Transactions of the Korean Nuclear Society Spring Meeting
Gwangju, Korea, May 30-31, 2013

Advanced Detection Technology of Trace-level Borate for SG Leakage Monitoring

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1. Introduction

EPRI (Electric Power Research Institute) reported that 187 NPPs, 80% of NPPs surveyed around the world, have been experienced the steam generator tube degradation and tube leakage occurred at the 20% of them [1]. If the tube leakage of steam generator cannot detect earlier, the operation of NPP will be stopped as well as occurs an economic loss due to the early replacement of the steam generator tube. Furthermore, it could lead to contamination of the environment with radioactive materials so the integrity of the steam generator tubes in NPPs is very important.

Many studies have been reported for monitoring technology of steam generator, however, all of these methods have their own limitations [1,2]. The leakage monitoring technology of steam generator of PWR has also got a limit due to the adoption of specific radionuclides (N-16, Ar-41, H-3, Xe, etc.) generated by nuclear fission, which are available only when reactor output is 20% or more. Most of domestic NPPs apply the N-16 technique for monitoring tube leakage but it has some problem that it is difficult to calculate the leakage rate because neutron flux are not completely formed during low power operation. For example, tube leakage of steam generator occurred in the Ul-jin nuclear power plant in 2002 during coast down operation for periodic plant maintenance. This plant could not prevent a rupture accident in advance because N-16 method is not possible the leak monitoring less than 20% reactor power.

The development of excellent alternative monitoring technology that can monitor the real-time leakage is required under a variety of operating conditions like start-up and abnormal conditions of NPPs. This study was performed to lay a foundation in monitoring the leakage of steam generator coping with the lower output and low power operational condition using trace level of boron which is non-radioactive nuclide to inject control neutron injection.

2. Materials and Methods

The boric acid have been injected into the reactor coolant systems (RCS) to control the neutron, which exist in the form of H_3BO_3 and in the range of 10-2500 ppm. The experimental procedure and samples, with almost the same condition as of the field are as follows.

2.1 Materials

In order to simulate the secondary system water matrix of the NPP, hydrazine hydrate ($NH_2NH_2H_2O$, 99.9%, Sigma Aldrich), ammonia solution (2M in ethanol, Sigma Aldrich) and ethanolamine (ETA; $NH_2CH_2CH_2OH$, 99.5%, Sigma Aldrich) was used 0.01, 1, 10 ppm with the liquid state, respectively. And it is investigated whether the effect of cation suspected interference factor for analysis of boron ions.

Also, boric acid (H_3BO_3, 99.5%, Sigma Aldrich), sodium acetate (CH_3COONa, 99%, Sigma Aldrich) and sodium fluoride (NaF, 99%) was selected each 1 ppm, respectively. By the way, glycol acid salt (1000 mg/L in H_2O) and formate (1000 mg/L in H_2O), which are generated ethanolamine (ETA) as a by-product, was diluted to 1 ppm, respectively, to research the effect of anion presented in the secondary system water.

2.2 Analysis

Boron ion was concentrated using the borate concentrator column (3×35 ㎜, 4000 psi) till a volume of 5 mL/min and analyzed by using the borate ion-exclusion column (9×250 ㎜, 1400 psi). By doing so, the resolution between fluoride and boron ions was confirmed. Also, the effect of anion separation was investigated using ion-exchange column (9×250 ㎜, 900 psi). As mobile phase, 40-70 mM polyol, which is more highly retained and conductive than borate itself, was injected along with 2.5 mM methanesulfonic acid (MSA) at the flow rate of 1 mL/min [3,4]. This eluent chemistry enhances the analytical separation and sensitivity of the conductivity detection.

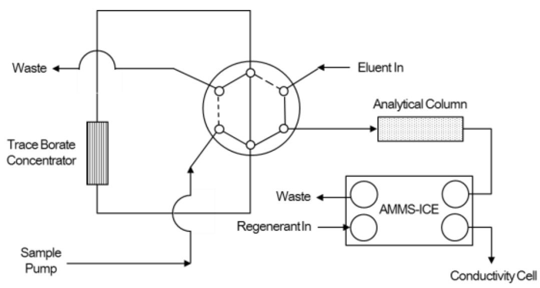

Fig. 1. Ion chromatography preconcentration system for trace-level borate determination

The suppressor is used to lower the conductivity of background and to deal with a small amount of cations. Schematic diagram of boron ion analysis system was shown in Fig.1.

3. Results and Discussion

3.1 Ion-exclusion Column

In Fig. 2, the detection time of boron and fluorine ions using borate concentrator column equipped with borate analytical column were 8.333 and 8.172 min, respectively. It is indicated that two peak values were overlapped (Fig. 2). If these columns were applied to nuclear power plants, there would have been difficulty while separating fluoride and boron ions due to the presence of approximately 0.01 mg/L or less fluoride ion in the primary system water.

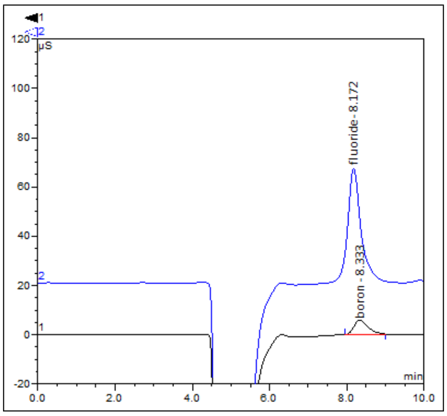

Fig. 2. Chromatogram of boron analysis by using borate concentrator column coupled with ion-exclusion column

3.2 Ion-exchange Column

In the case of ion-exchange column, analytical column with a low selectivity of fluoride ion was shown in Fig. 3 [5]. According to the results, the detection times of boron and fluorine ions were 9.676 and 7.832 min, respectively, proving excellent resolution.

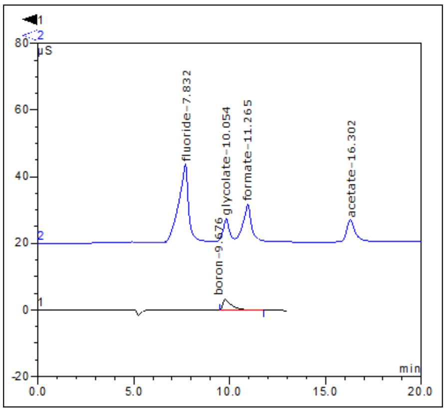

Fig. 3. Chromatogram of boron analysis equipped with ion-exchange column in complex cation /anion phase

4. Conclusions

In this study, non-radioactive nuclide boron ion, which existed in the secondary system water, as leakage monitoring indicator was investigated for the separation of complex cation and anion phase. Borate was detected by using borate concentrator column coupled with the ion-exclusion column analytical column, revealing the problem of overlapped peak between fluoride and boron ions. Meanwhile, ion-exchange column could confirm the possibility as a leakage monitoring indicator of steam generator, despite the peak of glycolic acid salts was slightly overlapped. It will be needed for further research regarding the selectivity of the mobile phase and column.

ACKNOWLEDGMENTS

This study was supported by Ministry of Knowledge Economy as the Project on Innovative Nuclear Power Plants (No. 20121620100010).

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