

EXPIRED

IAPWS Certified Research Need - ICRN

Sensors for use at Elevated Temperature in the Plant Cycle of the Power Industry

The IAPWS Working Group Power Cycle Chemistry has examined the published work in the area of high temperature water chemistry sensors for the power cycle and recognizes that there is a requirement for work to be pursued in this field and has prepared this document to assist potential investigators in obtaining sponsorship.

There is a need for the power industry to adopt the use of such sensors for monitoring corrosion and other issues in cycle chemistry. However, the availability of commercial products is limited. In addition, existing information for measurements made by sensors at room temperature cannot be adequately related to high temperature use.

This ICRN specifies the main questions that must be answered for the development of high temperature water chemistry sensors.

Although encouraging this work, IAPWS is not able under its statutes to provide financial support. The IAPWS contacts can provide any further development information and will act as a liaison between research groups.

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Background

Adequate water chemistry control is required for reliable operation of fossil and nuclear power plants, which is supported by suitable monitoring of water chemistry with on-line instruments [1-3].

Over the past two decades, attempts have been made to measure chemical variables at temperature (and pressure). Some sensors have been produced and several publications have been made on the theoretical calculation of a few values at temperature [4-8].

Although some sensors have been designed for operation at elevated temperatures, *e.g.*, for measuring temperature, pressure and flow, there are very few instruments for analytical measurements under similar conditions. There are several reasons for this situation:

- materials of construction of sensor
- actual construction
- inappropriate for measurements in low-density water
- handling
- long-term reliability of performance.

Due to the maintenance required for sampling and conditioning systems, it has been the desire of the plant chemistry personnel to install sensors directly into the process streams found in the plant cycle of power plants.

In several instances, chemists have been tempted to abandon the on-line analysis systems because of complexity and the need for intensive maintenance. This drastic measure can negate any warranty issues in the event of failure of materials and where no proof of adherence to manufacturer specifications can be provided.

In addition, according to EN12952-12:2003, it is now mandatory in Europe to measure (reported at 25 °C) at least conductivity after cation exchange (CACE) (cation conductivity), pH and dissolved oxygen in power plant cycles. Most countries in Europe have adopted this standard. The requirements contained in this document are in accordance with other international guidelines and manufacturer specifications.

In nuclear power plants, corrosive conditions in the primary cooling water are often determined by short-lived radiolytic species, *e.g.*, hydrogen peroxide, which are easily decomposed along the sampling line. It is then strongly required that the corrosive conditions

be determined by *in-situ* measurement at elevated temperature with high temperature water chemistry sensors, e.g., electrochemical potential (ECP) sensors and oxidation reduction potential (ORP) sensors. In addition, oxygen control in the PWR secondary cooling system for corrosion mitigation of carbon steel piping of the feed water line, e.g., AVT(O), must have no serious effects on the steam generator (SG) tubing. This means that although some oxygen should exist in the feed water line, minimal amounts can be accepted at the SG inlet. Since it is difficult to determine oxygen concentration at the SG inlet with conventional oxygen detectors due to the oxygen-hydrazine reaction along the sampling line, direct *in-situ* monitoring of oxidant existence by high temperature water chemistry sensors, e.g., ORP or ECP sensors, is strongly required. On-line water chemistry sensors applied in elevated temperature water, especially for nuclear power plants, are listed in Table 1 [9-56]. At the present time, only ECP and ORP sensors have been applied in operating power plants [27, 38, 48]. New sensors are required for monitoring material degradation in plants. Material testing is performed using material samples but no proven *in situ* technique is yet available for plant application [39].

Research needs

Questions to be answered (in order of priority)

1. Are suitable materials of construction available to manufacture high temperature sensors for pH (and ORP), conductivity, dissolved oxygen and corrosion rate?
2. How will these sensors be operated safely within the power plant environment?
3. How long will these sensors be operated continuously within the power plant environment?
4. How can these sensors be calibrated at the temperature of measurement?

Other Questions, on the interpretation of the data from such sensors (will be specified in a following ICRN):

- How will it be possible to relate CACE measurements to *in-situ* conductivity measurements?
- Are sufficient data available to characterize the measured values from 0 °C to the critical point of water?
- How may the measured values be corrected to ambient conditions so that the results at elevated temperature are meaningful to the plant chemist and operator?
- Can corrosion rates be directly measured in high temperature water?

Outputs

- Development of a repository of current knowledge (existing guidelines, instruction sheets, standards, research, plant experience, scientific papers)
- Investigation into results obtained using existing sensors – successes and failures

- Identification of shortcomings of existing materials of construction of high temperature sensors
- Development of a device to test sensors under simulated plant cycle conditions
- Development of new designs
- Determination of reliability of sensor materials for use under elevated temperature and pressure conditions
- Development of *in situ* calibration techniques
- Collection of data for each variable over the temperature range 0 °C to the critical point of water
- Development of suitable temperature-correction algorithms
- Evaluation of degradation of sensors during long-term exposure tests.

Beneficiaries

1. Plant manufacturers
2. Utilities and supporting organizations
3. Manufacturers of sensors for the power industry

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| Measured items | Instruments | Principal | Application status | | Further subjects |
|-------------------------------------|--|---|-----------------------------------|--------------|--------------------------|
| | | | 2000 [9,10] | 2010 [40-42] | |
| Radioactivity | | | | | |
| deposits on pipe | semiconductor detector | g-ray spectroscopy | Forsmark-2 [10] | | |
| Water properties | | | | | |
| [¹⁰ B] | Am-Be neutron source + neutron counter | measurement of neutron absorption by long counter | PWRs (Germany, Czech) [10,11] | | |
| [H ₂]/[D ₂] | Pd wire + electric resistance measurement | resistance of Pd as a function of [H ₂]/[D ₂] in Pd and temperature | CANDU (Point Lepreau) [10,12] | | |
| [O ₂] | pressure balance type | membrane polarography | Lab [13] | | |
| [H ₂ O ₂] | pressure balance type | membrane polarography | Lab [13] | | |
| conductivity | sensor array | a couple of ECP and FDC | Lab [43] | | |
| | coupled Pt electrodes | change in direct current | VVER (Lovisa-1) [10,14], Lab [15] | | |
| | triple Pt electrodes | Cole-Cole plot | Lab [15] | | |
| pH | YSZ type pH sensor | ion electrode | VVER (Lovisa-1) [10,16], Lab [17] | | continuous monitor [r |
| | Bi-Pb/PbO pH sensor | ion electrode | VVER [18] | | |
| Water/material interaction | TiO ₂ type pH sensor | flat band potential | Lab [19] | | for crevice pH [heat re |
| ECP | external electrode | Ag/AgCl | PWR 2ndary (Biblis) [20] | | |
| | internal electrode | Pt | BWR side stream (US) [21] | | |
| | | Ag/AgCl, | PWR primary (Ringhals) [22] | | PWR (Tsuruga-2) [44,45] |
| | | Fe/Fe ₃ O ₄ , | BWR (Barsebeck-1) [23] | | |
| | | Pd-hydride | BWR (US) [24], (Tokat-2) [25] | | |
| | | Ni/NiO | RR (Halden) [26] | | |
| ORP | internal electrode + Pt electrode | Ag/AgCl | FPP (US) [27] | | continuous monitor [r |
| corrosion rate | eddy current detector | wall thickness measurement | Lab [49] | | for crack size [heat re: |
| | DC current detector | Tafel plot | Lab [28] | | |
| | AC current detector | Nyquist and Bode diagrams | Lab [29] | | |
| surface properties | CDE detector | oxide film ER measurement | Lab [30] | | |
| | in-situ observation | laser Raman spectroscopy | Lab [50] | | |
| SCC | complex impedance | Cole-Cole plot | Lab [43] | | |
| | SSRT+SEM | SCC area ratio | BWR (US) [31] | | |
| susceptibility | dynamic ECP sensor | EC noise analysis | BWR [32-34] | | |
| crack initiation | direct observation | LFDMs | Lab [51,52] | | |
| | AE sensor | acoustic noise analysis | BWR (Taiwan) [53] | | |
| crack growth rate | CT specimen+PDM | crack depth measurement | Lab [51] | | |
| | Pt sensor+off-line | combined analysis of ECP, | Lab [54] | | |
| iron species | characterization | XRF, Mossbauer ¹ | RR [55] | | constant load [heat re |
| | AC: alternative current | BWR: boiling water reactor | PWR (Golfesh) [56] | | |
| | DC: direct current | DCB: double cantilever beam | | | |
| | FDC: frequency dependent complex impedance | EC: electrochemistry | | | |
| | PDM: potential drop method | EC: electrochemical corrosion potential | | | |
| | SSRT: slow strain rate test | LFDMs: long focal distance microscope | | | |
| | | Lab: laboratory test | | | |
| | | PWR: pressurized water reactor | | | |
| | | VVER: Russian type PWR | | | |
| | | XRF: X-ray fluorescence | | | |
| | | CANDU: Canadian heavy water reactor | | | |
| | | EC: electrochemistry | | | |
| | | LFDMs: long focal distance microscope | | | |
| | | RR: research reactor | | | |
| | | XRF: X-ray fluorescence | | | |
| | | CDE: controlled distance electrochemistry | | | |
| | | ECP: electrochemical corrosion potential | | | |
| | | MS: mechanical sealing | | | |
| | | ORP: oxidation-reduction | | | |
| | | SCC: stress corrosion cracking | | | |
| | | YSZ: Yttria sensitized Zirconia | | | |
| | | CT: compact tension | | | |
| | | ER: electric resistance | | | |
| | | SEM: scanning electron | | | |