Best Available Technology - Online Monitoring of Boron & Lithium

(Paper 423615)

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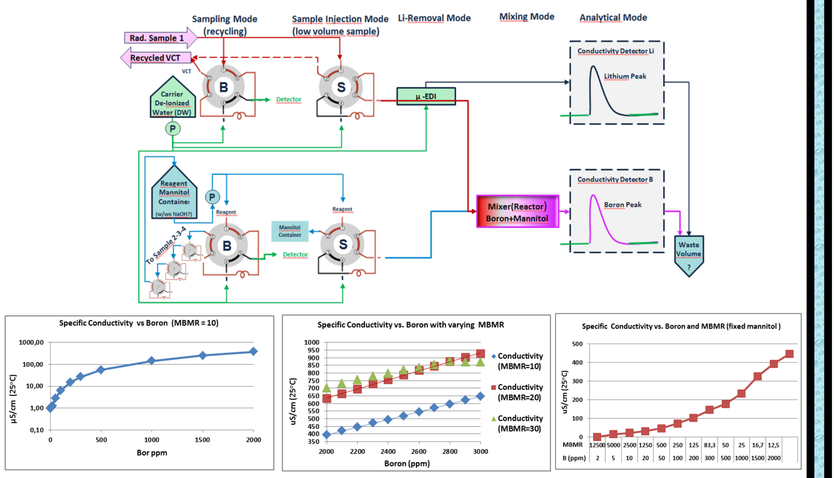
INTRODUCTION

Monitoring of boron and lithium in reactor coolant is most important to ensure a safe reactivity management and reduce risks of local & general material corrosion with radiation built up during operation of PWRs & VVERs. Natural Boron (NB) includes approx. 20% of ^{10}B and 80% of ^{11}B were the only important part for nuclear use is ^{10}B for its high neutron cross section to control fission. The ^{10}B could be monitored either as pure ^{10}B, or as total NB with a known or expected $^{10}B/^{11}B$-ratio. Boron online monitors are sometimes installed to support operators with more frequent information than ever possible with grab sampling followed by laboratory analysis. However, conventional online monitors such as automated devices for titration of boric acid or ^{10}B neutron absorption equipment may have drawbacks regarding sufficient accuracy or frequency, too frequent maintenance & calibration, or too high volumes of chemicals, sample and liquid radwaste. During a pre-study at Ringhals NPP-Sweden in purpose to decide equipment's for new boron online monitors to be installed, three new alternative technologies was suggested and demonstrated:

1. FIA-CONDUCTIVITY

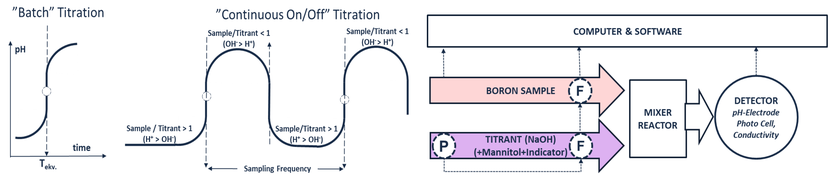
fisher scientific

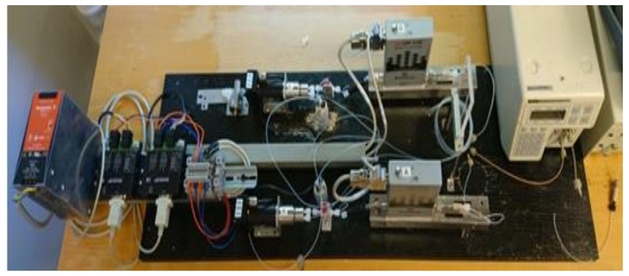


Boron measurements are based on a pure specific conductivity relation to the boron sample mixed with mannitol (fructose), where lithium is/could be removed. Some short demonstrations were performed at Ringhals together with Thermo Fisher Scientic-Denmark, using a slightly modified anion chromatograph (IC). Initial tests showed some difficulties to produce enough accurate results due to the varying influence of Mannitol to Boron Molar Ratio (MBMR). Therefore, frequent calibration will be needed, bringing more efforts and uncertainties to manage transients with large or rapid change of boron concentration in reactor coolant. Conclusion was that this principle may work out, but need further development not possible to finalize before the deadline of Ringhals installation.

2. CONTINIOUS ON/OFF TITRATION

Studsvik

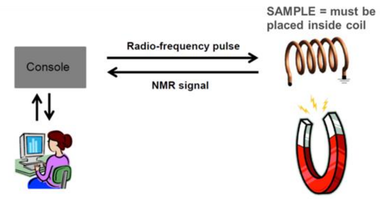


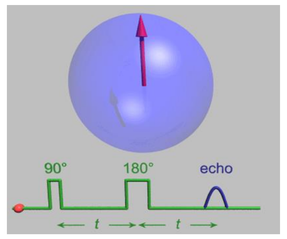


A pilot device to demonstrate a continuous repeated titration process was put together by Studsvik Nuclear-Sweden on request by Ringhals. The system was designed using high speed/low flow gear pumps with pulseless flows together with a Nano-Coriolis system, able to control and monitor the mass flowrates with very high accuracy and frequency A photometer in series with a conductivity sensor were both used for detection of the equilibrium point. The device managed to record very accurate boron results (0,1-0,2 % RSD) within every 2 minutes. Some minor concerns related to the shelf live of colour indicator and solubility of chemicals at high boron concentrations remained to be solved. Conclusion was that this technology is very promising, but that deadline for plant installation at Ringhals did not allow the required qualification.

3. LF-NUCLEAR MAGNETIC RESONANCE

NanoNord





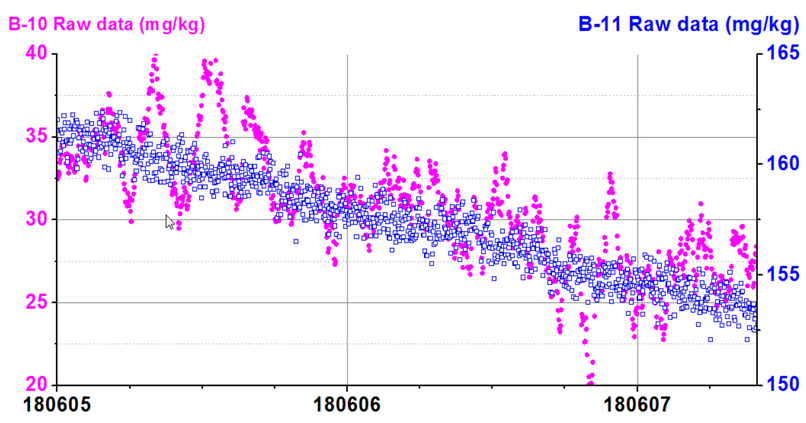
Demonstrations have been made by NanoNord A/S-Denmark together with Ringhals to qualify NMR technology for monitoring of ^{11}B, ^{10}B and ^{7}Li simultaneously. First demonstrations showed possibilities to monitor ^{11}B with accuracy of $\pm$ 1-2 ppm with 2-4 min frequency in the range of 2-2500 ppm ^{11}B (= 3-3000 ppm NB). ^{10}B could be monitored $\geq$ daily as an average value to follow ^{10}B-depletion (burnup) or $^{10}B/^{11}B$-ratio, and ^{7}Li with the accuracy and frequency to control pH_t at $\pm$ 0,025 units several times/day. Separate magnets/software optimized for each parameter may improve accuracy or frequency further. Conclusion was that LF-NMR was the most promising boron online monitoring technology on the market and needed only minor qualifications for final use.

CONCLUSION

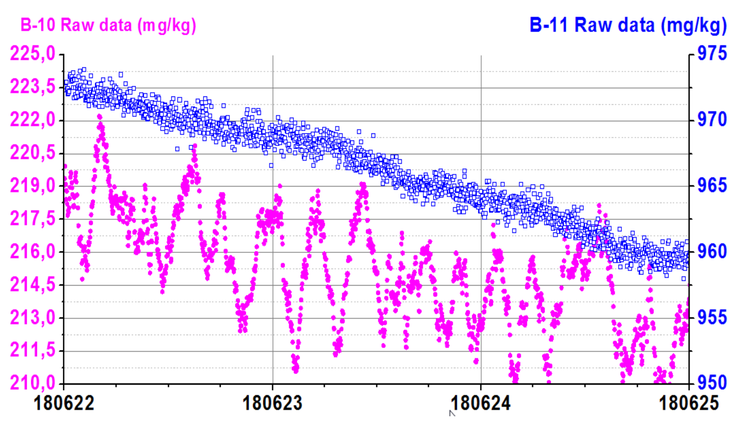
Results showed that all demonstrated technologies may be used for online boron analysis, but that LF-NMR showed the best potential to fulfil requests from operators, core physics and chemists. The main features with NMR compared to conventional and other demonstrated online devices are the possibilities to get high accuracy together with high frequency and simplicity to operate without chemicals where the radioactive samples could be recycled to the coolant without producing any liquid radwaste. Low needs for maintenance & calibration together with a low size and option to measure $^{10}B/^{11}B$-ratio and Li was considered useful. Since early 2018, NanoNord A/S in Denmark, have been worked together with Ringhals in purpose to optimise & qualify a NMR device and software for measurements of ^{10}B, ^{11}B and ^{7}Li. The first nuclear LF-NMR unit was installed at Ringhals in early June 2018, giving time only for limited experience and results before deadline of the 2018 NPC conference. Results below include a short period of EOC-operation at Ringhals unit 4, together with the start up with first days of operation from refuelling of unit 3. Results were very successful, but needs to be confirmed further for a longer period of operation including shut down and power transients. However, main conclusion is that results indicate that LF-NMR technology significantly may improve reactivity management and pH control, especially during transients and load follow operation of PWRs/VVERs with rapid variations of Boron & Lithium concentrations.

Online Measurements of Boron Concentrations using LF-NMR Technology

Ringhals Unit 4 - Daily dilution during end of cycle operation



Ringhals Unit 3 - Daily dilution during first days of operation post start up



Boron Dilution during Ringhals Unit 3 Start Up