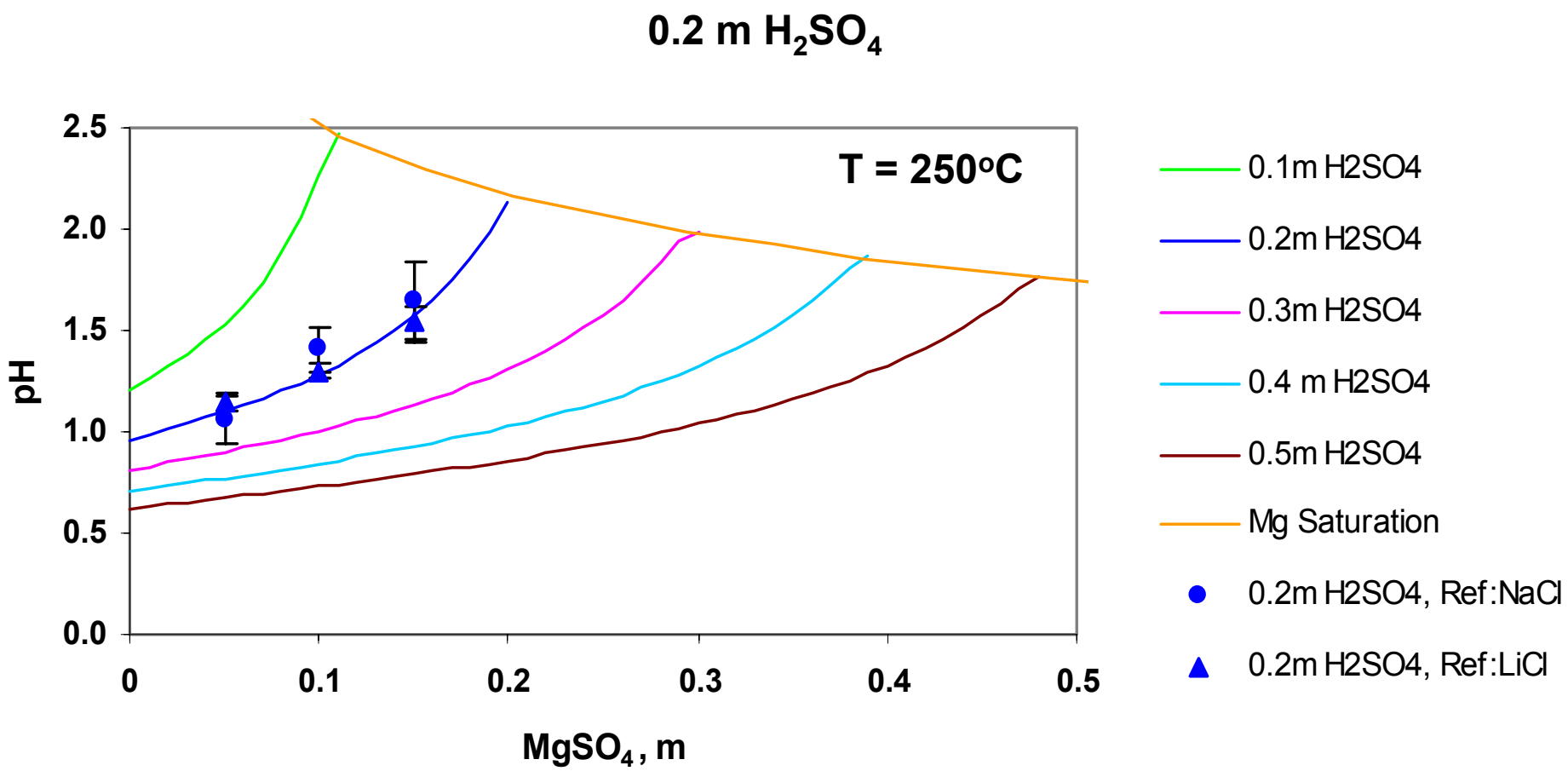
Artificial brine



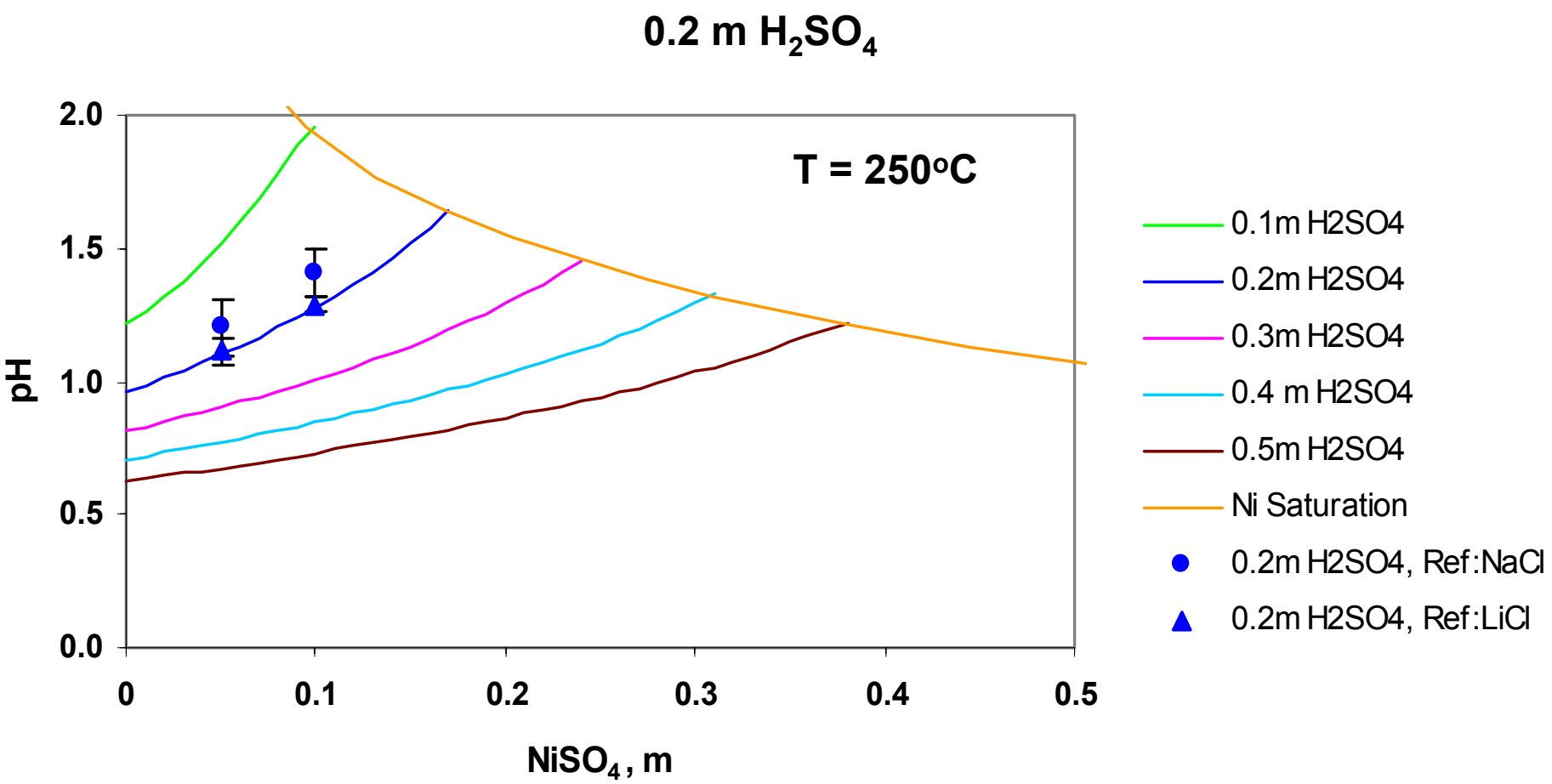
$Al_2(SO_4)_3$- H_2SO_4- H_2O solutions



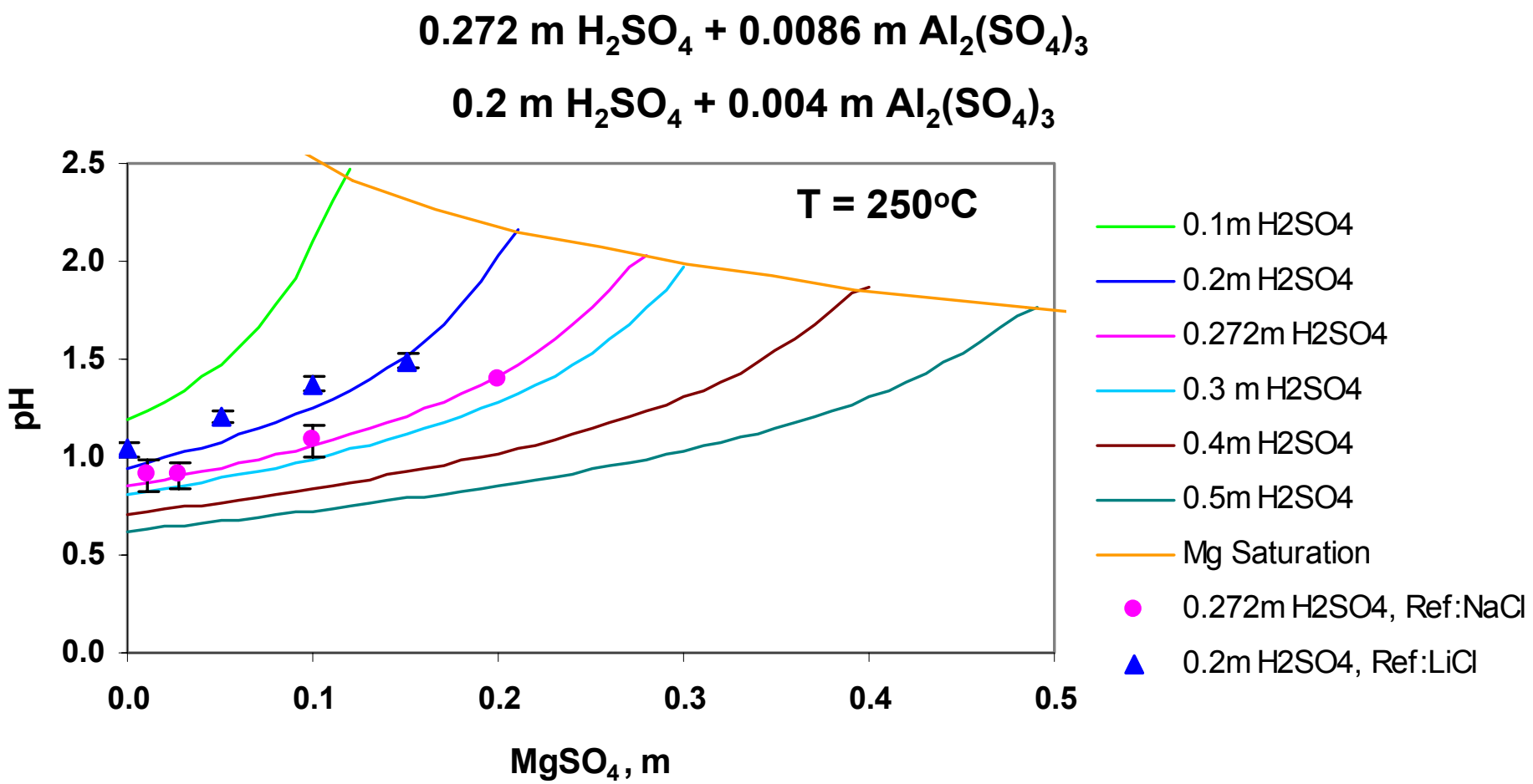
$MgSO_4$- H_2SO_4- H_2O solutions



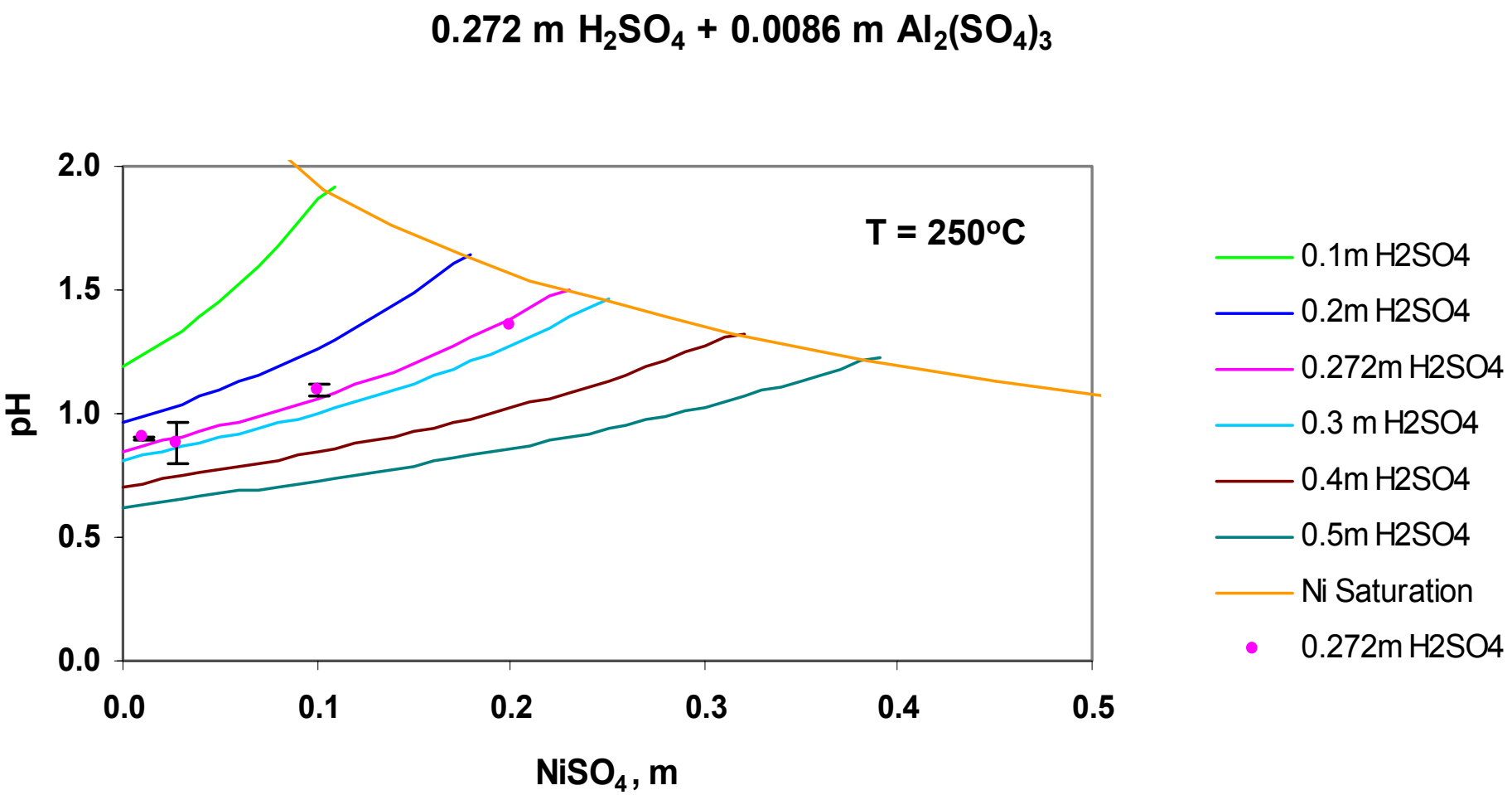
$NiSO_4$- H_2SO_4- H_2O solutions



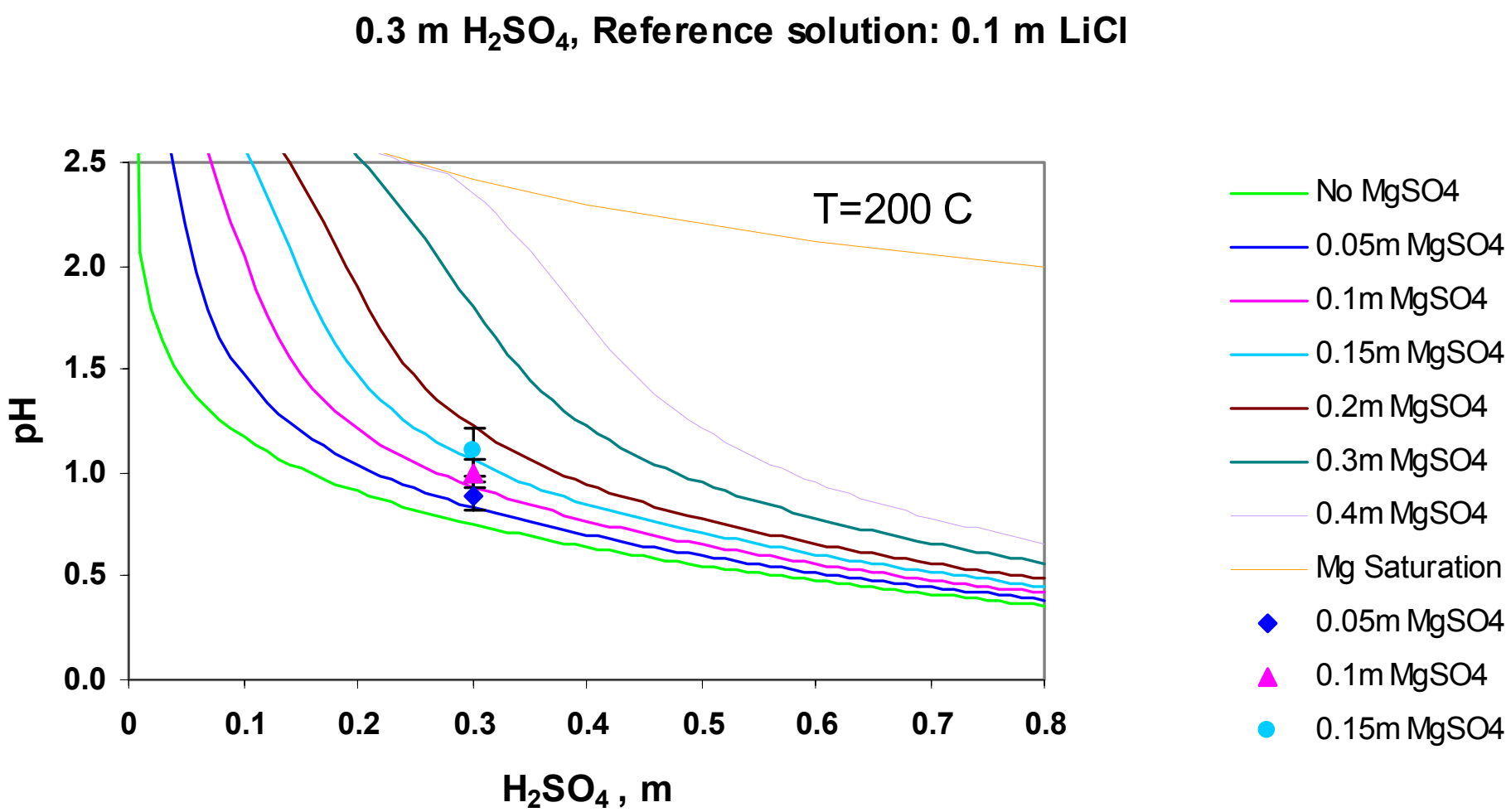
$MgSO_4$- $Al_2(SO_4)_3$- H_2SO_4- H_2O solutions



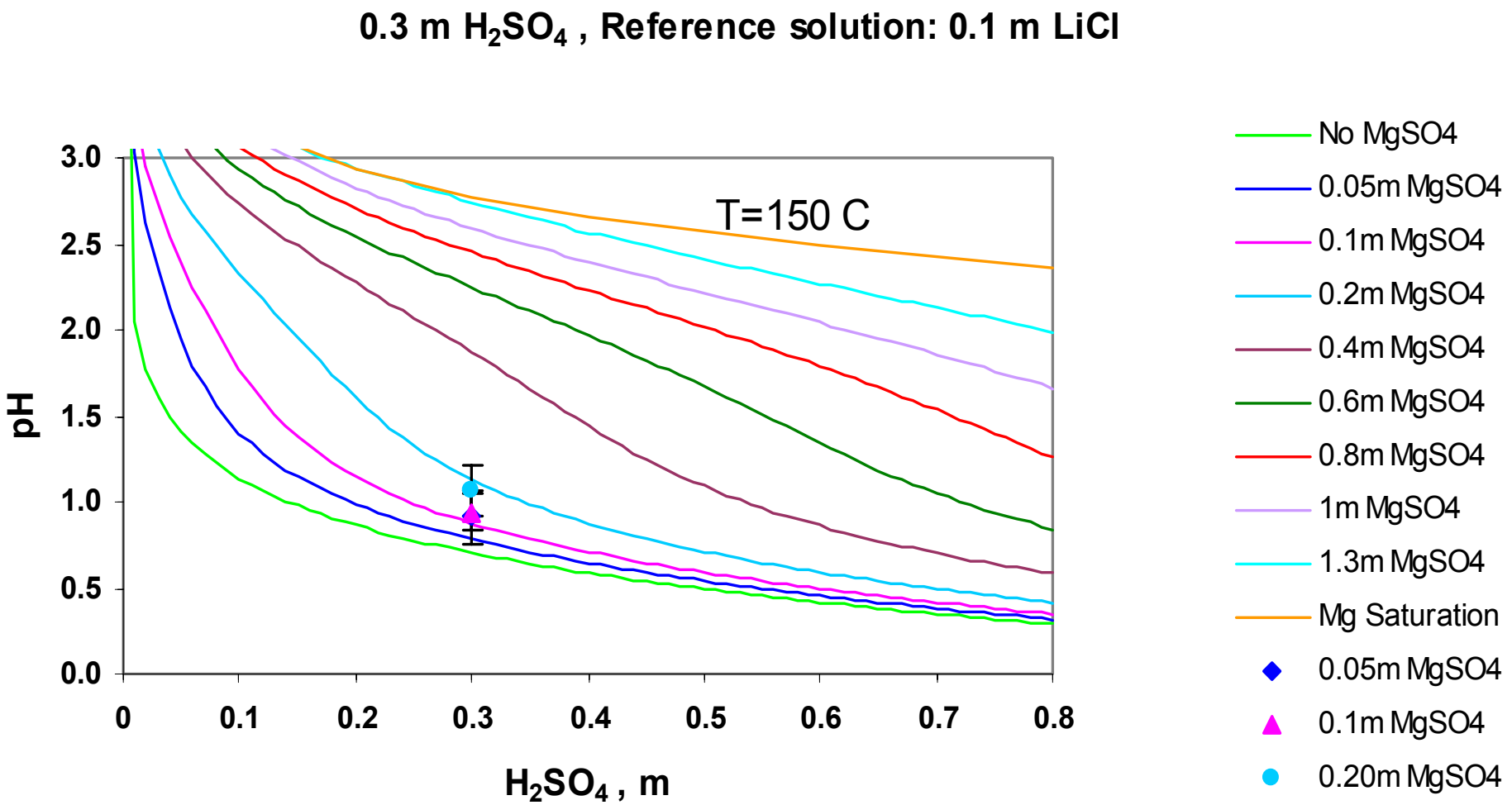
$NiSO_4$- $Al_2(SO_4)_3$- H_2SO_4- H_2O solutions



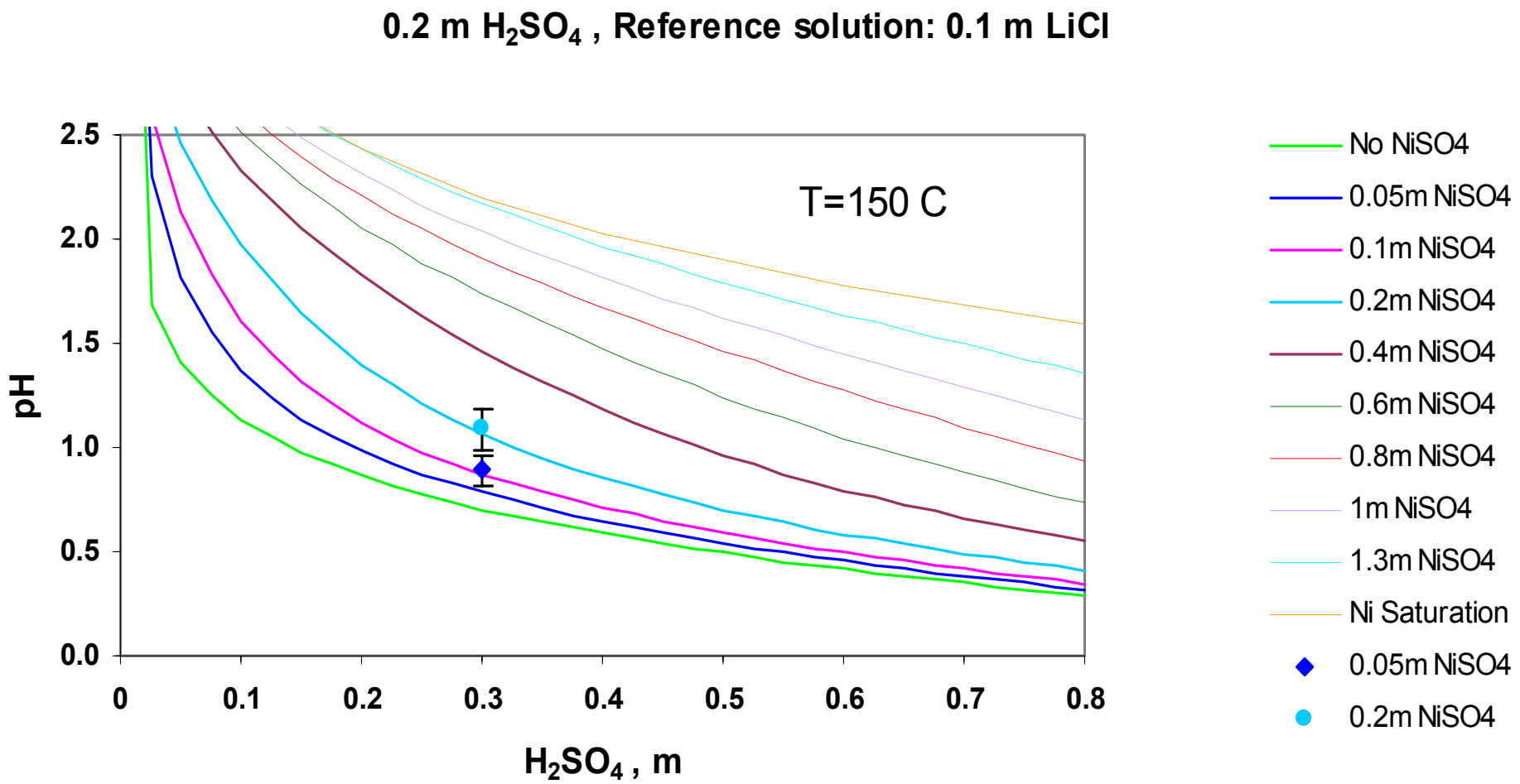
$MgSO_4$-H_2SO_4-H_2O at 200°C



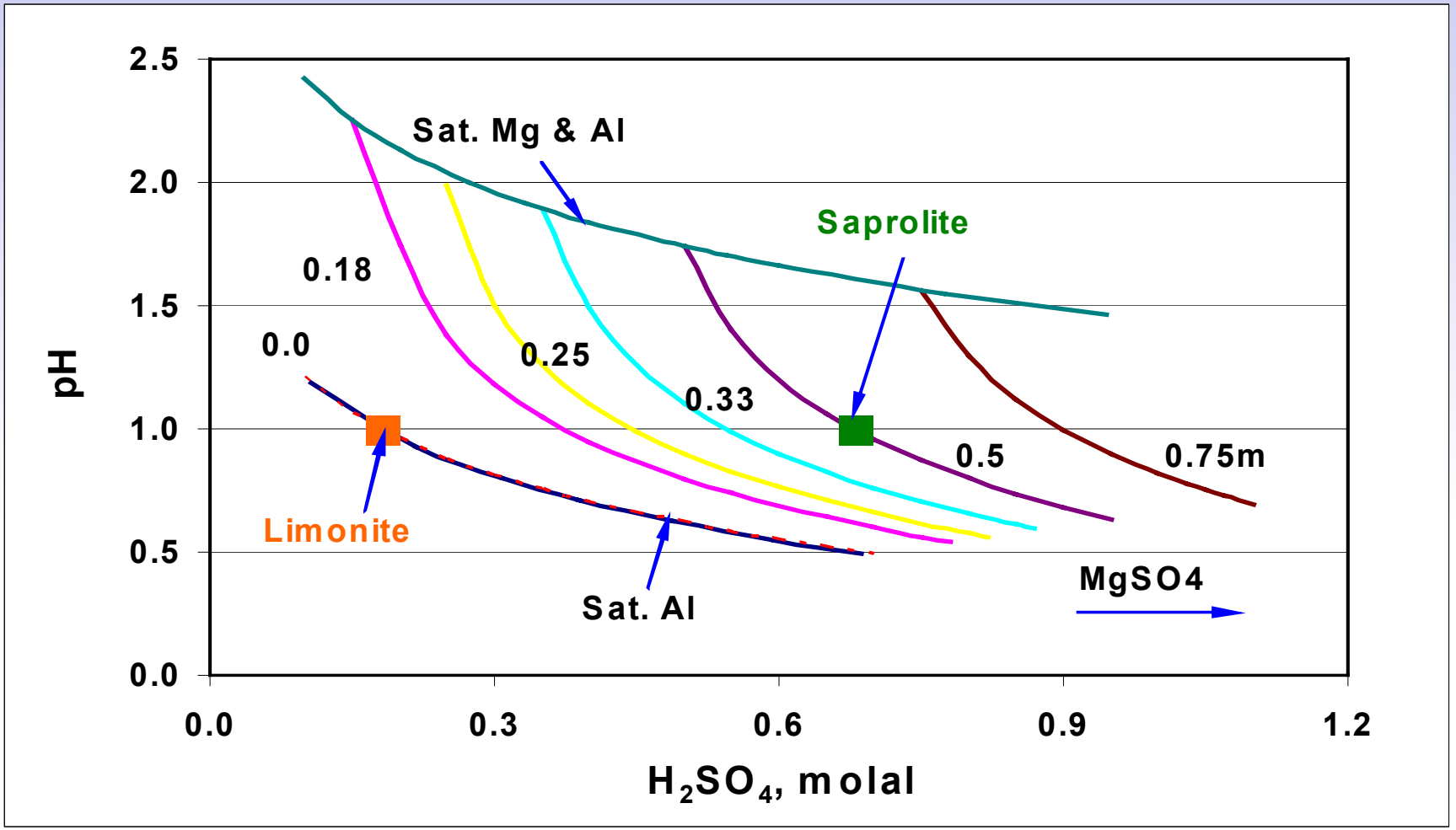
$MgSO_4$-H_2SO_4-H_2O at 150°C



$NiSO_4$-H_2SO_4-H_2O at 150°C



Calculated pH in $MgSO_4$- $Al_2(SO_4)_3$- H_2SO_4- H_2O solutions at 250°C in a PAL process



Conclusions

- A flow-through electrochemical cell with a YSZ electrode and a flow-through external Ag/AgCl electrode was employed to measure pH of **concentrated** chloride and sulphate solutions
- A reasonably good agreement was obtained between the experimentally measured pH values and those theoretically predicted (0.1-0.3 pH), suggesting that the cell can be utilized for **in situ** high temperature pH measurement in hydrometallurgical solutions