

SPECIAL PRINT

**Conventional resin cation exchangers
versus EDI for CACE measurement
in power plants –
Feasibility and practical field results**

by Manuel Sigrist

Conventional resin cation exchangers versus EDI for CACE measurement in power plants – Feasibility and practical field results

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Kurzfassung

Vergleich von Kationenaustauscherharz und Elektrodeionisierung mit dem Verfahren AMI CACE in der Anwendung in Kraftwerken

Die Leitfähigkeitsmessung nach einem Kationenaustauscher in Kraftwerken mit Dampfturbinen wurde in den 1950er Jahren von Larson und Lane eingeführt. Aufgrund der Einfachheit des Messprinzips, der Empfindlichkeit gegenüber ionischen Verunreinigungen und ihrer hohen Zuverlässigkeit ist die Leitfähigkeitsmessung nach starksaurem Kationenaustauscher (CACE) der wohl häufigste online gemessene Parameter der Chemie in Wasser-Dampfkreisläufen.

Der herkömmliche Messansatz erfordert die Verwendung eines passiven Kationenaustauscherharzes, um alle Kationen in der Probe gegen H^+ -Ionen auszutauschen. Ein Großteil der kationischen Belastung stammt von den Alkalisierungsmitteln, welche im Kreislauf verwendet werden. Die Harze werden daher permanent mit Kationen beladen und müssen periodisch ausgetauscht werden.

Austausch, Aufbereitung oder Entsorgung von gebrauchtem Harz ist eine zeitraubende und kostspielige Aufgabe für den Kraftwerkschemiker. Des Weiteren wird die Leitfähigkeitsmessung nach einem passiven Kationenaustauscherharz immer etwas verfälscht durch aus dem Harz ausgewaschene ionische Verunreinigungen, dies insbesondere unmittelbar nach dem Harzaustausch.

SWAN hat die Anwendbarkeit der Elektrodeionisierung (EDI) als Ersatz für das herkömmliche Kationenaustauscherharz untersucht und auf dieser Basis ein neues Leitfähigkeitsinstrument entwickelt. Dieser Artikel liefert eine Beschreibung des herkömmlichen Verfahrens für Kationenleitfähigkeitsmessungen sowie des neuen AMI CACE, welcher das EDI-Verfahren nutzt. Umfangreiche Feldversuche in verschiedenen Anlagentypen haben die Prozessstabilität und die Genauigkeit des Gerätes sowie die betrieblichen Vorteile gezeigt. Beispiele für Installationen und Prozesswerte werden gezeigt, wobei der Schwerpunkt auf den Austausch herkömmlicher Messaufbauten gelegt wird.

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Problem description

Conductivity is the most common sum parameter for the monitoring of ionic contaminations in water steam cycles. As volatile alkalinizing agents such as ammonia used to achieve alkali conditions in the cycle dissociate into cations, these substances contribute significantly to the base conductivity of the sample water, masking the contribution of unwanted contaminants (e.g. salts or acids).

Larson and Lane describe in their patent [1] from 1953 a measurement of conductivity downstream of a passive cation exchanger resin. This measurement arrangement has since then become the standard procedure to determine conductivity after cation exchanger (CACE) [2]. The measurement is not influenced by the baseline contribution of the volatile alkalinizing agent. Neutral salts are turned into their corresponding acid with a 3 to 4 times higher contribution to conductivity. This makes CACE a robust and effective parameter to detect unwanted ionic contaminations to a water-steam cycle.

The passive cation exchange resins have a limited capacity and require periodic replacement. The frequency of such replace-

ments depends on multiple factors, such as type, quality and volume of resin used, shape of the cation exchanger, pH, temperature and flow of the sample. (Figure 1)

The operator of a sampling system has the two following options to handle exhausted cation exchanger resins:

- Disposal to waste and replacement with new resin. This option is only viable for plants operating few measurements in samples with moderate pH (resins lasting more than 5 to 6 weeks).
- Regeneration of the exhausted resins with strong acid. This operation requires chemicals, labor time, demin water. Result is not always optimal (partially regenerated resins, resins with reduced capacity, resins with stronger leaching).

The cost and man hours required to refresh exhausted resins is significant in particular in larger plants operating multiple CACE measurements in samples with high pH.

Another draw-back of passive cation exchangers resins is the bias they introduce to the cation conductivity measurement. The three main sources of bias are:

- Partial cation exchange shortly before exhaustion
- Leaching of resin

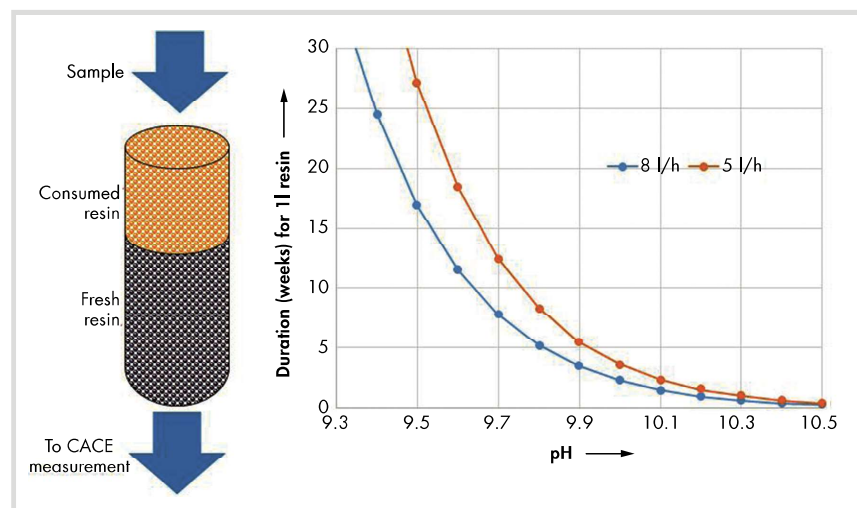


Fig. 1. Cation exchanger passive resin – duration versus flow and pH.

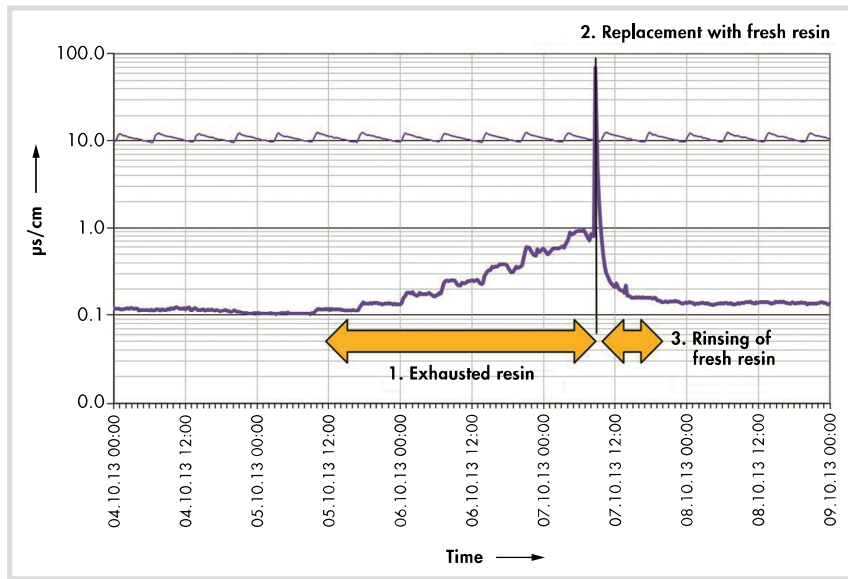


Fig. 2. Resin replacement – typical.

– The design of the cation exchanger column

Figure 2 shows a typical example of the first two effects. When the resin is nearly exhausted, some ammonia slippage occurs as the remaining active resin is no longer able to exchange all cations and the CACE measurement is biased. After replacement with fresh resin, the CACE values are also biased to high levels due to leaching products until the new resin is sufficiently rinsed by the sample. On each occurrence of such a replacement cycle, the CACE measurement of the particular sample is not useable for several hours or days. Detailed investigations have shown that even after long rinsing, many passive cation exchange resins are still leaching and causing a permanent offset of the CACE measurements [3]

Further bias is also induced by the mechanical designs of cation exchanger vessels and of their accessories. As these vessels are often designed by system integrators and not by instrument manufacturers, they come in a variety of shapes, sizes and connection schemes, as illustrated by the examples in Figure 3. Commonly known operational problems from such set-ups are long lag times or short operating time per resin batch, air accumulation at the top of the vessel, difficulties to access the vessel/column and to refill them with fresh resin. For a detailed investigation of the contribution of cation exchanger vessel design to CACE measurement, refer to [4].

A novel approach, keeping the same base principle

SWAN as instrument manufacturer has always considered the cation exchanger as an integral part of the CACE measurement chain. More than a decade ago, Swan introduced a simple resin bottle design which

screws directly onto the flow cell of the according conductivity measurements. This well established design requires no flexible connections, no special tooling and comes with features such as automatic de-aeration and permanent sample flow monitoring, all of which greatly facilitate the operation and maintenance of the instrument. However, the issue with periodic resin replacement remained.

To address the issue of limited capacity of the passive cation exchanger resin, SWAN developed an instrument combining cation exchanger resin and EDI technology. The cation exchange of the sample takes place in a compartment filled with cation exchanger resin, thus maintaining the same working principle than conventional cation exchangers upstream of CACE measurements.

The difference lies in the continuous regeneration of this cation exchanger resin: the patented design features a resin bed housed between the anode and the cathode of a EDI module with ion-selective membranes separating the resin from the electrode chambers. A schematic drawing of the instrument is shown in Figure 4.

This new technology is now available in the AMI CACE instrument released in 2016.

Extensive laboratory and field tests provided a clear understanding of the processes of cation exchange and resin regeneration as well as on leaching behaviour of passive cation exchanger resins and provided the basis for an CACE instrument using EDI technology. [3]

First units of this instrument were put in operation in selected power plants, providing an impressive demonstration of the viability and sturdiness of the new measurement method in a variety of condensate, feedwater, boiler water and steam samples.



Fig. 3. Examples of variety of cation exchanger designs.

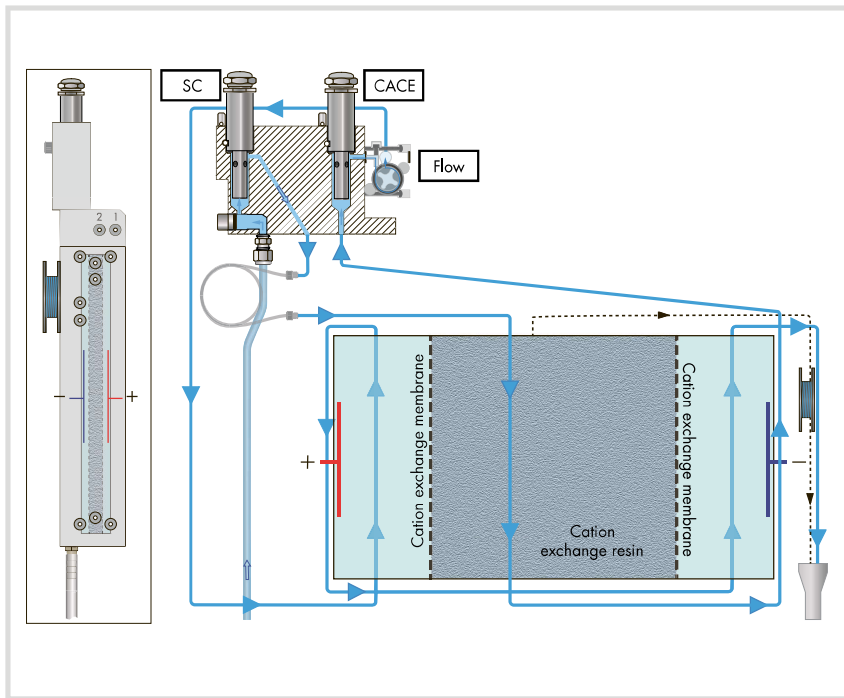


Fig. 4. AMI CACE schematics.

The next chapter shares some of the field data collected during these early product launches as well as from first sampling systems fully upgraded to AMI CACE instrumentation.

Field experience to date

Case 1: Feedwater in NPP

The first example shows acid conductivities measured in secondary cycle feedwater of a nuclear power plant (NPP). As many of these plants, the cycle is run on high AVT chemistry with a pH of 9.7 or above, combined with hydrazine as oxygen scavenger. The continuous base load operation provides for stable sample flow over extended time periods. The comparative measurements show an excellent match between conductivities measured after a conventional cation exchanger (CACE reference) and the AMI CACE. (Figure 5)

Case 2: Condenser hotwell measurement

As a result of the successful comparative trials in feedwater, the operator of the nuclear plant decided to upgrade at first some of the most time consuming and maintenance-intensive cation conductivity measurements. Beneath the two condensers of the LP turbines, two local sampling stations each monitor cationic conductivity in two samples extracted under vacuum from the condenser hotwells. In order to provide suitable hydraulic conditions for reliable sample extraction and measurement, these systems are located in a pit several meters

below the condensate water line. The passive cation exchangers need frequent replacement due to the high pH operation and accessing the confined space area of these sampling systems is a significant safety risk for the operator, in particular when carrying cation exchanger vessels with fresh and exhausted resin.

The new AMI CACE instrument in condenser hotwell (Figure 6) not only performed flawlessly compared to its counterparts using traditional cation exchanger resins but also contributes to a significant increase in operator safety and reduction of routine maintenance work related to resin replacement.

Case 3: Full system upgrade to AMI CACE instrumentation

The next case example is about a waste incinerator with two incinerator lines in a cycle with common feedwater and steam turbine. It is operated on AVT cycle chemistry using ammonia only. In 2012 one of the boilers and the steam turbine were replaced, and the EPC installed a sampling system that turned out to be quite maintenance intensive and not reliable.

Lack of stable pressure regulation combined with lack of remote sample flow monitoring was the main cause for unreliable measurements. Suboptimal flow cell and cation exchanger designs (two different types within the same plant) complicated routine tasks such as sensor maintenance and resin exchange.

Due to budget constraints and to the fact that the sampling system was rather new, a complete system replacement was not possible. The refurbishment executed in 2016 was thus focused on the cold sample side, with improvements to temperature safety, to sample pressure regulation and with replacement of all cation conductivity measurements with new dual conductivity instruments using EDI resin regeneration. In doing so, several maintenance-intensive pH sensors could be replaced with calculated pH from differential conductivities.

Figure 7 shows a before and after perspective of the main sampling system for feedwater, steams and condensates and illustrates how much simpler and readable a well refurbished system can be.

Figure 8 shows cation conductivity measurements in feedwater (conventional passive resin type with 11 resin as reference compared to CACE EDI type). Besides the excellent match between the 2 measurements, another interesting property of the CACE EDI is visible. On the process side,

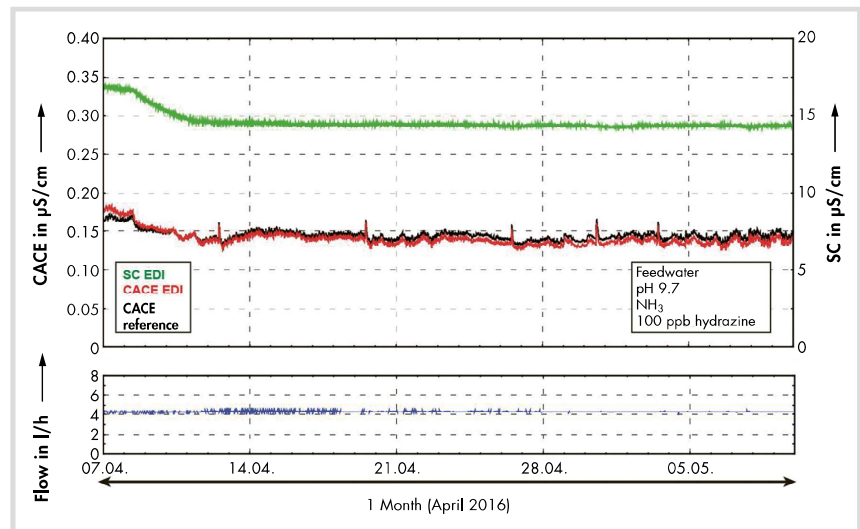


Fig. 5. Conductivity measurement of feedwater in a NPP.



Fig. 6. AMI CACE in hotwell station.

the EDI module is significantly smaller, the CACE measurement after EDI module picks up the change about 6 minutes earlier than the measurement downstream of a 1l passive cation exchanger (bottle type cation column with optimised hydraulic path).

In the case of a critical contamination event, this faster reaction time can be vital for a water steam cycle as these few minutes extra time may allow faster corrective action thus minimising the consequences of such contamination.

Compared to larger cation exchangers or to column designs introducing further lag time (e.g. with flex hose connections, dead space inside the column) the CACE measurement after EDI is expected to react 6 to 12 minutes earlier.

there are periodic fluctuations in the cationic conductivity, due to the addition of make-up water with higher CO₂ content than the feedwater. As the resin volume in



Fig. 7. Main sampling system for feedwater: Before and after.

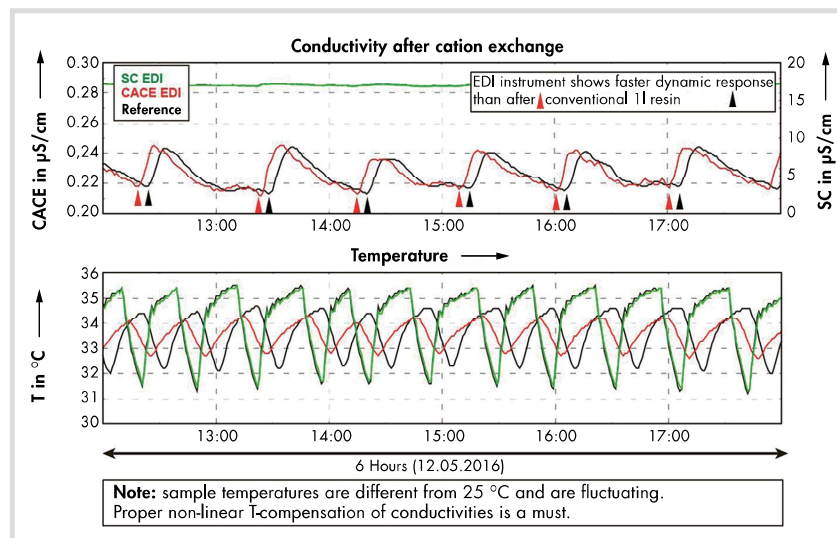


Fig. 8. CACE after EDI compared to conventional cation exchange.

Conclusions

Even simple online measurements benefit from standardised modular instrument design. Defining the cation exchanger as an integral part of the cation conductivity measurement chain was the first step of this standardisation. The use of EDI technology to continuously regenerate the cation exchanger resin is a second step in this development.

With the Swan AMI CACE, a proven alternative to cation conductivity after passive exchanger resins is now available, without the bias due to resin leaching, with significantly lower operating & maintenance costs and last but not least with faster reaction time than conventional measurements.

As cation conductivity is one of the most frequent online measurements in a water-steam cycle and with many cycles operating at high pH using volatile alkalization, this new development calls for a different approach for the refurbishment of conventional sampling systems: instead of replacing only individual sensors and transmitters or single analysers, the replacement of complete online instrumentation sets can be justified by the increase in reliability and the reduction of system operational cost.

For such larger scope refurbishment projects, it is worth checking and improving the safety and reliability of sample conditioning equipment and to adapt it to the requirements of modern instrumentation.

References

- [1] US Pat. 2832673 Larson Lane.
- [2] Standard Practice for On-Line Determination of Cation Conductivity in High Purity Water, ASTM D6504-11.
- [3] Julia Gath, *Conventional resin cation exchangers versus EDI for CACE measurement in power plants – feasibility and practical field results*, Swan Analytische Instrumente AG 4th International Conference on Flow Accelerated Corrosion (FAC 2016), Lille, France.
- [4] Heini Maurer, *Cation Conductivity: Facts and Fiction*, SWAN Analytical Instruments, PP-Chem Int., ISSN 1438-5325, November Volume 8 (2006), No. 11.

*Acid conductivity monitoring –
No more resin change*



Conductivity After Cation Exchange (CACE) has never been easier to measure than with the new EDI technology for cation removal from the sample.

The monitor AMI CACE is a key component in controlling water steam cycle chemistry. The AMI CACE continuously measures conductivity before and after cation exchange without the need to change resin columns every month or to replace/regenerate resin.

Its new EDI technology significantly reduces maintenance cost and the environmental impact, saving resin and regeneration chemicals.



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