Attachment 9

IAPWS WG PCC

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PROPOSAL FOR IAPWS SUPPORT TO INTERNATIONAL COLLABORATION PROJECT

Improved analysis of low concentrations of particulate metal oxides **in water/steam cycles**

PARTICIPANTS

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YOUNG SCIENTIST

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BACKGROUND

The formation and transport of corrosion products in water/steam cycles has been a major problem since the inception of thermal energy circuits. The determination of corrosion product concentrations has subsequently become a very important method of monitoring the chemical state of an operating unit. Since the solubility of the corrosion products is rather low at the conditions of the water/steam cycle, they appear mainly as particulates. This complicates the sampling, as the heterogeneous character of the system can easily lead to partial separation of phases resulting in non-representative sampling. This problem becomes particularly pronounced at low concentrations of corrosion products.

The subject has received attention in several publications and even specific procedural norms have been issued (1). However, the norms have found little application in practice because of their high cost and inability to achieve reliable results. The only comprehensive work concentrating on steam sampling, where most of the critical parameters are evaluated (2), deals with the design of sampling equipment. Most power utilities analyse the corrosion products at different places in the cycle and have different designs of equipment and use their own procedures. The reliability of the data is poor and outliers occur frequently.

Several members of IAPWS WG PCC are involved in minor investigations verifying the effects of different parameters on the reliability of corrosion product analyses; however, an overall evaluation of the sampling and analysis of corrosion products in water/steam cycles is missing. A general agreement on system design and operating procedures for sampling would be of great value to industry.

OBJECTIVE

The objective of this project is to assemble the experience within IAPWS WG PCC on the sampling of corrosion products from steam/water cycles, augment it with published information and then provide an assessment of the state of the art. WG PCC will on this basis issue a recommendation for reliable practice.

It is acknowledged that the overall subject of sampling and analysing corrosion products from coolant systems is extensive and complex. The scope of this proposed collaboration therefore concentrates on issues that are of immediate concern to both steam and water systems in operating plants, namely:

- how representative are measurements taken from cooled samples obtained at the end of a (usually) iron-containing-alloy sample line?
- how precise does a measurement of iron corrosion products need to be at the <1ppb and the >1ppb level?
- what is the partition of iron between particles and solubles at those levels?

COMPLETION

The young scientist will visit three members (Canada, Switzerland and Denmark) of the WG PCC, which are in possession of unpublished data and experience related to the sampling of corrosion products. He will on the basis of this material and the published work produce an assessment of the state of the art.

Deliverables

Report on “Assessment of the State of the Art of Sampling of Corrosion Products from Water/Steam Cycles”.

TIME SCHEDULE

The work will be done in autumn 2006. The stay in Canada, Switzerland and Denmark will take about one week in each country. The literature study and reporting will take 5 weeks.

Budget

Item	Cost ($US)	Sponsor
Travelling young scientist	3 500	
Cost of living young scientist	3 000	
Sub sum	6 500	IAPWS
Local costs	1 500	
Time participants	15 000	
Sub sum	16 500	Participants
Total cost	22 000	

Required contribution from IAPWS is $ 6 500.

References

1 Standard Practice for Sampling Steam, ASTM D-1066-97.
2 Jonas Inc., Development of a Steam Sampling System, EPRI TR-100196, Dec. 1991.

Attachment 10

YOUNG SCIENTIST IAPWS FELLOWSHIP PROJECT

Predictive Scheme for Standard Thermodynamic Properties of Aqueous Substituted Benzenes over a Wide Range of Temperatures and Pressures

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Background and Scope

This project is aimed at measuring the high-temperature thermodynamic properties of aqueous solutions of organic compounds. The development and application of instruments capable of operating up to and above 300°C at the University of Delaware, Blais Pascal University in Clermont-Ferrand, the CNEA (Argentina), the University of Guelph, the Institute of Chemical Technology in Prague, the University of Lethbridge and other laboratories during the last ten years has made it possible to launch a systematic evaluation and modeling of these systems. Because of the experimental difficulties of such measurements, much attention has been focused on the development of models that are based on a group contribution approximation. Such models are, however, often constrained by an incomplete experimental database and are applied only to the thermodynamic property (or properties) measured in the authors' own laboratories. The only group contribution schemes providing a complete description of standard state thermodynamic properties at high temperatures and pressures for a wide set of aqueous organics have been up to recently those by Amend and Helgeson (*Geochim. Cosmochim. Acta* 1997, **61**, 11-46) and Criss and Wood (*J. Chem. Thermodyn.* 1996, **28**, 723-741). The first method is based on the modified Helgeson-Kirkham-Flowers model for standard partial molar properties; the second is based on the "density" model. Both papers are based on data available in 1996. These are just a small fraction of experimental data available nowadays, leading generally to only semi-quantitative predictions. A new approach, which is based on the Sedlbauer-O'Connell-Wood (SOCW) equation of state, was published by Yezdimer *et al.* (*Chem. Geol.* 2000, **164**, 259-280). This treatment included simultaneous parameterization of the model by most available results on standard molar derivative properties (volumes and heat capacities): no other data were, however, taken into account. A systematic attempt to improve this method was initiated in the last few years, leading to exhaustive data compilation and model parameterization for aqueous aliphatic, aromatic and cyclic hydrocarbons (Sedlbauer *et al.*, *AIChE J.* 2002, **48**, 2936-2959), phenols and anilines (Censky *et al.*, *Cosmochim. Acta*, 2006, in press) and ketones, ethers and esters (Sedlbauer and Slavik, *J. Solution Chem.*, in press.).

The group contribution scheme based on the SOCW model has been designed from the beginning to incorporate three basic features:

1) It is extendable, i.e. new substituent functional groups can be added to the scheme with the properties of the hydrocarbon backbone and other already determined groups unchanged by this addition.

2) The extension is always based on careful compilation and presentation of available data on all standard molar thermodynamic properties (including their

3) evaluation from experimental results on related quantities such as Henry's law constants, phase equilibrium data, dissociation constants etc.). The data base is open to be used in the future for parameterization of other models, if proved more suitable than the SOCW model.

4) Adding just a few functional groups at a time and collaboration with the prime experimental laboratories specialized in high temperature thermodynamics of aqueous systems allows supplementing the existing data bases with targeted experimental efforts, needed for reliable representation of the new functional groups in a wide range of conditions. This approach was already used in case of anilines, phenols, ketones, ethers and esters (on-purpose experimental studies were published preceding the extension of the group contribution scheme).

Project Objectives

The purpose of the project is to extend the high temperature group contribution scheme by addition of nitro- functional group directly bound to aromatic ring and of phenolate (charged) functional group. Aromatic nitro compounds are often applied technologically and their effluents belong among the most environmentally sensitive systems. Phenolates appear in large amounts namely as intermediates in the production of phenol and due to their solubility constitute an important part of waste waters from such processes.

The project has two main objectives:

1) To develop the extended group contribution scheme by simultaneous treatment of all available standard thermodynamic data for nitro- and phenolate aqueous systems. In both cases it is expected that, in addition to NO_2- and -O^- first order groups, the second order functional groups will be also needed, correcting for near neighbor interactions (namely two substituents in *ortho*- position). The model extension will be based on literature compilation and data evaluation that will have to include high temperatures as well as the reference conditions (298 K, 0.1 MPa) used as integration constants in the SOCW model.

2) To supplement the existing scarce experimental results available for these aqueous systems at high temperatures by measurements of the ionization constants of isomeric ortho-, meta-, and para-nitrophenols up to 250°C using hydrothermal indicators and UV-VIS spectroscopy. A unique apparatus of this type is available at the University of Guelph, where the experimental part of the project should be accomplished. The choice of nitrophenols as target solutes had two reasons: i) their solubility is larger than solubility of non-polar aromatic

3) solutes, e.g. nitrobenzene, allowing measurements of the standard derivative properties to be made also. (It is expected that Ms. Ehlerova will complete the experimental study by measuring the standard molar heat capacities of nitrophenols to high temperatures at Universite Blaise Pascal, Clermont-Ferrand: this stay will be financed by the European exchange program Socrates); ii) as weak acids, nitrophenols are suitable for measurements of the ionization constants and include both functional groups of interest.

The work at Guelph will be carried out under the co-supervision of Dr. Sedlbauer, Dr. Tremaine and Dr. Liliana Trevani. The project will make use of the high-temperature UV-visible flow system developed by Trevani *et al*. (*J. Solution Chem.* 2001, **30**, 585–621) and thermally stable colorimetric indicators developed by Keith Johnston's group at the University of Texas (Austen), as used in our laboratory at temperatures up to 350 °C (Clarke *et al.*, *Geochim. Cosmochim. Acta* 2005, **69**, 3029-3043; Bulemela *et al*., *J. Solution Chem*. 2005, **34**, 769–788). The nitro-phenol UV-visible spectra overlap with the colorimetric indicator spectra, and it may be possible to measure the ionization constants at high temperature directly, by determining the ratio of the ionic and neutral forms in standard buffers with known pH. Both approaches will be tried.

Justification for IAPWS Support

The IAPWS funding will make it possible for the young scientist to spend at the University of Guelph for four months in a single stay starting in the fall of 2006. The purpose of this visit will be collaboration with Prof. Tremaine and Dr. Trevani on experimental determinations of the ionization constant of nitrophenols under a wide range of conditions using high temperature UV-visible spectroscopy. Subsequently the two teams from the University of Guelph and from the Technical University of Liberec will cooperate on development of the extended group contribution scheme for aqueous nitro-substituted aromates and aqueous phenolates. Involved in this part of the project will be also Prof. Mayer from the Blaise Pascal University in Clermont-Ferrand.

Budget (in $US)

Subsistence for 4 months: IAPWS Young Scientist Grant	*$6000*
Travel (round trip): to be paid by TU Liberec	*$1500*
Chemicals, supplies, equipment: to be paid by U. Guelph	*$4500*
Total	**$12000**