

## Minutes of PCAS, 2003

### Monday Morning (25 August 2003)

DP adopted as clerk of minutes

Minutes of previous IAPWS meeting in Argentina accepted without comment.

Participating members: Sergeui N. Lvov, Vladimir Mayer, Masaru Nakahara, Tomas Nemec, Donald A. Palmer, Masakatsu Ueno, Vladimir M. Valyashko,

#### ALS – IAPWS questionnaire

Crucial to the establishment of a better relationship with PCC and for the future of IAPWS is the increasing importance of aqueous chemistry rather than refinement of the properties of water and steam. We need to identify specific products from IAPWS WG's, particularly for industrial attendees. We need for PCC to prioritize a problem and with support from PCAS frame this problem (or more than one problem) during the course of this meeting. We need task groups that go beyond the membership of IAPWS to deal with common needs and future goals. There should be a slew of committees set up this week to treat a range of issues. For example, the first issue would be fuel cells with the aim of showing how IAPWS will play a role. This committee could be made up of SL, FM and Horacio Corti, and others. Electrochemistry at high temperatures is another topic (SL, DP, Digby Macdonald, and others). A subtask group would be to establish guidelines for pH measurements at high temperatures. The formation of this subtask group was mentioned at the PCAS WG meeting in Argentina and members were initially suggested (DP, SL, Peter Tremaine, MN, HC). SL asked if it is possible to attract chemists from the nuclear power industry. The answer is that nuclear is on the rise, and that IAPWS has had members in the past from the nuclear power industry so that we should be able to attract members in the future. ALS urges PCAS members to get involved in these task groups. Education is another issue that PCAS should consider having members on this committee. There are many good ideas in this area in the report that ALS described at the EC meeting on Monday morning. The subject was raised about our attempts to have PCAS and TPWS becoming interested in computer simulation modeling, but as no members with this expertise are currently in attendance, this subject will languish this year. How do we involve more "simulators" in IAPWS on a regular basis? Perhaps next year at the ICPWS the symposium on simulations will provide a basis for this area within IAPWS. DP suggested that we need to have more than one person responsible for new areas to avoid losing these initiatives.

VM asked if there were any applications for the collaborative young scientist program. However, there were none from PCAS this year.

VM raised the question of the symposia for the 2004 ICPWS. The list of symposia in the first circular was found to be no longer valid as it was revised on Sunday. SL proposed a rewording and recombination of two symposia into "Electrochemistry for Power Generation and other Technologies". This title would fit the currently proposed last topic on the current list from Sunday. It was decided to delay further discussion until Thursday.

### Monday afternoon – joint PCC/PCAS workshop

#### 1. Andre Zeijseink On the Importance of pH Measurements in Power Plant Cycles

Question: SL Why not add NaCl to the pure water samples to measure pH directly? AZ This has been tried sparingly, but not over a long period of time due to cost of probes. TP You give a value of 5.5 for the neutral pH of pure water at 350C. Was this an experimental or calculated value. The consensus of opinion was that this value was calculated based on fitting a large body of experimental data.

#### 2. Jim Bellows Calculation of pH from Specific and Cation Conductivity (no handout was available)

Question: MB Did you try the calculation of pH with NaCl added? Yes. EM confirmed that you can only calculate the pH in alkaline solutions as stated in the VGB guidelines.

## 3. Eric Maughan Practical Aspects of pH Measurement

Question: SL Have you considered diffusion potentials in your low temperature glass electrode measurements? By using KCl in the reference compartment, and dilute buffers and very dilute test solutions, the diffusion potential can be ignored. DP Do you recommend the use of Ross combination glass electrodes? Yes, and Equilthal electrodes are also very reliable.

## 4. Don Palmer Report on the pH of High Temperature Water

Question: SL Are there plans at ORNL to make a flow concentration cell for supercritical conditions? Yes, by replacing Teflon with ceramics a prototype as been made to go initially to 400C. VM How reliable are pH measurements at high temperature using spectrophotometric indicators? We could not find any complete estimate of experimental errors in the papers by Johnston and coworkers, but we estimate that these errors may be +/- 0.1 pH units. However, these researchers are no longer active in this area.

## 5. Serguei Lvov Can We Measure pH of High Temperature Water?

## 6. Yulia Zhgenti An Experimental Investigation of Borate/Lithium Adsorption from Solution onto Zirconium Dioxide in the Water-Steam Cycle of Power Plants

Question: SL Is knowledge of the zeta potential important to your study? Yes, because adsorption of ions changes the zeta potential. MB Do lithium cations adsorb because borate is adsorbed on the  $ZrO_2$  surface? No, lithium cations adsorb independently on the negative  $ZrO_2$  surface, and borate may be either adsorbed directly on the surface in place of hydroxide ions or are incorporated in the electric double layer.

## 7. Erik Maughan Theoretical and Practical Aspects for the Verification of Carbon Dioxide in the Water-Steam Cycle of Power Plants

Question: Is the instrument that you have described available commercially? Yes.

## 8. Shunsuke Uchida Development of High Temperature Water Chemistry Sensors

Question: SL You mentioned that ECP instrumentation has been installed in BWR's in Japan, what reference electrode was used and how do they allow concentrated solutions in the reference electrode to be used in the BWR environment? We use either an Ag/AgCl or Fe/Fe<sub>3</sub>O<sub>4</sub> reference electrode in a line where the water then goes to the drain and not back into the reactor.

## 9. Erik Maughan Automatic on-line Calibration Method for pH of Ammoniacal Water Circuits.

## 10. Geoff Bignold A Spreadsheet for Calculation of Speciation, pH and Conductivity from Measured Concentrations of a Range of Anions and Cations.

Question: MB A comment that spreadsheets will at least predict which are the important species in water at various conditions. DP A further comment that the reliability of these predictions depends on the reliability of the database on which they are based. For example,  $Mg(OH)^+$  is now believed not to be an important hydrolysis product of  $Mg^{2+}$  which rather hydrolyses directly to  $Mg(OH)_2$ .

**Monday afternoon final PCC/PCAS Discussion**

At the request of AZ for a combined action by PCC and PCAS, DP suggested that interested participants from both groups and invited specialists from outside IAPWS prepare a document for eventual publication on the subject of pH with particular emphasis on high temperature applications, comparison of techniques, equipment, calibration schemes and standards with consistent consideration of experimental uncertainties. MB noted that for power plant applications there was no need for uncertainty analyses as the expected reliability is only +/- 0.3 pH units at present. EM commented that although there is a critical need for reliable pH measurements in power plants, the task group must also consider the use of conductivity to predict pH. So a two-way approach should be adopted, conductivity and direct pH measurement. AZ commented that in Holland there was an attempt to use pH meters in power plants, but these were not successful (reliable) and therefore this approach was abandoned. SL claimed that chemists possess the technology to measure pH at high temperatures and this technology could be implemented now in a bypass mode to within a precision of 0.1 pH units. However, the equipment is bulky and expensive (ca. \$50,000). BD responded that this effort has been funded for over ten years and is still far too unreliable to be installed in working plants. Therefore power plants continue to use relatively inexpensive conductance monitors for fossil and BWR plants. He further stated that in terms of new instrumentation only ORP monitors have been adopted successfully through initial education by EPRI of the plant chemists and engineers. Forty percent of fossil plants with copper in their cycles now employ ORP monitors. Education of the power

industry following the publication of a comprehensive paper on pH measurements would be a logical next step. JB commented that information retrieved from power cycle monitors is now considered by plant operators in terms of the cost of shut down versus continued power generation and the resulting estimated cost of plant damage. BD said that corrosion fatigue is the most common and expensive problem facing the industry, but we should concentrate first on the question of pH as we have the expertise necessary within the two working groups. BS suggested that we also consider creating a task group to expand the spreadsheet presented by GB to extend the range to 120C and perhaps produce commercial software based on this model. However, BD quickly responded that there are too many legal barriers for IAPWS to go into such a venture.

It was concluded that an outline for the report by the pH/conductivity task group be prepared by two members of PCC and two from PCAS. Andre Zeijseink and Shunsuke Uchida (PCC), and Serguei Lvov and Donald Palmer (PCAS) volunteered to prepare this outline shortly after the Danish meeting. Others to be involved in this project are: Erik Maughan, Geoff Bignold and Horacio Corti with external help by Arthur Covington and Digby Macdonald, if they agree to participate. It is planned to have a draft of this report available by the next ICPWS meeting in Kyoto.

### Thursday Morning (28 August 2003)

The first item dealt with the recommendations for the restructuring of IAPWS (the following numbers refer to the recommendation numbers in the report).

1. No change
2. IAPWS name change: we should retain the general title, even though it does not reflect the exact nature of the organization, but we vote to insert “systems” instead of “mixtures” in the subtitle.
3. No change
4. PCAS would like to have more interaction with PCC, but we leave the recommendations for PCC to PCC.
5. We recommend a wording change to the recommendation “jointly and separately”.
6. Agree
7. Agree
8. Agree
9. We recommend a four year cycle for ICPWS. We do not wish to suggest changes to the forthcoming ICPWS meeting in Kyoto. We recommend publication of papers in special issues of journals in addition to or instead of the publication of the traditional ICPWS book/CD.

### Committees:

Nuclear – we support the establishment of the nuclear power task group (Palmer)

Fuel cell – accept

ICRN’s – PCAS members present report that they have had no direct or indirect benefit or use of ICRN’s. We feel further that the creation of task groups which are proactive substitute for ICRN’s in a positive way. For example, the task group on pH has been created, but we are about to close our ICRN on pH, because it has run its course and the same questions still remain.

Awards – agree (nomination of awards committee, PCAS recommends Mr. Okita)

Task groups

Properties and formulation for high temperature aqueous solutions – we need a co-chair from TPWS to serve with Vladimir Majer

Electrochemical processes in high-temperature aqueous systems – we recommend Masaru Nakahara and Shunsuke Uchida as additional members.

Education and Outreach – The Monograph is an educational tool and the Japanese national committee has a plan to include students in the forthcoming ICPWS.

Environmental Issues – PCAS nominates Masaru Nakahara and Vladimir Majer.

Metastability, nucleation, early condensate, droplet sprays and cavitation – PCAS has no further members to add.

## Attachment 7

Suggested symposium topics for the 2004 ICPWS meeting in Kyoto that involve PCAS directly

Thermophysical properties and phase equilibria in aqueous solutions: experiment and modeling (Harvey, Majer) - conditionally invited lecturer to be Dan Friend

Structure, dynamics and molecular simulation in aqueous systems (Ikawa and Okazaki, Mountain) - conditionally invited lecturer to be Guillot

Processes and chemical reactions in hydrothermal systems (Yamasaki, Palmer) – conditionally invited lecturer to be Yoshimura

Apparatus, materials and monitoring instrumentation for applications at high temperatures and pressures (Ueno, Sawamura, Maughan) - conditionally invited lecturer to be ?

Nonequilibrium, metastable and critical states (Marsik, Sengers) - conditionally invited lecturer to be Michael Anisimov

Fuel systems and electrochemistry of aqueous systems (Lvov, Japanese) - conditionally invited lecturer to be Robert Savenil

New task groups / committees

PCAS accepts participation in the project on the Data Book “Hydrothermal Experimental Data. Phase Equilibria and Solution Properties in Binary and Ternary Systems” edited by Vladimir Valyashko that contains eight chapters. The participating IAPWS members are H. Corti, S.N. Lvov, V. Majer, D. Friend and D.A. Palmer.

The Hydration Properties project, which is carried over from the previous year, continues with additional participation from Andre Plyasonov, Shedelbauer, Fernandez-Prini and Harvey.