
2006's Scientific and Technical Contributions

Eric Maughan

PPChem 2006, 8(1), 6–7

Summary of the Eskom International Chemistry Conference "Power Plant Chemistry and Process Water Treatment"

This paper is a very brief summary of the recent traditional and as always very successful Eskom International Chemistry Conference, which took place in Mabalingwe, South Africa, on November 9–11, 2005.

Karol Daucik

PPChem 2006, 8(1), 10–12

Decomposition of Chlorinated Hydrocarbons in the Water/Steam Cycle of a Power Plant

By mistake, a small amount of trichlorethane was injected into the condensate of a power plant unit with a once-through boiler. The gradual decomposition of the contaminant could be observed by measuring acid conductivity at different places along the feedwater and steam path. The ion chromatographic analysis showed that the increase in acid conductivity was attributable to chloride. The observations give a basis for simplified evaluation of the kinetics of thermal decomposition of trichlorethane in water.

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PPChem 2006, 8(1), 13–19

The Potential Use of Amines in High Temperature Once-Through Nuclear Power Plant Boilers

A project to implement amine dosing to the steam/water circuit in two of British Energy's nuclear power plants is underway, which, it is hoped, will arrest increases in boiler pressure drop. This paper summarises the reasoning behind the decision to go forward with amine dosing, the amine selection process, and progress to-date with the implementation project. Evidence from boiler rig testing is presented, which shows that amine dosing should be effective at arresting increases in boiler pressure loss. Results from a short plant trial with dimethylamine dosing are also presented, which show that amine decomposition under plant operating conditions is low.

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Thomas Blum*

PPChem 2006, 8(1), 21–30

Formation of Polyamine Films on Iron Surfaces under Power Plant Conditions – Laboratory Investigations

Polyamines have been used for more than two decades and are currently being applied to an increasing extent for successful conditioning of low, medium and high pressure boiler and steam/water cycles, this despite the fact that amines in general are comparatively reactive and in some cases less thermally stable. In some high temperature applications, polyamines and amines are repeatedly alleged in the literature to degrade into volatile organic acids, especially to form the very stable and corrosive acetic acid, in addition to dreaded sticky degradation products on metal surfaces.

In order to find a suitable response to these risky and long debated topics and to provide laboratory evidence to support the numerous practical successes and performance achievements obtained over more than 20 years, we have performed some laboratory experiments that address the origin of volatile acids, the question of stability of decomposition products and the film forming features of polyamines and their protection of metal surfaces. The estimation of low or residual concentrations of polyamines as typically encountered in practice is also discussed. These experiments were partly performed in open vessels at atmospheric pressure. Experiments involving polyamine stabilities were conducted in an autoclave at 175 °C and 400 up to 520 °C. Although laboratory experiments under such simple conditions are not always comparable to practical conditions, the results obtained still offer acceptable confirmation of the many positive practical observations and applications of polyamines in industry.

Kevin J. Shields
Dennis A. Frey
Robert D. Bartholomew
Gary H. Roberts

PPChem 2006, 8(1), 33–42

Chemical Cleaning of Fossil Steam Generators with Organic Solvents: North American Experience

Use of organic-based solvents as an alternative to inorganic solvents has been practiced in North America since the 1960s. Solvents in use include hydroxyacetic-formic acid, citric acid, and ethylenediaminetetraacetic acid. Initial applications were in the cleaning of waterwalls of conventional fossil fueled boilers, including drum-type boilers and once-through subcritical and supercritical steam generators, and subsequently in the cleaning of superheaters and reheaters. Most recently, organic solvents have been used in the preoperational cleaning of heat recovery steam generators of combined cycle units.

The organic solvents offer certain advantages as well as some limitations and these aspects must be considered during the selection process. Various characteristics and features of these organic solvents are considered and comparisons to commonly used inorganic solvents are made. Case studies based on field application of the organic solvents for specific purposes are presented to demonstrate the possible uses of these solvents and the required process conditions.

PPChem 2006, 8(1), 43–58

2005's Scientific and Technical Contributions

As every year, the January issue closes with abstracts of all the articles published in this journal in the last year. Back issues of our journal are – with few exceptions – still available; interested parties can receive PDF files of all articles by e-mail. The order forms may be downloaded from our homepage.

Geoff J. Bignold

PPChem 2006, 8(2), 68–73

The Behaviour of Ammonia, Amines, Carbon Dioxide and Organic Anions during Condensation in an Air Cooled Condenser

Air cooled condensers are being used increasingly frequently in new plants, not only in arid locations where supplies of large quantities of cooling water are absent, but also in many places where restrictions are being imposed on the issue of licences for abstraction of water for cooling applications. It is economically important to achieve the lowest practicable steam temperature and pressure in order to maximise the efficiency of the steam turbine. Heat transfer from the condensing steam to air, with only a small temperature difference, requires an air cooled condenser (ACC) with very large areas of finned tubing, which is normally made of carbon steel. Even with very modest corrosion rates, the very large area of steel can contribute a significant amount of iron to the condensate, and this can be a major source of iron rich deposits accumulating in the boiler plant.

The corrosion processes occurring in a steel air cooled condenser will inevitably be influenced by the chemistry of the condensate, which changes as the condensation process proceeds.

In a circuit where alkalinity is provided by the presence of ammonia, the early stages of condensation in the ACC will have a relatively low ammonia concentration in the liquid phase and correspondingly low pH. Any organic anions such as acetate or formate found in the steam will suppress the pH further. Carbon dioxide will also have this effect. Thus it is the upstream ends of the ACC tubes that will be expected to contribute most to the iron level in condensate. As steam passes further along the condenser tubes, the pH in the condensate rises, so that any dissolved iron may become supersaturated and some particulate iron is produced.

If the steam contains an amine with a distribution coefficient that favours the water phase, then the water in the early stages of condensation may have an appreciably higher pH and the loss of iron from steel surfaces may be suppressed. However, the interactions are complex. Amine decomposition elsewhere in the circuit is likely to cause the concentrations of carbon dioxide and organic anions in the steam to rise, and these will be less volatile in the condenser and consequently more difficult to expel from the circuit. An initial approach to understanding these interactions is set out in this paper.

S. Ronnie Pate
Sam J. McChesney
Randy C. Turner

PPChem 2006, 8(2), 74–81

Southern Company's Approach to Cycle Chemistry

The Southern Company has long sought to develop water chemistry treatment philosophies and out-of-specification actions that ensure long-term operations and availability of the fossil-fueled steam units. This has been accomplished by utilizing the best known science from world class chemists, both academic and from original equipment manufacturers, and from organizations such as the Electric Power Research Institute (EPRI), as well as the personal experience of the chemistry practitioners. This paper explains the results sought and basic steps on how to achieve these ends. Some of the concepts covered include minimum qualifications for plant chemists, chemistry control philosophies, and annual peer reviews, including EPRI Benchmarking of each unit's chemistry program.

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PPChem 2006, 8(2), 82–88

Water Chemistry Control of an Ultra-Supercritical Boiler – Avedøre Unit 2

Avedøre Unit 2 is an ultra-supercritical boiler with an integrated steam cycle that includes a biomass boiler and two heat recovery steam generators. The unit is only equipped with a condensate polishing capacity of 14 % at full load. This results in chemical excursions during startup of the boiler, when salt deposits are washed off the turbine. Initiatives are being taken to eliminate a high content of impurities in the condensate and feedwater at startup.

Michael A. Sadler
Kevin J. Shields

PPChem 2006, 8(2), 95–104

Minimizing Levels of Volatile Organic Acids and Carbon Dioxide in Steam/Water Circuits

Low concentrations of weak organic acids such as acetic and formic acids are commonly found in water sampled from the steam/water circuits of boilers and steam generators. The debate concerning their influence on corrosion in these circuits continues, but there is agreement that their presence is a nuisance and if reasonably possible levels of these impurities in steam/water should be minimized. The main origin of these volatile organic acids has been shown to be traces of more complex organic impurities present in makeup water. Improved techniques of deionization such as the use of reverse osmosis will significantly reduce the organic contaminant levels in makeup water. There is clear evidence that levels of weak organic acids can be effectively removed from the steam/water circuit by the use of condensate polishing operating in its conventional H-OH mode. Polishers operating in the economical ammonium form will in most cases also successfully control these impurities, but, in some circumstances, difficulties could arise, so care in monitoring their performance is recommended.

Stefan A. Huber

PPChem 2006, 8(2), 105–116

The Behaviour of Natural Organic Matter in Water Treatment and the Water/Steam Cycle: Deeper Insights

The paper focuses on specific components of natural organic matter (NOM) whose molecular charge densities are too low to allow efficient removal by ion exchange. This fraction of NOM is mainly polysaccharidic in nature. It does not contribute much to conductivity in the makeup water, but in the water/steam cycle the reaction products are decomposed to organic acids (pathway: polysaccharides → monosaccharides → organic acids). In the past, non-ionic NOM was largely overlooked because it was not accessible to analytical techniques. Only recently has a new technique, called LC-OCD (liquid chromatography – organic carbon detection), allowed rapid identification and quantification. The paper describes in detail the behaviour of polysaccharides during pre-treatment, demineralization and in the water/steam cycle. Strategies on how to remove polysaccharides in the makeup water are also presented.

Volker Ender
Björn Kettner
Thomas Schumann
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PPChem 2006, 8(2), 117–125

The Influence of Temperature on the Removal of Organics from Natural Waters by Ion Exchange – Laboratory and Pilot Plant Experiments

In laboratory and pilot plant experiments we investigated the influence of temperature on the removal of organics from natural waters by ion exchange resins and three types of scavenger resins. The temperature was varied during the loading phase as well as during the regeneration process (20 °C, 30 °C, and 40 °C in the laboratory experiments;

30 °C, 40 °C, and 50 °C in the pilot plant). The water quality was analysed using the liquid chromatography – organic carbon detection (LC-OCD) method.

The following main results were found:

- Neither the variation in the loading temperature nor the variation in the regeneration temperature could influence the removal of total organic carbon (TOC) before the breakthrough point. The reaction enthalpy of the removal of TOC from natural waters by ion exchange resins is therefore about zero.
- A higher loading temperature leads to a later TOC breakthrough point. Higher regeneration temperatures give better TOC regeneration rates.
- The most important potential for the improvement of the retention of organic matter by ion exchange resins is a better understanding of the relation between TOC ion exchange and the adsorption mechanisms regarding their individual fractions. This seems to be valid especially for the hydrophobics fraction.

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PPChem 2006, 8(3), 132–136

Effect of Amines on the Surface Charge Properties of Iron Oxides

Large-scale, flow-through experiments were conducted at Chalk River Laboratories [1,2] in which the deposition rate of suspended magnetite (Fe_3O_4) particles onto Inconel boiler tube walls was determined in water at 270 °C with the pH controlled nominally at 6.2 (at 270 °C) by the use of potassium hydroxide and various amine buffers (morpholine (MOR), dimethylamine (DMA), ethanolamine (ETA), and ammonia). Relative to the deposition rates in KOH solutions as the control, MOR was found to result in the highest magnetite deposition rates among the various amines, and DMA the lowest. A hypothesis was developed from this work that sorption of the protonated form of the amine onto negatively charged magnetite surfaces might enhance the deposition rate by reducing electrostatic repulsion between the magnetite particles and the boiler tube walls. This paper summarizes results of potentiometric titrations performed in 0.03 molal NaTr to determine whether MOR (200 and 250 °C) and DMA (150 and 200 °C) or their protonated cations significantly alter the proton-induced surface charge of magnetite over the range of pHs of interest in PWR secondary cycles [3]. However, in order to measure these effects, it was deemed necessary to first establish the hydrolysis constants of MOR and DMA over the entire range of experimental conditions of the magnetite surface titrations, and in the same ionic medium.

Anton Banweg

PPChem 2006, 8(3), 137–140

Organic Treatment Chemicals in Steam Generating Systems – Using the Right Tool in the Right Application

Nalco has developed organic treatment chemistries for many applications in steam generating systems to provide better performance than the traditional alternatives. Several specific applications are discussed: fluorescent organic materials for monitoring and diagnostic applications, all-polymer internal boiler water treatment for deposit inhibition, hydrazine alternatives, and engineered multiple amine products for optimal condensate system corrosion protection.

Wayne Micheletti

PPChem 2006, 8(3), 141–150

Atmospheric Emissions from Power Plant Cooling Towers

Power plant recirculated cooling systems (cooling towers) are not typically thought of as potential sources of air pollution. However, atmospheric emissions can be important considerations that may influence cooling tower design and operation. This paper discusses relevant U.S. environmental regulations for potential atmospheric pollutants from power plant cooling towers, and various methods for estimating and controlling these emissions.

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PPChem 2006, 8(3), 159–168

Corrosion Product Sampling at Koeberg Nuclear Power Station

Corrosion and corrosion product transport have a negative impact on the performance and reliability of secondary cycle systems and components. Taking a grab sample, acidifying it and measuring the iron and copper concentrations is not an effective method to measure corrosion products as the sample is not representative and results are limited to the detection level of the analytical technique employed. Koeberg has installed fixed corrosion product sampling equipment at several strategic points in the secondary system. The technique involves accumulation of the insoluble material on a filter paper over a period of time and then analysis of the deposit. A cation resin impregnated filter collects the soluble ionic material which is analysed separately. The filter papers are digested with acids and chemical analysis is performed to determine insoluble and soluble iron and copper concentrations by flame and graphite furnace atomic absorption spectrophotometry.

The sampling equipment, sample collection, analysis method, operating experience and some further developments are discussed.

Neil B. Caris

PPChem 2006, 8(3), 169–174

The Changing Role of Chemistry in the Power Industry

Corrosion costs the U.S. electricity industry between five and ten billion dollars a year. In steam generating plants it is estimated that over half the forced outages are caused by corrosion, and in the U.S. industry, corrosion increases the cost of electricity more than it increases the cost of any other product, adding over 10 % to its price. The total cost of corrosion to U.S. industry is in excess of \$276 billion annually, of which more than 30 % could be prevented through the use of optimum corrosion management practices [1].

In order to effectively deal with these issues it will require a coordinated approach throughout the industry, in which chemistry has a major role to play. Chemistry has effectively moved from being a problem to being a solution for materials and corrosion issues, and judging by the current advances and initiatives, will continue to do so. The window of opportunity to positively influence the entire industry is here. This will be especially challenging for us as chemists in Eskom, with an ageing fleet and lack of excess generating capacity. The spin-off of taking up this challenge to "get our chemistry right" and take a quantum step forward would be a significant positive effect on the unit capability factor (UCF) and the forced loss rate (UCLF) for the Generation Division. This could, in turn, influence issues as far reaching as the cost of electricity for the South African consumer and when the construction of new generating plant is scheduled.

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PPChem 2006, 8(3), 180–189

The Potential of Alternative Sorbents for Desulphurization – From Laboratory Tests to the Real Combustion Unit

At present, natural limestone is used for the desulphurization of waste gases from the combustion of fossil fuels. However, it is important to save all primary resources for the future, and this applies for limestone as well. The research discussed in this paper focused on finding potential alternative sorbents for the purpose of desulphurization using the dry additive method. The article primarily describes desulphurization tests of selected substances, starting from tests in the laboratory and in pilot scale units, through tests in real combustion facilities.

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PPChem 2006, 8(4), 197–202

The Behavior of Organics in a Makeup Water Plant

It is well known that organic compounds are decomposed in the water/steam cycle and affect the cation conductivity of the steam. KEMA and others have demonstrated that acid decomposition products like acetate and formate are enriched in the early condensate. KEMA has found strong indications that these organics played a role in a low

pressure turbine blade failure. As a measure to prevent future damage, the Dutch power industry asked KEMA to carry out research to assess the behavior of organics in makeup water plants based on ion exchange resins. A survey has been conducted of the raw water sources used by the Dutch power industry. It appears that not only the concentration of the organics (total organic carbon, TOC) is different but also the composition. Because most of the TOC could be classified as natural organic material (NOM) the seasonal influence on the TOC composition has also been addressed.

The performance of a demineralization plant is influenced by the quality of the raw water, the composition of the TOC playing a very important role. The research revealed a seasonal influence on the TOC concentration and composition in the makeup water after mixed bed. With the results it is now much easier to predict the possibility of operational disturbances and/or decreased makeup water quality and to implement the technical alternatives to prevent these.

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PPChem 2006, 8(4), 203–207

The Results of Chemical Cleaning by Organic Chemicals of Boiler Tubes of a Plant Operated on OT

In December 2003, Unit 1 of the Chita Second Thermal Power Plant underwent chemical cleaning; the first time our company has chemically cleaned a plant operated on oxygenated treatment (OT). The cleaning resulted in the complete removal of scale using the procedure typically applied in units operated on all-volatile treatment (AVT), and there was no corrosion caused by excessive cleaning. However, we discovered that the acid cleaning process requires more time than in plants operated on AVT, and consequently this must be reflected in future chemical cleaning processes of units operated on OT.

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PPChem 2006, 8(4), 208–214

Aspects of the Distribution of Volatile Amines in LP Turbines

Minor amounts of acids have frequently been identified in various areas of LP turbines that are exposed to initial condensation processes. To avoid the general use of highly corrosion-resistant materials in such areas, an optimal precautionary measure is to provide for sufficient alkalization of the initial condensates. The effectiveness of the alkalization in preventing corrosive attack by contaminants is dependent on a number of factors. Several related problems are discussed.

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PPChem 2006, 8(4), 224–233

TOC: The Contaminant Seldom Looked for in Feedwater Makeup and Other Sources of Organic Contamination in the Power Plant

All life forms, their wastes and their decomposition products fall into the category of naturally occurring organic matter (NOM). Furthermore, man also contributes to the overall load with synthetic organic compounds such as plastics, organic solvents, pesticides, organic coatings and polymers, which do not occur in nature.

At face value the majority of organic compounds appear to be insoluble due to their non-polar nature and are therefore considered to be immiscible in water. Nevertheless, water as the universal solvent will retain certain fractions, whether as trace soluble compounds or due to electrostatic forces, e.g., van der Waals.

NOM and man-made organics are difficult to detect by conventional means, e.g., by conductivity or pH measurements, and specialised equipment is required. Once a contaminant is identified as such, steps must be taken for effective removal before it enters the power plant cycle. However subsequent contamination within the plant cycle should not be overlooked.

This presentation explores:

- The nature of organic matter found in water supplies
- Identifying whether contamination by organic matter is taking place in the pre-treatment plant as well as the power plant cycle

- Measurement of organic matter, i.e., different methods
- Effects of organic matter on the plant cycle chemistry
- Effective measures to attempt to counteract any detrimental effects
- Case studies
- Organic contaminants which might be introduced into the plant cycle

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PPChem 2006, 8(4), 234–243

Concentrations of Total Organic Carbon and Trihalomethanes in Feedwater of a Nuclear Power Plant

A UK Magnox coastal power station was found to experience organic fouling of the condensate polishing plant resins, leading to impaired anion resin kinetics. After 25 years of operation it also began to experience some on-load corrosion boiler tube leaks from a source of halide. Dry primary coolant of carbon dioxide has to be maintained, and each boiler tube leak requires that power must be reduced to plug the leaking tube. Sources of the organic materials were investigated and trihalomethanes (THMs) were identified in the station 'Town's Main' water supply. Seasonal variations and the change in concentration through the make-up water treatment plant and in the steam/water circuit were investigated. Approximately 4 % of the total organic carbon (TOC) and 80 % of the THMs passed through the water treatment plant (WTP) with some of the remaining THMs breaking down in the once-through boiler, in this case releasing halide into the boiler. This required palliative measures for boiler alkalisiation and an upgrade to the WTP.

Robert Svoboda

PPChem 2006, 8(4), 244–248

Down Under – The ESAA's Conference "Power Station Chemistry 2006"

This paper reports about the last Power Station Chemistry Conference organized bi-annually by the Energy Supply Association of Australia. This year, thirty technical papers were presented to 121 participants from 9 countries. In addition, two interesting training courses were offered to the conference participants. The topics of the conference, especially the advanced considerations on water resource management, are of worldwide relevance.

Robert Svoboda

PPChem 2006, 8(5), 270–276

Chemistry in Steam Turbines

The local chemical environment in steam turbines is governed by the solubility and the volatility of substances in the steam. Both are influenced by steam expansion and condensation. Nowadays there is sufficient knowledge to predict, quantify and experimentally verify these effects. Basic data and experimental results as well as their practical application are discussed.

Shunsuke Uchida

PPChem 2006, 8(5), 282–292

Latest Experience with Water Chemistry in Nuclear Power Plants in Japan

Water chemistry control in nuclear power plants (NPPs) is principally based on experience with such control in fossil power plants (FPPs). However, the much more severe targets for integrities of fuel assemblies and structural materials, accumulation of radioactive species involved in the primary cooling water and irradiation-induced degradation of component materials cause major differences in the control of the two plant types.

In this article, major cooling systems of NPPs are compared with those of FPPs and then the latest experiences with water chemistry in NPPs, especially evaluation and control of radiolytic species for mitigating corrosion damage of structural materials in primary cooling water of boiling water reactors, are summarized. Procedures of radioactive corrosion product control for moderating shutdown radiation levels and radwaste source reduction are also introduced.

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Danial Quigley

PPChem 2006, 8(5), 293–297

A New Generation of Automated Water and Steam Sampling

Flow control of water and steam samples is important to help assure the quality of the samples and repeatability of the analytical results. Constant velocity in the sample line maintains the integrity of the sample even with the entrapment and/or release of both soluble and insoluble species deposited within the system piping.

Sample inlet temperature and flow are easily controlled under constant conditions. Since sample pressures typically fluctuate, specifically at the time of startup and shut-down or at peaking power plants, maintaining a representative sample can be difficult and labor intensive. The traditional manual sample conditioning system requires constant adjustment during startup or as plant conditions change. With plants continually operating with limited maintenance and operational resources, an automated sample conditioning system is essential. Previously available flow sensing and automated sample conditioning technologies required maintenance on sample lines with high levels of crud. A new automated sample conditioning system continually adjusts a pressure-reducing valve in order to maintain a constant sample flow rate. By automatically maintaining the sample flow rate, unattended representative sampling is achieved. Automatic startup including a controlled blowdown sequence can be initiated from sample conditions or remote commands. Additional features and benefits of an automated sample conditioning system are discussed. System operation, instrument diagrams and results from field trials are presented.

Des McInnes

PPChem 2006, 8(5), 298–302

Stator Cooling Water Deoxygenation Control at Tarong Power Station

Large electrical generators are normally cooled by circulating deionised water through hollow strands in the stator bars. Corrosion of the copper strands can lead to restriction of the cooling water flow through the strands, resulting in reduced cooling and consequently reduced output, or in the worst case catastrophic failure due to local overheating. Two key chemical parameters which can be managed to minimise the risk of flow restriction due to deposition of corrosion products are the dissolved oxygen concentration and the pH of the cooling water.

Tarong Power Station has four 350 MW Hitachi generators and is currently completing generator stator rewinds on all units. In conjunction with the rewind, Tarong has installed a deoxygenation system to provide low oxygen make-up water to the stator cooling systems. The stator cooling water systems have operated for twenty years under low oxygen neutral pH conditions, however the make-up water has always had up to $8 \text{ mg} \cdot \text{kg}^{-1}$ of dissolved oxygen.

This paper briefly discusses the corrosion issues and provides an overview of the modified make-up system at Tarong.

Massalha Loay
Aharon Grabli

PPChem 2006, 8(5), 303–305

Experience with Organic Treatment at American Israeli Paper Mills (AIPM)

The nature of a paper mill, generally, creates a challenge for the water cycle treatment, which must be based on different considerations. An illustration of these considerations is provided and discussed briefly throughout the presentation of American Israeli Paper Mills' experience with amine treatment. Encouraging as well discouraging results of such a treatment are described. Moreover, it is shown that the VGB range values for the water cycle parameters are achievable even in a paper mill.

Eric V. Maughan
David Dalgetty

PPChem 2006, 8(5), 306–310

The On-Line Measurement of Silica in the Power Plant (Part One)

The measurement of silica has always been a core measurement in the plant cycle. However, owing to the perceived complexity of the measurement and the maintenance requirements, many of these on-line analysers have fallen into disuse. The purpose of this paper (in two parts) is an attempt to dispell these notions. A review of the principles of measurement, calibration and troubleshooting is presented in this two-part paper.

David Addison

PPChem 2006, 8(6), 332–343

Improving Chemical Planning Aspects of New Generation Plant – Huntly e3p Project Experience

Modern Engineer, Procure and Construct (EPC) contracts can, at times, lack suitable thermal power station chemistry expertise, resulting in less than best practice design choices being made. It is the responsibility of thermal power station chemists within organisations that are the clients of EPC contracts to ensure that thermal power station chemistry knowledge and good practice is utilised for new projects. This approach has been followed with Genesis Energy's new "Energy, Efficiency, Enhancement" 385 MW combined cycle gas turbine (CCGT) plant (e3p), located at its Huntly Power Station site in New Zealand. This project has also shown that the inclusion of condensate polishing for CCGT units is economically viable with significant long term benefits in terms of lower plant operating costs and improved plant reliability.

Wolfgang Leye
Eric Maughan

PPChem 2006, 8(6), 349–352

The Removal of Magnetite to Protect On-Line Analysis Equipment

The transport of corrosion products through the steam-water circuit is of major importance to the power plant chemist. Several devices are commercially available to perform on-line sampling of corrosion products with subsequent analysis in the laboratory. However, the bulk of the corrosion product (mainly iron oxides) found in the sampling lines for on-line analysis is transported to the chemical analysers, resulting in deposition and blinding of the sensors. This results in additional maintenance.

This paper describes a device for the removal of iron oxide (magnetite) in the sample lines prior to on-line analysis.

David J. Knights

PPChem 2006, 8(6), 353–360

Water for Power Generation in Australia – Now & into the Future

Australia is the driest inhabited continent on earth. This paper summarises the current water usage for electricity generation in Australia and explores the future alternatives for water resources. Many power stations use large volumes of good quality water for cooling, most of which is simply evaporated into the atmosphere. The author examines the community's awareness of the volume of water used for electricity generation and attempts to determine the value of this lost water.

As water resources in Australia are stretched to their limit and the urban and rural users compete for the resource, power generators will need to look for water savings, alternative water supplies, improvements in generating efficiency and other forms of cooling in an attempt to save water. Whilst generators have made water savings, many of the alternative cooling processes and water saving alternatives result in a net increase in carbon emissions, or have other environmental impacts.

The author highlights the issues associated with making water savings, and discusses the water options available in the future for electricity generators.

Dumitra Lucan

PPChem 2006, 8(6), 361–369

Behaviour of Steam Generator Tubing in the Presence of Silicon Compounds

The chemical reactions that take place between the components of concentrated solutions generate an aggressive environment. The presence of this environment and of the tubesheet crevices lead to localized corrosion and the affected tubes cannot ensure effective heat transfer between the fluids of the primary and secondary circuits. Thus, it becomes necessary to understand the corrosion process that occurs on the CANDU steam generator secondary side. The purpose of this paper is the assessment of the corrosion behaviour of the tube material Incoloy 800 at the normal secondary circuit parameters (temperature = 260 °C, pressure = 5.1 MPa). The testing environment was demineralized water containing silicon compounds, at a pH = 9.5 regulated with morpholine and cyclohexylamine. The paper presents the results of metallographic, electronic microscopy and X-ray diffraction examinations, as well as the results of electrochemical measurements.

Eric V. Maughan
David Dalgetty

PPChem 2006, 8(6), 370–373

The On-Line Measurement of Silica in the Power Plant (Part Two)

In Part 1 of this paper, the rationale for the measurement of silica, on-line methods and troubleshooting were presented. In this second part more detail is given on the theory of measurement, the chemistry of the reaction and the calibration of on-line analysers.

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Harald Thorwarth
Günter Scheffknecht

PPChem 2006, 8(6), 374–381

A Thermodynamic Study on the Effects of Individual Flue Gas Components on Mercury Speciation

Thermodynamic equilibrium calculations have been carried out to investigate the effect of common flue gas components on mercury behaviour under oxidising conditions in coal-fired power plants. The calculations were implemented based on the free Gibbs energy minimisation method. Considering homogeneous and heterogeneous reactions the shares of the different elements/compounds were varied over a wide range. The coal mercury content does not show any impact on its own speciation along the temperatures under study. The weak influence of O₂ (g) on the oxidation of elemental mercury, the importance of the coal chlorine content as well as the inhibiting effect of H₂O (g) in the conversion of Hg⁰ (g) to HgCl₂ (g) have been found to be the major flue gas influencing factors.

Josef Denk
Robert Svoboda

PPChem 2006, 8(7), 401–408

Stress Corrosion Cracking due to Carbon Dioxide and Organic Impurities in the Steam/Water Cycle

Carbon dioxide and organic species such as formates or acetates are present in many steam cycles of power plants. However, there is only limited knowledge available concerning their effect on stress corrosion cracking of turbine steels. In the case of CO₂ these data are often controversially discussed. Based on the known mechanisms of stress corrosion cracking of low pressure rotor steels, literature results, company-internal investigations and service experience, the effects of carbon dioxide and organics are discussed.

It is known that both types of impurities can reduce the pH of the condensed steam if this is not compensated by a proper water treatment and may enhance most types of aqueous corrosion of steels, including stress corrosion cracking. The scope of the present investigation was the identification of specific corrosion effects, other than the pH effect. There are some indications of such ion-specific effects, especially for acetate, under very specific test conditions. However, the relevance for real service conditions seems to be limited.

Plant experience feedback indicates that the pH effect of organics has caused some failures in steam turbines, but specific corrosion effects could not be identified unambiguously. It is therefore concluded that specific corrosion effects of these substances are not of prime importance. The priority for protecting the steam turbine against corrosion by carbon dioxide and organics is therefore maintaining a sufficient local pH value.

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PPChem 2006, 8(7), 409–414

The Role of Metal Complexes in Nuclear Reactor Decontamination

Chemical decontamination is the process of removal of radioactivity from corrosion products formed on structural materials in the nuclear reactors. These corrosion products cause problems for the operation and maintenance of the plants. Removal of the radioactive contaminants can be achieved by dissolving the oxide from the system surface using organic complexing agents in low concentrations known as dilute chemical decontamination (DCD) formulations. These organic complexing agents attack the oxide surface and form metal complexes, which further accelerate the dissolution process. The stability of the complexes plays an important role in dissolving the radioactive contaminated oxides. In addition, the DCD process is operated through ion exchange resins for the removal of the dissolved metal ions and radioactive nuclides. In the present study, the kinetics of dissolution of various model corrosion products such as magnetite (Fe₃O₄), hematite (α-Fe₂O₃) and maghemite (γ-Fe₂O₃) have been studied in the presence of complexing agents such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), hydroxyethylethylenediaminepentaacetic acid (HEEDTA), and 2,6 pyridinedicarboxylic acid (PDCA). The reductive roles of metal complexes and organic reducing agents are discussed.

Troy Walker
Les Lloyd

PPChem 2006, 8(7), 415–420

Alternative Water Sources for Industry

Australia's record-breaking drought has placed increasing emphasis on the importance of the security of water supplies for both domestic use and industry.

The decrease in the availability of water that has traditionally been seen as easy to treat is driving some users to investigate alternative sources of water. Developments in water treatment technology have enabled the use of a range of processes to produce this water reliably at ever decreasing costs. This increasing acceptance of new technologies has seen recycling of plant waste streams, municipal wastewater re-use and sea-water desalination, among others, become commonplace.

This paper surveys the trends in water treatment for industry both in Australia and internationally with a review of technologies and case studies of operating plants.

Tamara I. Petrova
Valery I. Kashinsky
Viktor A. Rogovoy
Aleksander E. Chub
Aleksander A. Kryuchkov

PPChem 2006, 8(7), 421–424

The Effect of Temperature on the Contamination of Condensate with Organic Impurities

The results of tests on the effect of condensate temperature on the washing out of organic and inorganic impurities from anion resins used in condensate polishing units at fossil power plants are presented. It is shown that elevated condensate temperature results in increased washing out of these impurities.

Boris Michailovich Larin
Anatoli Stepanovich Sedlov

PPChem 2006, 8(7), 425–429

An Investigation of the Sorption/Desorption of Organics from Natural Waters by Solid Adsorbents and Anion Exchangers

The results of laboratory and operational tests at thermal and nuclear power stations on anion exchangers and solid adsorbents of makeup water treatment plants with regard to the sorption/desorption of organic substances in natural water and condensate are presented. The resins Amberlite™¹ IRA-67, IRA-900, IRA-958Cl, Purolite®² A-500P, Dowex™³ Marathon, and others were tested. Retention of up to 60–80 % of the "organic" material on the anion exchangers and organic absorbers installed at different places in the technological scheme of the water processing unit was attained. The possibility of a partial "poisoning" of the resins and the degradation of the working characteristics over the first year of operation are discussed.

¹ Amberlite is a trademark of the Rohm and Haas Company.

² Purolite is a registered mark of the Purolite International Ltd.

³ Dowex is a trademark of the Dow Chemical Company.

Tomáš Blejchař
Rostislav Malý
Pavel Kolat
Martin Dluhoš

PPChem 2006, 8(7), 438–445

Plasma Systems in Power Engineering

Plasma technology is currently being investigated as an alternative to heavy fuel oil and gas in the process of ignition of pulverized-coal/air mixtures at the start-up of pulverized-coal boilers and in the stabilization of combustion. Low-temperature plasma generators have been successfully tested at a Czech power plant and have now been handed over to the operator for further application. The process of ignition with plasma technology is described, as well as the results of the on-site tests. The development and application of mathematical modelling of the flow in the design of the generators is discussed.

PPChem 2006, 8(8), 452–459

Eighth International Conference on Cycle Chemistry in Fossil and Combined Cycle Plants with Heat Recovery Steam Generators

June 20–22, 2006, Calgary, Alberta, Canada

The EPRI International Conferences on Cycle Chemistry in Fossil and Combined Cycle Plants with Heat Recovery Steam Generators are the most important conferences dealing exclusively with fossil plant cycle-related topics worldwide. This contribution is a compilation of the abstracts of all the papers presented at this year's conference in Calgary, Alberta, Canada.

Brian Hoffman
J. Denis Aspden

PPChem 2006, 8(8), 460–468

Critical Aspects of Ion Exchange Resin Performance in High Temperature Condensate Polishing Applications

As more fossil-fired power stations are constructed in hot and dry regions, there is an increasing desire to practice condensate polishing at temperatures which approach and exceed 60 °C. In some cases, the condensate temperatures are even reaching the limits which are set by allowable back pressure on the steam turbine. This paper discusses the fundamental behavior of ion exchange resins in condensate polishers at high temperatures. The critical degradation mechanisms for both anion and cation exchangers are examined in terms of both resin life and, more importantly, their effect on overall process performance. The critical issues of silica, sulfate, and resin kinetic performance are discussed. Although routine operation of ion exchange resins above 60 °C is very stressful, suggestions are made for optimizing polisher performance and minimizing risks. By selecting the correct resins and applying good process design and operating practices, deep bed condensate polishing has been successfully practiced for many years at elevated condensate temperatures in fossil-fired generating plants.

David M. Gray

PPChem 2006, 8(8), 470–478

A Multiparameter Instrumentation Approach to Makeup and Cycle Chemistry Measurements

With fewer personnel to operate today's generating stations, on-line chemistry instrumentation becomes more critical. A practical approach to improving installed reliability and accuracy is the use of a high-performance multiparameter instrument platform. Its commonality of installation, functions, calibration and maintenance plus the availability of on-line computed parameters can have far-reaching benefits. Parameters of specific, cation and degassed cation conductivity, pH, dissolved oxygen, oxidation reduction potential and total organic carbon as well as the benefits of having them available within a common instrument platform are discussed. Also addressed are good sampling practices and appropriate sensor design, installation and maintenance.

Michael Sheedy

PPChem 2006, 8(8), 482–488

Short Bed Ion Exchange Technology Produces Ultrapure Water without Using a Mixed Bed

Conventional practice when producing water with a conductivity of less than $0.1 \mu\text{S} \cdot \text{cm}^{-1}$ is to use a mixed bed ion exchange unit. This paper describes a novel short bed ion exchange technology that produces water of this quality using separate columns of cation and anion resin. The principle features of this technology include the use of compressively packed beds only 7.6 cm to 15.2 cm (3 in to 6 in) in depth, fine mesh resins that improve exchange kinetics, countercurrent regeneration, and low exchanger loadings. This results in a system that is much smaller and less complex than an installation with a regenerated mixed bed unit. Case studies are presented that describe operation of this technology for the treatment of a surface water source, a municipally treated water source, and reverse osmosis permeate.

Stephen Kerr
Brett Connor

PPChem 2006, 8(8), 489–499

Life without Mud – The Installation of Clarification Pre-treatment for Fitzroy River Water Make-up to Stanwell Power Station Cooling Water Systems

The design and operation of a new clarified raw water plant at an Australian power station using a proprietary Actiflo clarification arrangement are discussed with respect to plant priorities of water conservation, cooling efficiency, microbiological control efficacy and operational costs. Plant experiences with achieving a low suspended solids regime and new challenges and opportunities for this plant are presented.

Robert Svoboda
Frank Gabrielli
Herbert Hehs
Hans-Günter Seipp
Frank-Udo Leidich
Bruce Roberts

PPChem 2006, 8(8), 502–509

Organic Impurities and Organic Conditioning Agents in the Steam/Water Cycle: A Power Plant Manufacturer's Point of View

Power plants are designed to run with pure water and steam. For simple cycles (no export steam) no other products should be necessary. If organic additives are used, the possible side effects have to be carefully addressed.

Possible side effects include corrosive degradation products, interference with monitoring cation conductivity, influence on boiling and on condensation, and fouling. Examples from boiler and turbine operation are given.

Organic amines produce volatile acidic degradation products, but the amine provides cations for pH counterbalance.

In contrast, organic oxygen scavengers, dispersants, chelants as well as organic impurities generally produce volatile acidic degradation products, but with no cation for counterbalance. For this reason, such products must be considered as potentially corrosive.

From a power plant manufacturer's point of view, any organic matter in the steam/water cycle brings the risk of detrimental side effects. The general use of organic additives should thus be avoided and restricted to specific needs and situations, as for example in certain process steam systems.

Andrew G. Howell
Robert Pritekel

PPChem 2006, 8(9), 516–525

Turbine Deposition: Two Cases

Two coal-fired drum boiler units of similar vintage experienced both similarities and differences in turbine deposition patterns. Deposits containing copper, sodium, phosphate, sulfate, iron, chloride and silica resulted in damage and performance problems of varying extent for the two units. Root-cause problem evaluation, actions taken, and recommendations for further actions to address causative issues are discussed.

Emory H. Hull
Robert D. Bartholomew

PPChem 2006, 8(9), 526–535

Rigorous Calculation of Sodium-to-Phosphate Mole Ratios for Phosphate Treatment Programs

The sodium-to-phosphate (Na:PO₄) mole ratio and/or free caustic concentration is the primary control parameter for most phosphate-based treatment programs. Traditionally, these have been determined by comparison with graphs of pH versus phosphate for various sodium phosphate solutions. Approximate methods of estimation have also been used. This paper presents a more rigorous calculation method of the Na:PO₄ mole ratio and free caustic concentration (which has been used for about a decade by Sheppard T. Powell Associates LLC and some of our clients). Calculated Na:PO₄ mole ratios and free caustic concentrations based on the method presented in this paper are then compared to those calculated using the approximate method published by Verib.

Volker Ender
Thomas Schumann
Susanne Sachs
Gert Bernhard

PPChem 2006, 8(9), 541–549

On the Uptake Mechanisms of Organics from Natural Water – Investigations with Strong and Weak Base Ion Exchangers and Their Corresponding Copolymers

In laboratory column experiments, ion exchange resins and the corresponding non-functionalized copolymers were compared in order to investigate the uptake mechanisms of organics during the water demineralization process. To improve the detection limit, ¹⁴C-labeled model substances (β-alanine, starch, synthetic humic acid type M42) were used. These compounds are supposed to represent the TOC fractions of neutrals/amphiphilics, polysaccharides and humics following the LC-OCD method. The uptake was investigated depending on the salinity and pH, the concentration of the organics, and the loading temperature. The main results are:

- At neutral pH, a near 100 % removal of β-alanine and starch by ion exchange and/or adsorption was observed, whereas humic acid was taken up by ion exchange to an extent of about 10 %.
- In acidic conditions, β-alanine and starch were completely removed up to the breakthrough point of the sulfate ions. These elute the organics. Humic acid will be removed owing to precipitation.
- The last mechanism allows the removal of humic acid by the copolymers too. These are inefficient in regard to the uptake of β-alanine and starch.
- The variation in the concentration of the organics as well as that in the loading temperature have only a subordinate influence on the uptake.

Pavel Hübner

PPChem 2006, 8(9), 551–557

The Fate of Organics in the Water-Steam Cycle

The behaviour of organic matter in power plants has been examined. The samples were taken from water treatment plants producing make-up water for boilers as well as from water-steam cycles and cooling cycles. The power plants examined were Czech power plants, both fossil and nuclear, and one Slovakian nuclear plant.

The tests were performed by the liquid chromatography – organic carbon detection (LC-OCD) method at a subcontractor lab. This method enables distinguishing between different groups of organic matter and from experience the effectiveness of water treatment technologies and the possible influence on the water-steam cycle of the power plant can be estimated.

It has been confirmed that by using appropriate flocculation the problems in water treatment plants diminish and the VGB limit for total organic carbon (TOC) concentration of $200 \mu\text{g} \cdot \text{L}^{-1}$ in boiler feedwater may be reached. The lower limit following EPRI recommendations of $100 \mu\text{g} \cdot \text{L}^{-1}$ is hardly achievable using existing water treatment technology. This provides an open field for reverse osmosis technology that is able to remove organics completely.

Hao-Feng Zhang

Li-Bin Niu

Shuji Oishi

Hiroshi Takaku

Kunio Shiokawa

Mitsuo Yamashita

Yoshihiro Sakai

PPChem 2006, 8(9), 558–564

Influence of Chloride and Carbon Dioxide on General and Crevice Corrosion of Steam Turbine Materials for Geothermal Power Plants

The influence of chloride and CO_2 on general and crevice corrosion of steam turbine materials for geothermal power plants was investigated in two simulated geothermal waters. The general corrosion rates of the rotor steels with a lower Cr content were accelerated due to the CO_2 in the water, while the corrosion rates of the blade steels with a higher Cr content were controlled mainly by the chloride concentration in the waters. Concerning the crevice corrosion behavior, the galvanic corrosion effects in each of the waters were confirmed for the rotor steels with lower corrosion potentials than those of the blade materials, and almost no difference in corrosion behavior was observed between the two waters tested. Regarding general and crevice corrosion in the two simulated geothermal waters, it was determined that a newly developed rotor material and also an improved heat-treated blade material are promising for actual usage in geothermal power plants.

Bradley Buecker

PPChem 2006, 8(9), 570–573

Water Pre-Treatment with Membranes: A Developing Technique for the Power Industry

The paper describes the successful application of new microfiltration technology for suspended solids removal in a U.S. power plant in lieu of clarification/sand filtration. The process, results and problems encountered are discussed.

PPChem 2006, 8(10), 580–587

A Look Back at the International Conference "Instrumentation for Power Plant Chemistry"

On September 19–21, 2006 the PowerPlant Chemistry International Conference "Instrumentation for Power Plant Chemistry" was held in Zurich, Switzerland. This paper gives an overview of the conference, with abstracts of the 27 technical presentations, brief reports on the panel and breakout sessions, and a review of the conference exhibition of manufacturers of power plant chemistry-related instrumentation.

Daniel E. Meils

Joseph A. Mastroianni

PPChem 2006, 8(10), 596–602

On-Line Instrument QA/QC Standard Practices

This paper has been written to assist nuclear power plant laboratories in establishing a laboratory quality management system (QMS) to assure that the accuracy and precision of analytical data produced meets operational needs. Without such a QMS, data produced in a laboratory may not have the sufficient accuracy and precision, leading to inappropriate operational decisions being made. The paper addresses all the necessary requirements a nuclear power plant laboratory needs to fulfill to be able to establish a successful QMS, provide adequate analytical procedures, demonstrate adequate instrument capability, demonstrate laboratory capabilities, and demonstrate individual analyst capabilities.

Frank A. Dunand
Nicolas Ledermann
Serge Hediger

PPChem 2006, 8(10), 603–608

Luminescent Oxygen Sensor to Monitor Power Plant Water and Steam Cycles

The majority of existing dissolved oxygen analyzers use polarographic sensors. These are well recognized for their accuracy and reliability, but maintenance complexity and frequency, as well as flow dependence and calibration needs are among the issues encountered by users. A new oxygen sensor has been developed based on luminescent technology. The main advantages of luminescent technology over electro-chemical cells are the operator independence of the calibration, the low flow requirement, the absence of flow dependence, and of course the drastic reduction of the maintenance activities. The application of luminescent technology to accurately measure low ppb oxygen concentrations is demonstrated based on laboratory and field experience in both all-volatile treatment (AVT) and oxygenated treatment (OT) environments.

Richard A. Breckenridge
L. Joseph Hancock
Robert L. Bryant
John W. Clark

PPChem 2006, 8(10), 609–615

A Method for Continuously Monitoring and Selectively Sampling Plant Cycle Water for Metal Oxide Transport Analyses

Results from analytical methods for monitoring iron and copper transport through the plant cycle water may include dissolved species, but more typically detect insoluble compounds of metal oxides [1]. Since the presence of these insoluble particulates can be indicative of serious system problems, the methods provide useful quality control and troubleshooting information. However, the data is "averaged" over some time period, e.g., one day or one week. This is better than a single "grab sample," but these methods do not necessarily enable plant operators to identify when large "spikes" occur or what causes them. If information could be available, corrective or preventive actions could possibly be taken at the time of the incident.

An instrument that continuously samples plant cycle waters, detects very low levels ($< 2 \mu\text{g} \cdot \text{kg}^{-1}$) of particulate metal oxides and automatically obtains a sample for laboratory analysis when the reading exceeds a preset threshold has proven to be very helpful in operating and maintaining reliability of steam generation systems.

Robert Svoboda
Geoff Bignold

PPChem 2006, 8(10), 624–627

Meetings of the IAPWS Working Group 'Power Cycle Chemistry' in Witney, UK, September 3–8, 2006

This paper reports on the sessions of the IAPWS working group "Power Cycle Chemistry" at the 2006 Annual Meeting of the International Association for the Properties of Water and Steam (IAPWS) in Witney, United Kingdom, September 3–8, 2006. It discusses, among other things, the 2006 working group Priority List of areas in need of basic research, the proposals for IAPWS Certified Research Needs developed from the priority list, a proposal for international collaboration, and presentations made at the meeting.

Miroslav Štastný
Olga Bláhová
Ivo Jiříček
Bohumil Lorenc

PPChem 2006, 8(10), 629–634

Effects of Steam Chemistry on the Turbine Blades in the Phase Transition Zone

This paper discusses the relationship between the concentration of corrosive anions in the steam and the occurrence of stress corrosion cracking of LP turbine moving blades. Although the titanium alloy (Ti6Al4V) proved stress corrosion resistant in the phase transition zone even with non-optimum chemistry, optimization of cycle chemistry and improvement in the quality of steam create conditions under which steel moving blades may also be applied in the phase transition zone without risk of stress corrosion cracking.

The deposits on the LP turbine blades in the phase transition zone significantly increase the surface roughness and lead to energy losses.

Philippe Dudouit
Pierre Guillou
Eva L'Hostis

PPChem 2006, 8(11), 645–650

Sodium Monitoring in the Water and Steam Cycle of Power Plants

Today sodium concentration has become one of the most important indexes for quality control of water and steam at power plants; however, measurement of this parameter can be difficult in practice. The use of ion selective electrodes means that analyzers are sensitive to pH shifts, and constant exposure to very low concentrations of sodium ions in ultrapure water conditions can lead to electrode desensitization. In addition, there is

a need to address drift through regular calibration. This paper discusses the technical challenges in low level sodium analysis and the required features for a practical and accurate analyzer to provide trouble free, sub $\mu\text{g} \cdot \text{kg}^{-1}$ (sub ppb) measurement.

Beverly J. Newton
Detlef Jensen

PPChem 2006, 8(11), 652–657

Advances in Ion Chromatography for Power Plant Operations

Ion chromatography is used in the power industry to monitor and minimize corrosive ions in the steam generator, turbines, steam and feedwater piping, and protect against cooling water impurity ingress. This paper includes a review of the recent advances in the science of ion chromatography which are aimed at improving trace analysis of corrosive ions in power plant waters and chemicals. An overview of hardware and column advances for these applications is presented. Included are details on lowering detection limits through the use of automated eluent generation and specialty columns. The emphasis is on advances in the science which will help extend the operating life of steam generators, secondary systems and turbines. Examples of the use of ion chromatography for troubleshooting corrosion problems in power plants are given.

Heini Maurer

PPChem 2006, 8(11), 658–664

Cation Conductivity: Facts and Fiction

Cation exchangers are of paramount importance to reliable conductivity readings. They come in all shapes and sizes and each and every type has its advocates. The purpose of the paper is to separate facts from fiction and shed light on such issues as rinse down, temperature effects and response time.

Frank I. H. M. Oesterholt
Jo Savelkoul
Antoine I. van Hoorn
Lambèr L. M. J. Paping
Johan W. G. van Mourik

PPChem 2006, 8(11), 666–673

Dutch Approach to *Legionella* Control in Cooling Water Systems: History and Perspectives

Cooling systems with recirculating open cooling towers represent a considerable *Legionella* risk. The Dutch Policy Rule 4.87 forces employers to carry out a risk assessment and establish a control plan for their cooling towers. This legislation only gives general descriptions and no standards. However, to provide employers with more detailed information on how to control and maintain their system, the Information Report AI-32 was written as a Dutch Code of Practice. The biggest problem for cooling tower owners is obtaining accurate data on *Legionella* concentrations in their cooling systems. The results of different methods in use to quantify *Legionella* differ to such an extent that it is very difficult to make a realistic estimate of the risk of *Legionella* infection to employees and the environment, and to adequately decide on corrective actions to be taken. More and more industries and laboratories are affected by the same lack of a reproducible analytical technique. It has become clear that the existing methods were developed primarily for relatively clean water systems with a limited lifetime, like potable waters, and not for industrial cooling systems. Especially for these industrial waters, which are re-used many times, the same analytical method cannot consistently deliver the necessary degree of reproducibility. Two cases at Corus and Dow in their industrial water systems demonstrate that there are differences in accuracy between laboratories using the same analytical method as well as between analytical methods themselves. Future work should result primarily in a new analytical method which is faster, more reliable and better reproducible compared to the current methods. Secondly there is a need for a protocol on the method for obtaining a representative sample from a complex cooling system.

Albert Bursik

PPChem 2006, 8(11), 679–690

Some Questions and Answers on All-Volatile Treatment

PowerPlant Chemistry has received a multitude of questions regarding currently used feedwater and boiler water treatments. This contribution addresses many of the inquiries about all-volatile treatment, giving general information on the subject and providing references where the questioners and readers of this paper can find more detailed information on the topics discussed.

Richard Woodward

PPChem 2006, 8(11), 694–698

Online Coal Analyzers Bring Benefits to the Utility Industry

Online coal analyzers have been in commercial use for more than two decades now, with coal producers accounting for most of the units purchased. In the past three years or so, coal-fired power plants have shown an increasing share of the analyzers bought. This article explains the most common applications of analyzers at power plants, ranging from boiler optimization to compliance with emission regulations. The article also provides a brief overview of different analyzer types, their principles of operation, and typical performance achieved.

Steven West
Xiaowen Wen
Charles Baer

PPChem 2006, 8(12), 709–712

Methods for Verification of Low Parts-per-Trillion Sodium Determination by On-Line ISE-Based Sodium Monitors

As needs and capabilities for the production of ultrapure water advance, the analysis technology for determining contaminant levels is continuously challenged to keep pace. In water used for steam generation, maintaining the lowest possible levels of sodium ion is of great importance for the prevention of damage to turbine blades. Today, sodium levels in water and steam are being pushed lower and lower, making validation of readings from on-line analyzers increasingly difficult. In this paper, we compare two methods of validating on-line, ion-selective electrode-based analyzer performance at low $\text{ng} \cdot \text{kg}^{-1}$ (low parts-per-trillion, ppt) sodium concentrations. Dynamic dilution and recovery and grab sample analysis by inductively coupled plasma mass spectrometry are applied to analyses by a recently introduced sodium monitor and to an existing monitor provided by another manufacturer. Verification studies in the range of $1\,000 \text{ ng} \cdot \text{kg}^{-1}$ down to less than $10 \text{ ng} \cdot \text{kg}^{-1}$ are described. Results of this study and discussion of analyzer design features that enable such low-level analysis are presented, and techniques available to plant operators for on-site verification of low-level chemical analyzers are discussed.

George J. Licina

PPChem 2006, 8(12), 718–726

Monitoring Biofilms in Real Time for Control of MIC and Heat Exchanger Fouling

Microbiologically influenced corrosion (MIC) of piping and heat exchanger materials in power plant cooling waters can cause expensive unplanned outages, the need for local repairs, and, in some cases, the need for complete system replacement. Biofouling of heat exchanger tubes also decreases overall plant efficiency and power output. The biocide additions necessary to mitigate biofouling and MIC increase costs, raise concerns over effluents, and can even increase corrosion.

In this paper, an electrochemical biofilm sensor with integrated data acquisition and data analysis capabilities for monitoring biofilm activity on metallic surfaces is presented. Power plant and other industrial experience with this tool, including biocide optimization projects in plants, is described.

Thomas Kappes

PPChem 2006, 8(12), 727–731

State of the Art in Flue Gas Analysis Technology for Emission Monitoring and Combustion Control

The continuous monitoring of gaseous emissions of power plants is gaining more and more importance worldwide, not only in industrialized countries, due to stringent environmental legislation and the need for efficient use of resources. An outline of modern exhaust gas analysis instrumentation is given together with applications for emission monitoring as well as for the optimization of combustion and exhaust gas treatment processes in fossil- and biomass-fueled power plants. Further, an overview of the amendment to the German federal immission control regulations for large combustion plants and gas turbines is presented.

Xueyong Guan
Ting Zhu
Digby D. Macdonald

PPChem 2006, 8(12), 732–741

Application of Electrochemical Noise Analysis in High Subcritical and Supercritical Aqueous Systems

In this study, electrochemical noise analysis (ENA) is used to identify corrosion mechanisms and to analyze the effect of pressure on corrosion reactions in high subcritical and supercritical aqueous systems. Two corrosion mechanisms, "chemical oxidation"

(CO) and "electrochemical oxidation" (EO), are used to describe the corrosion reactions in supercritical aqueous systems, depending upon the density and dielectric constant of the fluid. ENA is used to differentiate the two corrosion mechanisms by postulating that only the electrochemical mechanism gives rise to spontaneous fluctuations in current and potential. A rugged electrochemical noise sensor has been developed to monitor the fluctuations in the coupling current between two identical specimens. Experiments show that the electrochemical mechanism is the dominant corrosion process when the temperature is less than 350 °C and that it becomes of progressively lower importance as the temperature increases above the critical temperature ($T_c = 374.15$ °C). ENA is also used to explore the effect of pressure on the rate of corrosion of metals at supercritical temperatures. As predicted by the pressure-effect model, the experimental data demonstrate that the electrochemical corrosion rate increases with increasing pressure in low-density supercritical systems, corresponding to an increase in the density and the dielectric constant.

*Troels Mathiesen
Torben S. Nielsen
Jan Elkjær Frantsen
John Kold
Anne R. Boye-Moeller*

PPChem 2006, 8(12), 742–750

Influence of Various Surface Conditions on Pitting Corrosion Resistance of Stainless Steel Tubes of Type EN 1.4404

The pitting resistance of pickled, ground and electropolished surfaces of EN 1.4404 (AISI 316L) tubes was tested using cyclic polarization and ASTM G150 for determination of the pitting potential and critical pitting temperature, respectively. The materials were tested in chloride-containing solutions with 0.05 to 5.0 % chloride. Crevice corrosion was avoided using a flushed port cell with a specially cast gasket. A ground finish with low surface roughness shows no improvement over the coarse pickled finish, while an electropolished finish provides considerably higher resistance but at the same time scattered results. The two testing techniques give almost identical critical pitting temperatures that show only little dependence on chloride concentration. The variation in pitting resistance has been correlated to the surface morphology of the different surface conditions.

*Charles Laire
Raymond De Graeve
Yves Comptdaer
Philippe Gilbert*

PPChem 2006, 8(12), 756–762

Experience with Titanium Condensers in Belgian Nuclear Power Plants

In Belgium, five nuclear power plants are equipped with titanium condensers of different designs. At the Doel sites, where the cooling water is very corrosive, full titanium condensers have replaced the original condensers. The cooling water is brackish water; a cooling tower is installed for two units.

At Tihange, one unit is equipped with a replaced condenser in titanium, although the cooling water is less aggressive compared to Doel.

At some units, small leaks have occurred during service and the causes of these leaks could be related to the following mechanisms:

- Steam droplet erosion at the tube outer surface; inspections with eddy current and a visual inspection have drastically reduced the occurrence of small leaks at the Tihange 1 unit.
- Mechanical wear due to foreign objects blocking the tube entrance on the raw water side. Small debris coming from the cooling tower has generated wear and this type of degradation has resulted in the installation of protective short sleeves at one unit (Doel 4). After 8 years of operation with these sleeves, the absence of degradation was verified on pulled tubes. Despite the aggressive water, no corrosion under the sleeves has occurred, and erosion behind the sleeves – possibly due to local turbulence – has not been observed. This experience confirms the excellent corrosion resistance of titanium.

The paper summarizes the results of the different inspections and investigations on pulled tubes.