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Experimental Approaches to Predict the Behavior of Liquid Films

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Date of presentation: May 21, 2005
Location of presentation: Moscow ID

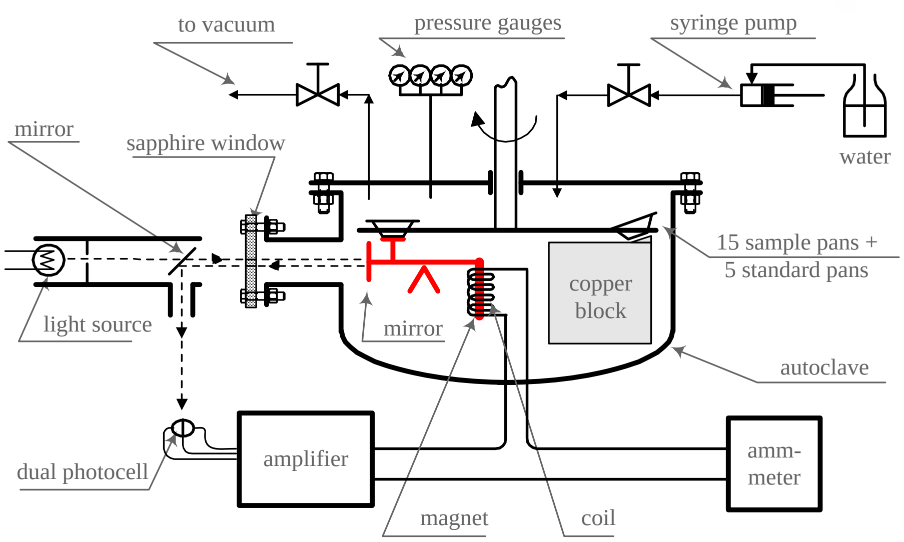
This presentation has been funded in whole or in part by the U.S. Department of Energy

Presentation Outline

- **The OCRWM OST&I Material Performance ORNL Project, which was begun in 2004, is made up of six main tasks.**
  - **The primary functions of each task will first be presented.**
  - **Next, the preliminary results of some scoping experiments (*i.e.*, those performed prior to the establishment of the ORNL Quality Assurance Program) in Tasks 1-3 will be described briefly.**
  - **Finally, a summary of the current status and future direction of the project will be presented.**

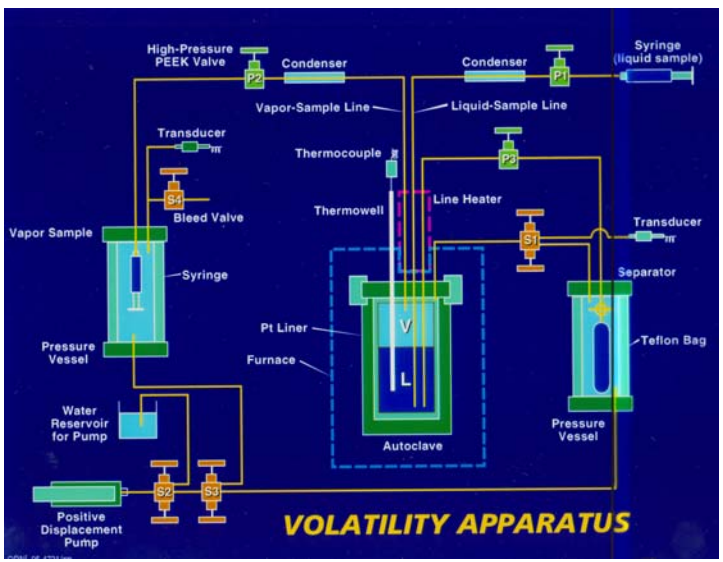
Task 1

- **A one-of-a-kind “Isopiestic” Apparatus allows solution masses to be monitored directly.**
  - **We measure the composition of liquid-films (including deliquescence) on metal alloy coupons with and without a coating of dust. Temperatures of 200°C or higher can be attained.**



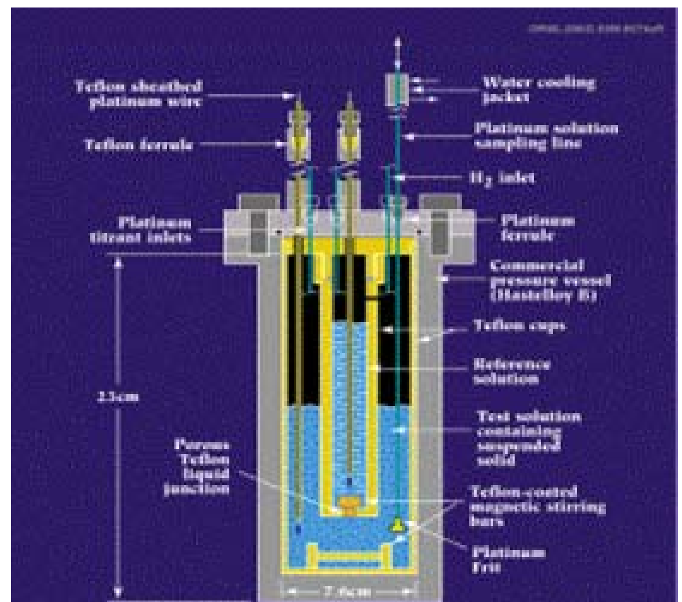
Task 2

- **A "Volatility" Apparatus provides a measure of the equilibrium compositions of co-existing liquid and vapor phases to very high temperatures, even for highly corrosive solutions**
  - **We will quantify the extent to which corrosive HF, HCl, HNO_3, and H_2SO_4 partition to the vapor from concentrated liquid films from 60 to 170°C**



Task 3

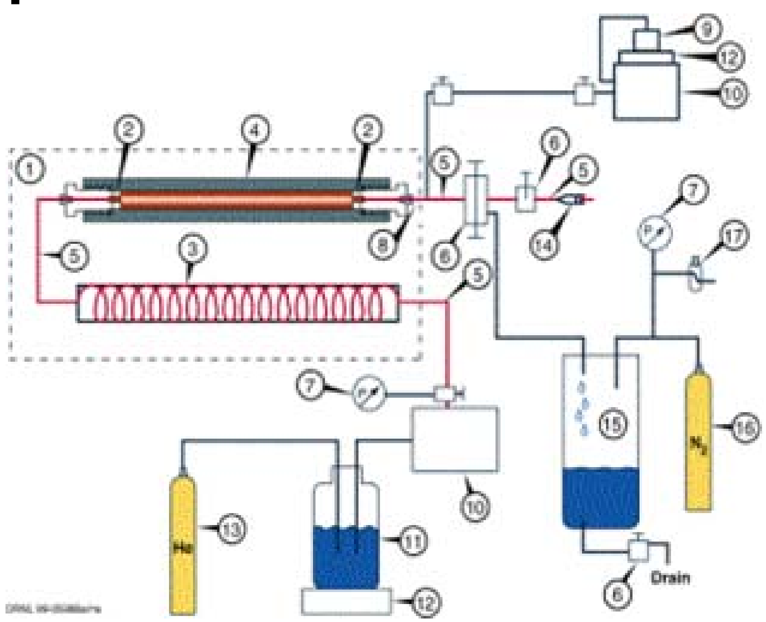
- **Our hydrogen-electrode concentration cells for highly accurate pH measurements (80 to 200°C)**
  - **We monitor the pH and solution compositions over time to high temperatures; measure the solubilities of solid phases; measure the adsorption of ions on mineral and metal oxide surfaces; monitor the solution chemistry in the presence of rock particles.**



Hydrogen-Electrode Concentration Cell for Solubility Measurements

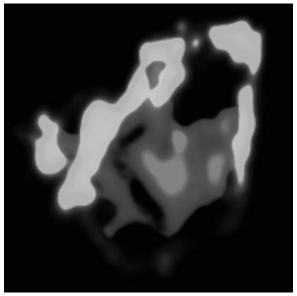
Task 4

- **A corrosion-resistant flow cells to monitor dissolution and/or corrosion.**
  - **We will monitor metal concentrations, *in-situ* pH and corrosion potential resulting from the exposure of metal alloy coupons to various solutions as a function of time and temperature**

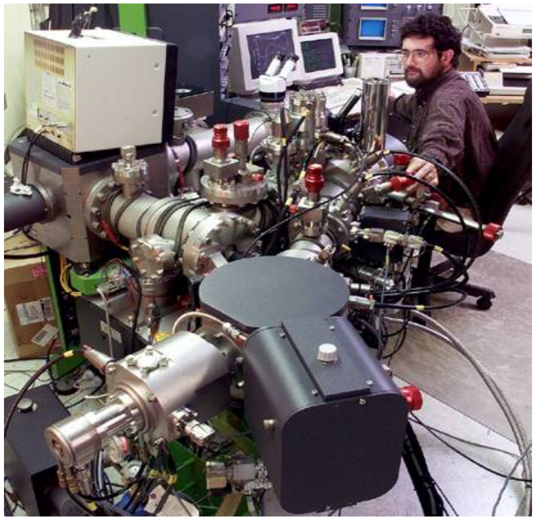


Task 5

- **Secondary Ion Mass Spectrometry (SIMS)**
  - **A surface analytical technique which uses an ion beam to remove material from a surface. It will be used to trace the transport of material at metal surfaces and through corrosion layers in order to assess the nature of reactions at the metal alloy-rock particulate-solution interfaces.**
  - ***ORNL Cameca 4f ion microprobe:*** **A unique capability which can chemically and isotopically finger print major, minor and trace elements in minerals, metals and glasses either atom layer by atom layer (in depth profiling mode) or laterally (in ion imaging mode)**



Na-feldspar reacted with ^{18}O rich 2 *m* KCl at 600ºC, 200 MPa for 6 d; note ^{18}O rich tracer penetrating solid that accompanied the reaction ofNa-feldspar to K-feldspar.

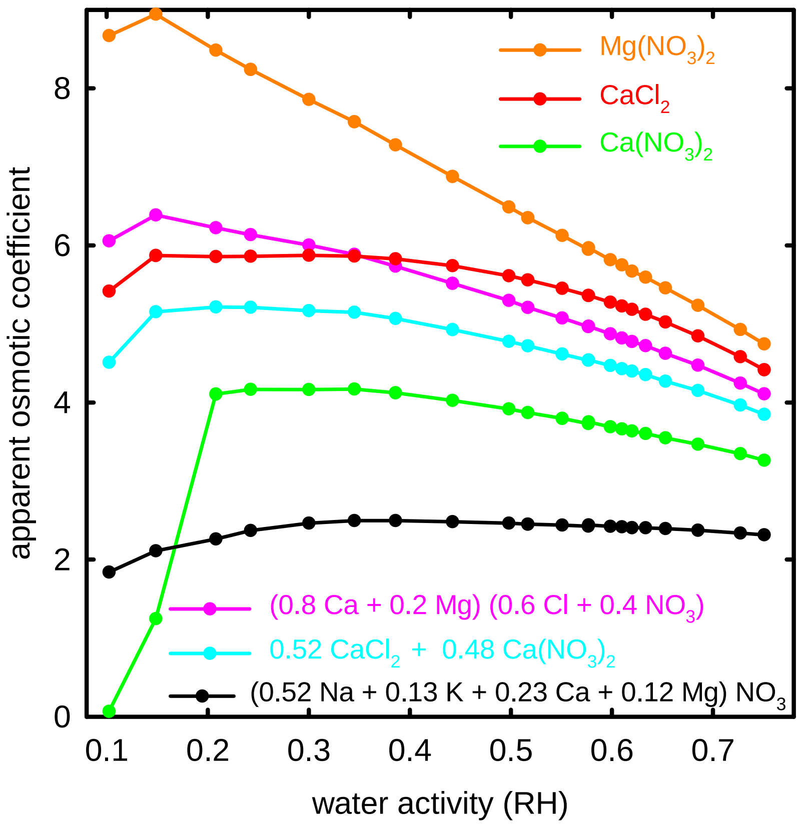


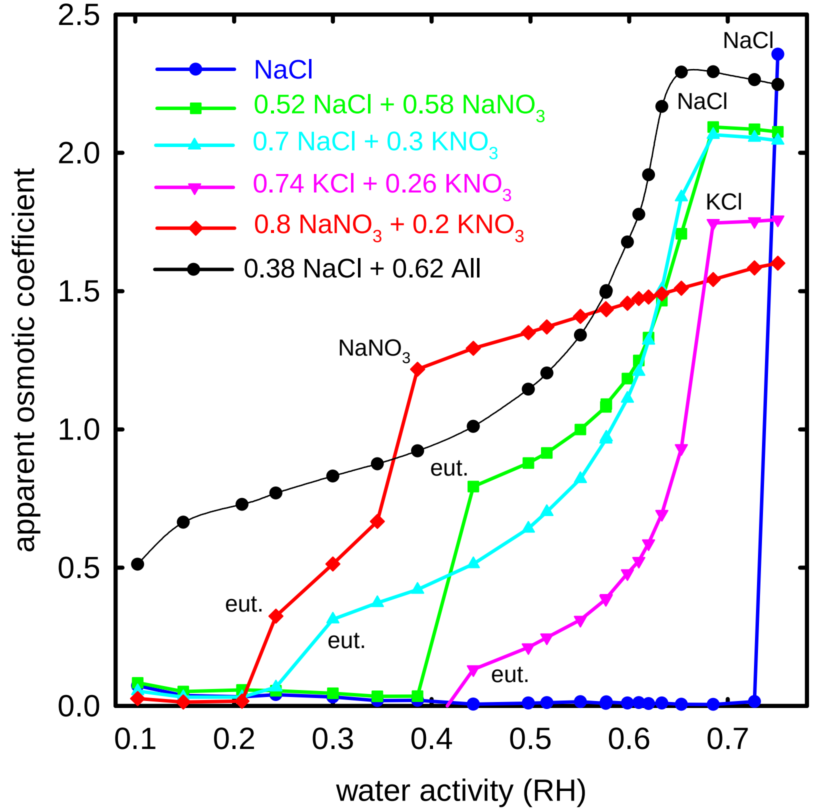
Task 6

- Modeling of the Corrosion Evolutionary Path (CEP)
  - This modeling effort is being performed under subcontract with OLI Systems with Digby Macdonald (PPSU) as an OLI consultant.
    - They utilize experimental results obtained from the literature, their own extensive database and those obtained at ORNL to bound the solution compositions and chemical environments which need to be considered for predicting the CEP on a given alloy.
    - They will also provide feedback to ORNL as to chemical conditions which need to be investigated.

Task 1: Phase Diagrams

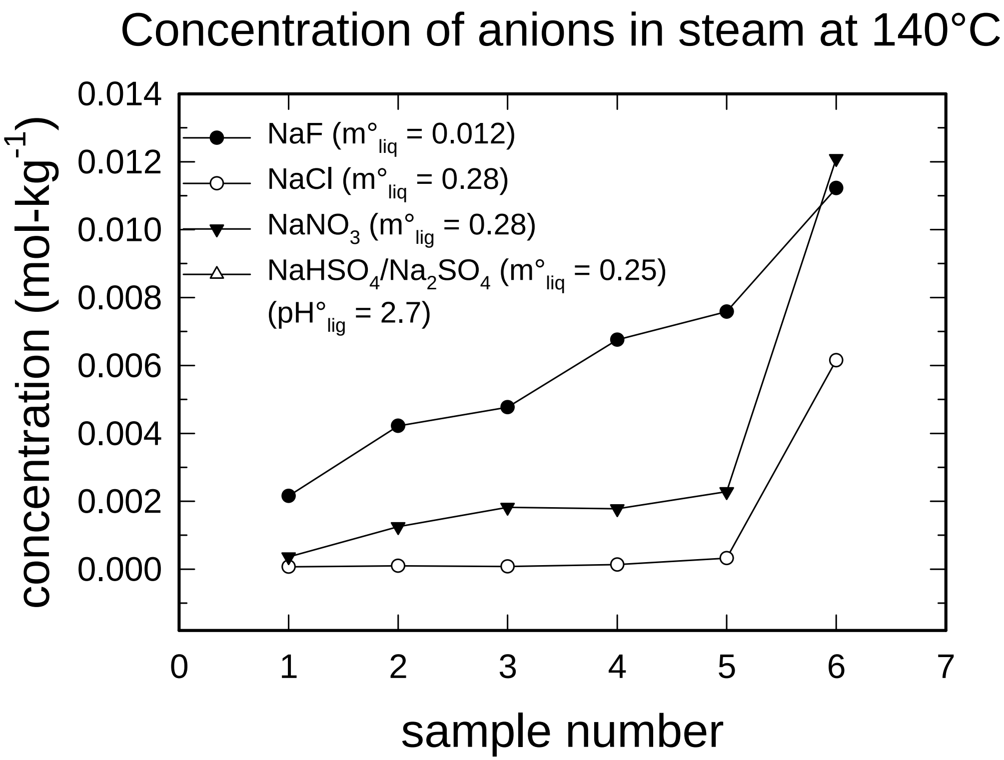
- **Preliminary results at 140°C: Deliquescence points and relative-humidity phase diagrams for electrolyte mixtures, *e.g.*, for equimolar $NaNO_3$ + NaCl solution, deliquescence RH decreases from 67% at 25 °C to < 43% at 140°C.**





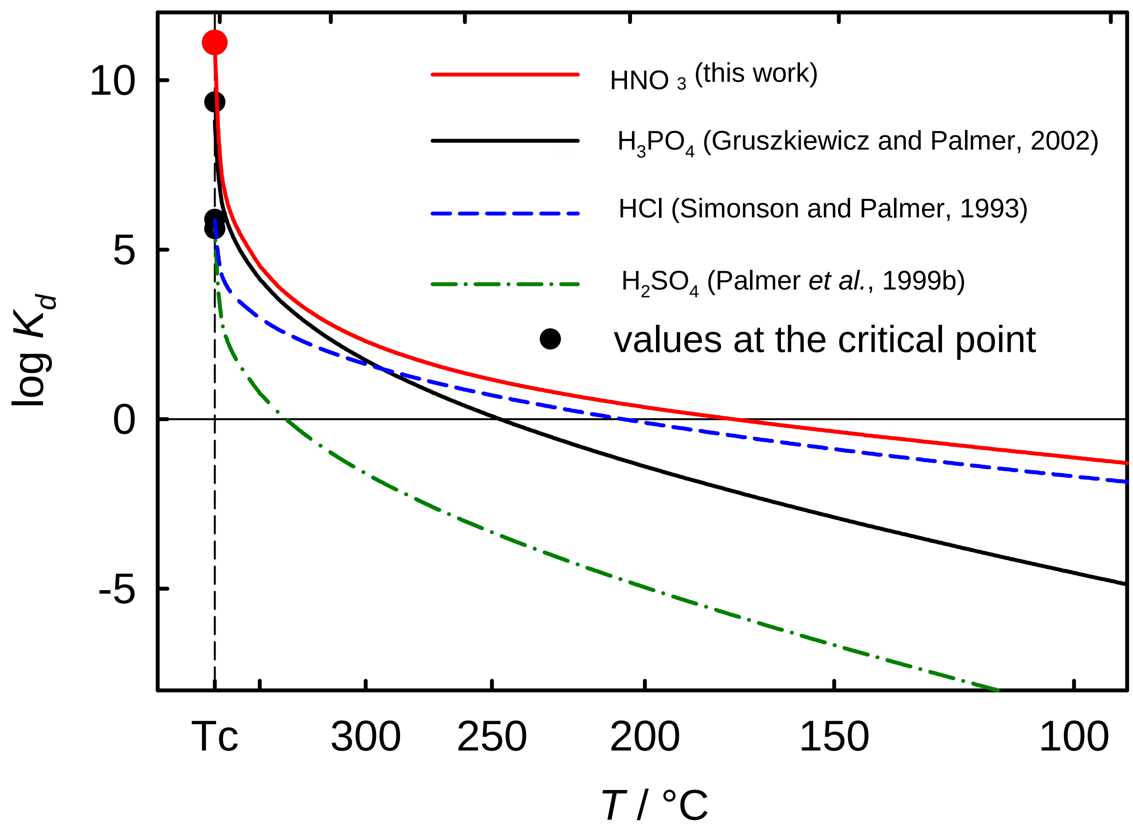
Task 2: Partitioning Equilibria

- **Preliminary Results at 140°C:**
  - **Measured concentrations in the liquid and vapor phases at the initial liquid composition shown in the figure.**
  - **The pH of the solution was controlled by the HSO_4^-/SO_4^{2-} buffer (pH_T = 2.7).**
  - **The order of volatility is F >> NO_3>Cl>>SO_4 which is consistent with previous results obtained at ORNL and with HF being a relatively weak acid.**



Task 2: Previous ORNL Results

- **Partitioning Constants for Mineral Acids**
  - **Comparison of the relative volatilities where each acid is considered to be a 1:1 electrolyte such that: *Kd* = m(HXvap)/{m(H+liq)m(X-liq)}**



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Task 3: Mineral Solubility Measurements

- **pH Measurements of Selected Brines:**
  - pH of Ca-Mg-Na-SO_4-K-F-Cl brines were monitored for 7 days at 80-200ºC – slow drifts from pH 7 to 8.4 were noted.
  - Precipitation of largely crystalline fluorite, CaF_2, and kogarkoite, Na_3FSO_4, was observed.
  - Solubilities of kogarkoite were measured in two brines at 80-200ºC and pure crystalline Na_3FSO_4 was synthesized independently.
  - Preliminary solubility constants for kogarkoite were obtained as a function of temperature and ionic strength.

Summary

- Measurements as described above for Tasks 1-3 will continue under the approved ORNL QA Plan and subsequent measurements will focus on the effects of added ground rock particles.
- Task 4 will be initiated with newly developed pH sensing electrodes in line at temperature.
- Metal alloys obtained following QA Procurement procedures will be fully characterized and samples will made available for insertion into Tasks 1-4.
- The CEP will be defined through an interactive modeling and experimental program.
- The results will be made available to the members of the OST&I Materials Performance group mainly to define the aqueous solution chemistry behavior that will prevail.