Development and Demonstration of Online Boron Monitor

Background

The Japanese national effluent standard for boron has been effective since July 2001; it is set at 10 mg/l for effluents discharged to terrestrial water bodies and 230 mg/l for effluents discharged to coastal water bodies, respectively. Thus, low-cost wastewater treatment and process monitoring are in high demand for controlling boron in wastewaters. CRIEPI has already developed a rapid determination method in potentiometric measurement with a tetrafluoroborate (BF_4^-) ion selective electrode (ISE). Since this method promises a compact and low-cost automated measuring equipment, CRIEPI started R&D to translate the determination method into practical use as a process monitor.

Objectives

To develop an automated measuring equipment for monitoring boron concentration in process effluents and natural waters and to demonstrate its effectiveness as a process monitor.

Principal Results

1. Development of online boron monitor

CRIEPI and DKK-TOA Corp. have jointly developed a fully automated measuring equipment (see Fig.1 and Table 1, this is referred to as online boron monitor) for monitoring aqueous boron which usually exists as boric acid. The specification targeted for development was to automate all procedures required for the measurement, that is, sampling of a solution, addition of the chemicals, acquisition and processing of data, rinsing out a measurement cell, and automatic calibration of the ion-selective electrode. The online boron monitor measures boron in the range of 1-500 mg/L for 15 min without any pretreatments, which covers the Japanese effluent standards for boron. We have established the injection procedure of samples, the settings of sample dilution ratio, and the conditioning method of the ISE for long-term operation. We also manufactured the data processing software.

The consumable supplies for the measurement are ion electrodes and low-cost chemicals, thereby enabling large reduction in the running cost as compared with the existing automated measuring equipment based on conventional spectrophotometry.

2. Application to coal-fired power plant

The online boron monitor was installed at a coal-fired power plant and measured flue gas desulfurization (FGD) wastewater. A boron profile for 4 months is shown in Fig.2. The online boron monitor was successfully operated for the initial 2.5 months. A quite good correlation was obtained in the measurements between the monitor and the Japanese official method (ICP-AES). Thereafter large discrepancies were observed for 2 weeks, which is depicted as A in Fig.2. We speculated that the discrepancies were caused by bubbles attaching on the ISE membrane. In the fourth month, fluctuated measurements were observed with the monitor, which is depicted as B in Fig.2. This is due to the life of the ISE membrane and can be solved by exchanging the membrane at intervals of three months. The boron concentration varied drastically in the range of 100-500 mg/l [*1], reflecting the boron content in coal. This detailed behavior of boron in the FGD effluent has never been grasped before, because the measurement of boron at a power plant is usually carried out a few times a week at most.

The online boron monitor offers the real time data of the boron concentration and serves as a powerful tool to manage and control boron in process effluents. It is now commercially available from DKK-TOA Corp. since January 2007.

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Reference

K. Abe, et al., 2007, "Development and demonstration of online boron monitor," CRIEPI Report V06008 (in Japanese)

H. Ohsumi, et al., 2003, "Development of simple and rapid determination method of boron in wastewater using ion-selective electrode," CRIEPI Report T02012 (in Japanese)

＊1：The effluent was properly treated at a downstream facility and discharged to public water bodies at below the effluent standard.

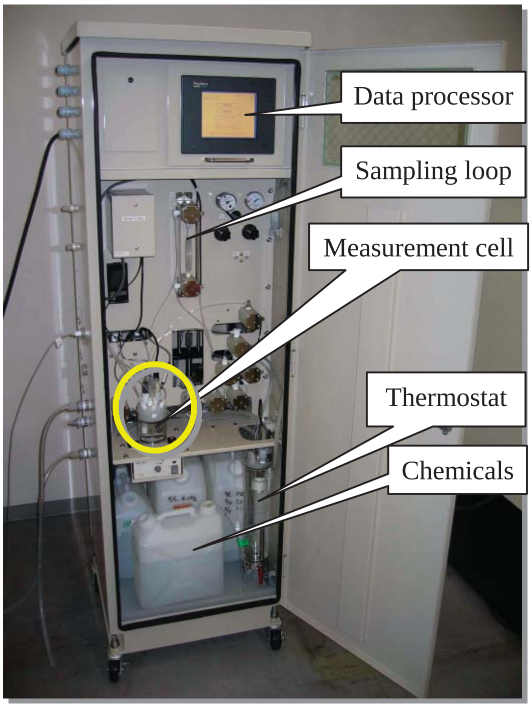

Fig.1 Online boron monitor

Table 1 Specifications of online boron monitor

Measurement principle	Potentiometric analysis with BF_4^- ion selective electrode
Measurement cell	Internal volume: 40 ml (maintained at 40˚C with circulating hot t)
Measurement range	1-500 mg/l (adjustable by sample dilution ratio)
Measurement time	15 min
Repeated accuracy	± 10% full scale
Dimensions	Width 500 × depth 500 × height 1500 mm
Utility	Power supply (100V 500VA); compressed air (0.4 to 0.7 MPa); deionized water

The interfering ions to the BF_4^- ISE are, iodide ion (I^-), cyanide ion (CN^-), nitrate ion (NO_3^-), sulfide ion (S^{2-}) and brormide ion (Br^-). We have to confirm the sample properties before measurement.

The running cost for the online boron monitor is expected to decrease to one-ninth of that for the existing automated measuring equipment based on the conventional spectrophotometry.

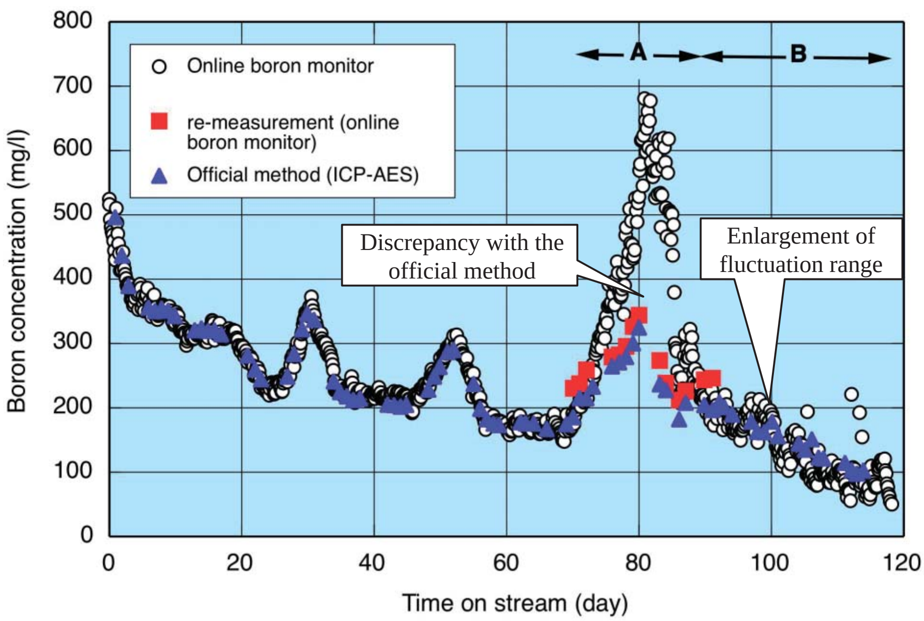

Fig.2 Boron concentration in the effluent from the flue gas desulfurization unit.

A quite good correlation was obtained for the initial 2.5 months in the measurements between the monitor and the Japanese official method (ICP-AES). Then large discrepancies were observed for 2 weeks, (depicted as A), which is considered to be caused by bubbles attaching on the ISE membrane. This phenomenon can be avoided by heating the utility water thoroughly.