
Working group 'Power Cycle Chemistry' (PCC)

IAPWS PCC WG Meetings in Santorini, Greece

3-8 July, 2005

MINUTES OF MEETING

1. Amendments / Adoption of Agenda

The meeting was chaired by Robert Svoboda. A draft agenda was discussed, amendments agreed and the revised agenda is set out in **PCC Attachment A**.

2. Election of Clerk of Minutes

Geoff Bignold agreed to record the minutes.

3. Approval of Minutes of 2004 Meeting in Kyoto, Japan, action points

The minutes of the 2004 meeting were approved without any corrections.

4. International Collaborations

Progress report by **Tomonori Satoh**:

Summary of FAC work as a result of Canada-Japan Collaboration Program

Professor Ushida introduced the background and key aspects of the project which had benefited from \$5000 funding from IAPWS for Mr Satoh to spend a period at the University of New Brunswick at the outset of the study.

Mr Satoh then gave a detailed presentation of the considerable progress that had been achieved within one year. A report of the study was made available to the PCC. He included information on the fatal accident at Mihama Unit 3, and showed how corrosion rate measurements based on electrical resistance of a tubular specimen could be used to deduce when FAC is actively occurring. Support is being sought from the main sponsors to continue the work for a further two years.

Answering questions, Mr Satoh indicated that the work had been performed in neutral pH conditions as a first step.

Barry Dooley commented that PWR apply reducing agents. Further studies should also include such.

Robert Svoboda summarised that this work was an excellent example of international collaboration and congratulated Mr Satoh on making such rapid progress.

Professor Lister expressed his thanks to IAPWS for their part in support of the work.

Derek Lister:

Water Chemistry Issues and Corrosion Research at University of New Brunswick, Canada

Professor Lister gave a description of his department and of the work in support of CANDU, PWR and BWR systems that is conducted.

The list of CANDU related work was extensive and included cracking of carbon steel outlet feeders, FAC in LiOH dosed systems, deposition under boiling heat transfer conditions, solubility of hydrogen and deuterium in H₂O and D₂O and exchange processes between particulate oxides and surface deposits.

In PWR chemistry there is work on the kinetics of iron and nickel exchange relative to water circulation rate. In the BWR work on the influence of zinc on corrosion and release processes is being undertaken.

Robert Svoboda thanked Derek Lister and asked that further consideration be given to these topics after consideration of the priority list.

One new topic for potential international collaboration in 2006/7 was identified (Priority List item number 4).

5. Priority List Review (see also PCC Attachment B)

The priority list set out in 2004 was reviewed and updated. A number of overlapping topics were merged and some additional topics were introduced after thorough and extensive debate. The agreed revised list is given as PCC attachment B.

Arising out of the discussions the following actions were agreed:

- To develop an ICRN on “Interfacial situation in advanced ultra supercritical plants” in collaboration with PCAS.

Barry Dooley to Liaise with Don Palmer

- To develop an ICRN on “Mechanism of Decomposition of Ion-exchange Resin”

Karol Daucik

- To develop a joint PCAS/PCC ICRN on “Development / Application of Sensors (Ambient and High Temperature Sensors)”

Maughan, Lister, Uchida, Lvov

- To develop an ICRN on “Improved analysis of low concentration of metals (Fe, Cu, Co, etc)”

Derek Lister + Karol Daucik

- To formulate a brief description of the problem of the relationships between the chemistry of the contaminants and their concentration at point of measurement, for presentation to IAPWS executive with the aim of potential introduction of a new ICRN proposal in 2006.

Task group: Bellows + Maughan+ Hughes + Bignold

Draft prepared and presented to PCC on 7 July 2005. **PCC Attachment C.**

- To progress the work on a method to quantify mechanical carry-over by the establishment of a guidance document. Robert Svoboda will propose two alternative approaches to the IAPWS executive:
 - o Development of a PCC guidance document
 - or
 - o Preparation of a paper for publication in the open literature (e.g. PowerPlant Chemistry) under IAPWS PPC team membership.

Team/task group: F.Gabrielli +J.Bellows, S.E.Therkildsen + M. deWispelaere + R.Svoboda

INTERMEZZO: Joint workshop with PCAS:

Research Presentations on Physical Chemistry for Power Generation

- a). **D. Palmer** - The Solubility of Zinc Oxide with Reference to Mitigation of Cobalt-60 Deposition and SCC in the Primary Circuit of PWRs

Don Palmer described work on the solubility of zinc oxide as a function of pH and temperature. The aim was to identify the maximum concentration that can safely be used in PWR primary water to displace active cobalt and reduce radiation fields. Details of zinc speciation had been evaluated from the results which now extended up to 350°C.

- b.) **S. Lvov** - Development of Zirconium Oxide Coating Technology to Mitigate Intergranular Stress Corrosion Cracking in BWRs

Sergei Lvov described work on the hydrothermal deposition of zirconia coatings on BWR materials for protection against IGSCC of stainless steels. He showed that, by careful control of deposition conditions, a 2 to 3 µm coating of high density and very good adhesion could be attained. Such a coating was able to suppress the free corrosion potential into a region where the probability of IGSCC was reduced.

- c.) **Stastny, M.**, Sejna M.: The Effects of Steam Chemistry on Condensation Process

Mr Stastny described an advanced theoretical study of condensation processes in expanding steam flows (modeling conditions in the later stages of LP steam turbines) and showed excellent correlations with the limited supporting experimental data. The work showed that the kinetics of droplet formation are too fast for all non-volatile solutes in the steam to be absorbed in early condensate. He confirmed previous conclusions on the very low solubility of NaCl in LP steam.

- d.) **R Svoboda** : The solubility of copper as a function of temperature

Robert Svoboda made a presentation which questioned the apparent inconsistencies between plant observations and published data on the solubility of copper in power plant circuits. Whereas ammonia corrosion of copper alloys in condensers occurs preferentially at the hotter end of the machine, an interpretation of the published data could suggest that copper oxide solubility falls with temperature. In the case of deposition in stator coils, although the solubility data would suggest a risk of blockages developing at the outlet end, the practical experience shows vulnerability at the inlet.

Don Palmer questioned whether just cuprous or cupric ion solubility was being considered and commented on the temperature dependence of the equilibrium constants for the ammonia complexes of both oxidation states. There was a consensus that, although sufficient data may exist, there is a need for clarification of the various dependencies in order to make the information more useful to the power industry.

Action: Svoboda will submit the references to Palmer, who will respond.

Sergei Lvov announced that PCAS had decided to terminate the work of two of its Working Groups and to replace them with a single new group on Interfacial Chemistry and Electrochemistry in High Temperature Fluids. He invited PCC participation in this working group. One of the issues addressed would be the establishment of an international conference to be held in juxtaposition with a relevant conference of the Electrochemical Society.

Action: Interested PCC members to contact Lvov.

7. IAPWS Certified Research Needs

Active ICRNs:

ICRN 13 on Surface Tension of Aqueous Solutions is due for closure. It was agreed that consideration should be given to results from the forthcoming conference in Stuttgart in October 2005. The ICRN therefore to be extended until September 2006.

Action – F.Gabrielli

Closed ICRNs reconsidered:

The ICRN on Evaluation of Binary Nucleation Models is no longer active but the progress has been covered in the IAPWS book. A closing statement is requested from Dr Marsik.

The ICRN on the Origin and Fate of Organics, which was issued originally in 1993, is likely to need to be readdressed after the forthcoming conference in Stuttgart in October 2005. ICRN reconsideration therefore to be done in the 2006 PCC meeting.

Action - E.Maughan

Proposed new ICRNs (to prepared for approval at the 2006 meeting):

Interfacial situation in advanced ultra supercritical plants

Joint PPC/PCAS ICRN: Palmer, Dooley

Mechanism of Decomposition of Ion-exchange Resin

Daucik

Development / Application of Sensors (Ambient and High Temperature Sensors)

Joint PPC/PCAS ICRN: Maughan, Lister, Uchida, Lvov

Improved analysis of low concentration of metals (Fe, Cu, Co, etc)
Lister, Daucik

New Issues:

Dr Safarik asked that PCC consider the need for support for work on the Thermophysical data on Moist Air at up to 10MPa / 1000°C and Steam at up to 50MPa / 1800-2000°C.

Jim Bellows explained the relevance of this to potential developments in hydrogen burning advanced gas turbines.

PCC concluded that the subject was not sufficiently urgent to introduce a further topic into the priority list at this time. It remains important that the necessary work should be undertaken before the practical hardware is developed.

8. Progress on committee work

Progress on the international collaboration within the nuclear committee had been fully reported by Professors Uchida and Lister. The need for further involvement and interest on nuclear plant topics was debated. This group is providing a strong interaction between fossil and nuclear power cycle chemistry, which is rarely found at other technical venues. Strong arguments in support were set out, with no members expressing any disagreement.

New task groups are indicated in the action list.

8. Focused topic: Nuclear Chemistry:

The following presentations were made:

- **Shunsuke Uchida:** Latest Experience with Water Chemistry in Nuclear Power Systems
- **Bernhard Stellwag:** Injection of Methanol at a Boiling Water Reactor as an Alternative to Hydrogen Injection (with Wilfried Ruehle)
- **Donald Palmer:** Zinc oxide solubility
- **Robert Svoboda:** Amine chemistry: blessing or curse for the steam turbine?

9. Focused topic: Combined cycle and fossil cycle chemistry:

The following presentations were made:

- **Robert Svoboda:** The "baby boom" (1988-2003) of combined cycle power plants is over what were the chemistry related teething troubles?
- **Geoff Bignold:** High iron levels in feedwater derived from steel air cooled condensers
- **Richard Harries:** LP steam carryover during load changes
- **Robert Svoboda:** Consequences of upset chemistry during plant startups, required restrictions
- **Marc deWispelaere:** Boiler tube failures – relation to Aluminium in the cycle?
- **Barry Hughes:** Cycle chemistry control automation while cycling at Teeside
- **Sonja Vidoikovich:** Steam purity control in Serbia power plant Nikola Tesla A
- **Karol Daucik:** Sampling for Iron in power cycles.
- **Svend-Erik Therkildsen:** Laboratory analysis for power plants

10. Update on International Power Cycle Chemistry guidelines

Karol Daucik introduced the new EBA / EPPSA / VGB guidelines on the quality of feedwater, boiler water and steam "Guidelines for Feed Water, Boiler Water and Steam Quality for Power Plants / Industrial Plants".

Differences with previous guidelines include a revised philosophy of action levels.

Alignment with the current EN guidance has been optimized.

Some parameters have no recommended upper action levels.

No endorsement from IAPWS is sought. The material was presented for information. The opportunity for information presentations on new guidelines should be allowed for future meetings.

11. Membership

The PCC unanimously supported the membership of:

Derek Lister
Sonja Vidoikovich:
Marc de Wispelaere
Berhard Stellwag (reinstatement)

Eric Maughan recorded the recent death of Barry Conlin. The PCC expressed its regrets and appreciation for the input to the working group, which Barry had contributed in the past.

12. Preparation of next year's agenda

The Priority List will be promoted to the earliest possible point in the next agenda.

Presentations preferably directed on items on the current priority list, or on items that members wish to advocate for the priority list. Any other technical presentations should be limited to no more than ten minutes each.

Time in the programme is to be allowed for working subgroups to undertake the agreed tasks.

Draft documentation for discussion and potential endorsement at the next meeting to be made available from working group chairmen by March of next year (for consideration by national committees and PCC members in advance of next IAPWS meeting).

13. Election of Officers

No requirement for immediate changes, but consideration of future officers will be required during the next year for discussion in 2006.

14. Preparation of the Report to EC

See IAPWS Minute 10.

15. Miscellaneous and Adjournment

The work of this year's meeting includes the proposal for four new ICRNs, two of which are joint with PCC and PCAS, and the intent for two PCC guidance documents.

Seven of the technical presentations are given consideration for publication.

Robert Svoboda thanked all PCC members for a very positive meeting.

Eric Maughan expressed the thanks of the members to Bobby for the excellence of his chairmanship.

Agenda for Working group 'Power Cycle Chemistry (PCC)

IAPWS PCC WG Meetings in Santorini, Greece
3-8 July, 2005

PCC Starting time 10:00 on Monday July 4. Joint WG topics are still to be decided upon (see general schedule)

1. Amendments/Adoption of Agenda
2. Election of Clerk of Minutes
3. Approval of Minutes of 2004 Meeting in Kyoto, Japan, action points
4. International Collaborations, the process
 - Progress report **Tomonori Satoh**: Summary of FAC work as a result of Canada-Japan Collaboration Program
 - **Derek Lister**: Corrosion research at University of New Brunswick, Canada
5. Priority List Review,
6. Progress on committee work

Intermezzo: joint workshop with PCAS:

- Research Presentations on Physical Chemistry for Power Generation

- a). **D. Palmer** - The Solubility of Zinc Oxide with Reference to Mitigation of Cobalt-60 Deposition and SCC in the Primary Circuit of PWRs
- b.) **S. Lvov** - Development of Zirconium Oxide Coating Technology to Mitigate Intergranular Stress Corrosion Cracking in BWRs
- c.) **M.Stastny**, M.Sejna: The Effects of Steam Chemistry on Condensation Process
- d.) **R.Svoboda** – Opening a discussion on the Solubility of Copper and Copper Oxides in Dependence of Temperature

7. IAPWS Certified Research Needs, Closing statements

8. Focused topic: Nuclear Chemistry:

- **Shunsuke Uchida**: Latest Experience with Water Chemistry in Nuclear Power Systems
- **Bernhard Stellwag**: Injection of Methanol at a Boiling Water Reactor as an Alternative to Hydrogen Injection (with Wilfried Ruehle)
- **Robert Svoboda**: Amine chemistry: blessing or curse for the steam turbine?
- **Barry Dooley**: [discussion on FAC on Thursday, as required]

9. Focused topic: Combined cycle and fossil cycle chemistry:

- **Robert Svoboda**: The "baby boom" (1988-2003) of combined cycle power plants is over what were the chemistry related teething troubles?
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- **Richard Harries**: LP steam carryover during load changes
- **Robert Svoboda**: Consequences of upset chemistry during plant startups, required restrictions
- **Marc deWispelaere**: Boiler tube failures – relation to Aluminium in the cycle?
- **Barry Hughes**: Cycle chemistry control automation while cycling at Teeside
- **Sonja Vidoikovitch**: Steam purity control in subcritical power plant

- **Karol Daucik:** Sampling for Iron in power cycles.
 - **Svend-Erik Therkildsen:** Laboratory analysis for power plants
10. Guidelines from EBA/EPPSA/VGB, status on guideline for boiler water (Daucik)
 11. Membership
 12. Preparation of next year's agenda
 13. Election of Officers
 14. Preparation of the Report to EC
 15. Miscellaneous and Adjournment

For more information:

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Working group 'Power Cycle Chemistry (PCC)

*IAPWS PCC WG Meetings in Santorini, Greece
3-8 July, 2005*

PCC Priority List

1. Interfacial situation in advanced ultra supercritical plants

Formation and exfoliation mechanism of scale (oxide films) in steam lines
effects of chemistry (oxygen, ammonia ?)

Corrosion interactions materials / steam, influence / effect of
supercritical parameters, protective layers, radiation

Faster decomposition of chemicals (TOC, ammonia etc)?

Joint PPC/PCAS ICRN (Palmer, Dooley); draft: Mar 06

2*. Mechanism of Decomposition of Ion-exchange Resin

Operating conditions, quality control of resin; leak rates are slow, but sulfate is
one of the products, organic leachables, oxidation

Additional information has to be researched

ICRN Daucik -> PCC guidance document; draft: Mar 06

3*. Development / Application of Sensors (Ambient and High Temperature Sensors)

ECP (nuclear, fossil application), ORP,

problem: abstract parameters, acceptance by plant operators

Joint PPC/PCAS ICRN (Maughan, Lister, Uchida, Lvov) ; draft: Mar 06

4*. Improved analysis of low concentration of metals (Fe, Cu, Co, etc)

Techniques for analysis are known, but problems with implementation

Additional problems with adequate sampling

ICRN: Lister + Daucik; draft: Mar 06

(possibly international collaboration 2006: Lister, Daucik, Svoboda)

5*. Corrosion mechanisms that are related to the presence of contaminants in

steam/water circuits, particularly in boiler-water

Define critical species / quantify critical quantities of steam generator water impurities, synergy
with other species (e.g. oxygen), consideration of the materials

**6*. The relationships between the chemistry of the contaminants and their
concentration at point of measurement**

Detailed definition of the problem

*Task group: Bellows + Maughan + Hughes + Bignold (short document
attached, ICRN proposal 2006?; interim report to PCC: Mar 06)*

7*. The quantification of risk of asset damage

problems of getting background data, important long-term issue
need: tool for operators, design engineers & commercial persons

8*. Method to determine the mechanical carry-over?

Outline established in PPC minutes 2004

Guidance document is needed;

PCC will propose to EC establishing a PCC guidance document.

If positive: task group; if not: publication by IAPWS team in e.g. PPChem. Team/task group: F.Gabrielli, J.Bellows, R. Harries, S.E.Therkildsen, M.DeWispelaere, R.Svoboda; draft PPC guidance document:Feb 06.

9*. Improved understanding of condensation mechanisms

- dropwise vs filmwise condensation in condensers (improve heat transfer)
- heterogenous – homogeneous nucleation models for prediction of condensation in steam turbines (chemistry, electrostatic,...)
- chemistry of the phase transition zone in nuclear turbine systems

To be considered in 2006 for ICRN

10*. Deposition of contaminants and corrosion products in steam and water circuits

- supersaturation,
- mass transfer,
- adsorption,
- crystal nucleation,
- deposit re-dissolution,
- scouring and exfoliation,
- activation and activity transport in reactor systems
- Mechanism and Influence of Cu Deposition :
(essentially a solved problem from a scientific viewpoint)
 - mechanism of deposition on a turbine blade is not understood
 - discrepancies in temperature influence on deposition (?)

To be considered in 2006 for ICRN

11. High pressure / high temperature steam and humid air (24 MPa and up, 2000°C), thermophysical properties and chemistry formulation

Long term interest in power industry, should be included in update of ICRN #14

12*. Radiation chemistry of water

Radiolysis

To be expanded in 2006, together with PCAS?

*** includes input from the nuclear group**

The numbering in the list is made for reference only and does not contain any information on actual priority

**Working group 'Power Cycle Chemistry' (PCC)
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Proposal for new task group within PCC

Guideline on changes in samples between sampling point and analysis.

Samples can change in two modes between the sample point and the analysis. Samples may change chemically at constant overall composition. One example of this mode is the change of phosphate from a dibasic acid to a tribasic acid as it cools from boiler temperature to analytical temperature of 25°C. Crystal species may change crystalline form, disproportionate or react in other ways. Hydrogen peroxide may decompose in the sample line.

The second mode of change is to alter the sample. Examples of the mode are deposition or and release in sample lines, refluxing in sample lines, reaction of oxygen with sample line deposits, and entry of oxygen through apparently, but not completely, tight compression fittings.

A related issue is non-representative sampling. Blowdown samples collected from a blowdown header that is not flowing may be hours old before they are analyzed.

The task group believes that much, if not all of the issue has been dealt with in the literature, but that it needs to be collected and disseminated.

A collection of sample changes would provide guidance to people less familiar with these issues than PCC. We suggest that this task group collect the available literature and prepare a draft guideline.

Is the Daucik-Lister task group doing similar work and should the work be combined?

Note: "Guideline" is used in a sense somewhat different from the usual IAPWS guideline. It may be that a new type of document if the EC so chooses. It could also be an expansion of the meaning of Guideline.

Jim Bellows Geoff Bignold Eric Maughan Barry Hughes