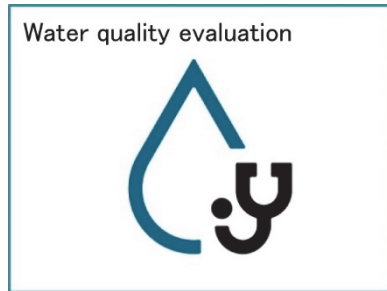


Development for Novel Identification Method of Seawater Contamination into Steam-Water Circuit Including Carbon Dioxide of Power Plants Based on Chemical Equilibrium Calculation



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In the steam-water circuit of thermal power plants, cation conductivity is measured to detect at an early stage the leakage of seawater into the condenser. However, there is the problem of carbon dioxide interfering with the measurement. To address this issue, a novel model for identifying seawater leakage has been devised. It is a model based on chemical equilibrium calculation considering not only cation conductivity but also pH and electrical conductivity. This novel identification model was verified using chemical equilibrium calculation software and water quality data from the actual unit. The results show good accuracy with an error of 0 to 20 % with chemical equilibrium calculation software. It has also been confirmed that trace seawater leaks can be detected before reaching the reference value prescribed by JIS B 8223 for feedwater control (i.e., cation conductivity of 0.5 $\mu\text{S}/\text{cm}$), which makes it possible to detect seawater leakage promptly and easily even in the presence of carbon dioxide.

1. Introduction

In thermal power plants, boilers and piping are made of iron-based materials such as carbon steel and low-alloy steel. Corrosion is therefore one of the major issues to deal with. Being in contact with feedwater, boiler water and steam flowing inside, equipment such as boilers and piping are subject to corrosion. The resulting adhesion of corrosion products (scaling) hinders efficient operation or, in the case of excessive progression of corrosion, may lead to serious damage such as holes and ruptures in piping/equipment. For prevention, impurity contamination is monitored by continuously measuring the water quality of the steam-water circuit. However, if more renewable energies are introduced and thermal power plants are started up/shut down more frequently, the effect of carbon dioxide, which is also present in the circuit, will have more impact on the measurement. This results in delay in detecting impurity contamination, raising concerns about increasing risk of damaging thermal power plants. Therefore, a novel identification method was devised to make it possible to detect impurity contamination promptly and easily even in the presence of interfering chemical components, and is presented in this report.

2. TOMONI® an intelligent solution powered by ΣSynX

TOMONI is an intelligent solution that accelerates decarbonization through power plant design, operation and maintenance and know-how about various systems with strong cooperation from customers and partners⁽¹⁾⁽²⁾. Our aspiration is to help operate power generation facilities by offering a menu of services including power plant remote monitoring and realize a sustainable society by means of stable power supply and reduced impact on the global environment.

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In TOMONI, wide-ranging solutions are available, covering the entire power plant, not just the turbine, which is the main component of a power plant. **Figure 1** shows examples of corrosion incidents in the steam-water circuit. When corrosion of the materials used in the steam-water circuit has developed, the resulting scaling may lower operation efficiency or damage to equipment may bring the plant to a halt. There is a possibility of causing an adverse impact on the environment or a large financial loss owing to equipment restoration or decreased power generation. As a preventive means, a water quality evaluation app has been developed to support water quality control for the steam-water circuit. **Figure 2** gives an example of the screen display of the water quality evaluation app. One of the main functions is guidance, through which water quality data and the relevant operational parameters are constantly monitored online and are quantified in real time for evaluation. If any abnormal sign is observed, guidance about the cause and how to respond will be shown. In this way, it becomes possible to promptly deal with the situation in a timely manner, before the affected area expands, thereby maintaining appropriate water quality and preventing serious incidents from happening. There are also other functions available, including the detailed offline evaluation of water quality based on the water treatment expert knowledge, on-site technical assistance system, and additional technical support. By making use of these services, we contribute maintain the integrity of the plant.

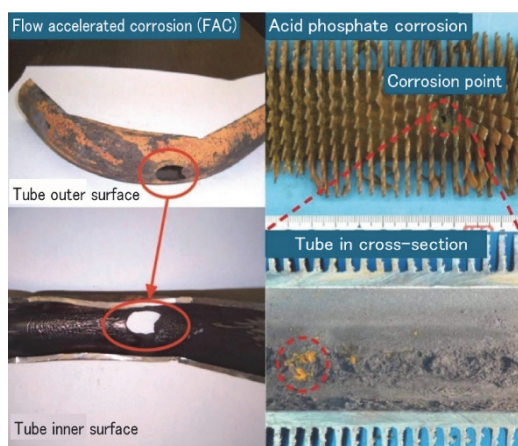


Figure 1 Examples of corrosion incidents

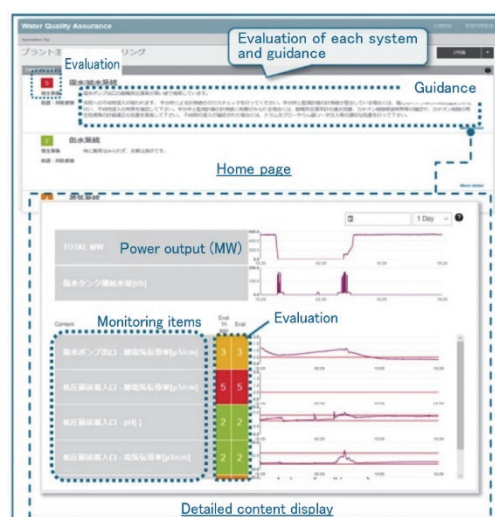


Figure 2 Example of screen display of Water quality assurance

3. Major problems in steam-water circuit – leakage of seawater into condenser

One of the serious problems in thermal power plants is the leakage of seawater into the condenser. **Figure 3** shows a schematic diagram of the steam-water circuit system of a combined-cycle power plant. When seawater is used as cooling water, a cooling water tube or tube sheet may be broken because of corrosion or damage. If this happens, seawater enters and gets mixed with the condensate, gradually making its way into the entire steam-water circuit. This may cause the following serious failures or equipment damage⁽³⁾:

- (1) Scale formation and heat transfer inhibition in boiler water tubes, caused by calcium and magnesium components
- (2) Low pH levels of boiler water and corrosion as a result of hydrolysis of magnesium chloride
- (3) Steel corrosion causing hydrogen attack by generated hydrogen corrosion of steel materials and triggering cracking
- (4) Contamination and corrosion of superheater tubes and turbine blades, caused by salts that have entered the steam system as the carryover from boiler water or the supply of spray water from the desuperheater

As more time passes after the occurrence of seawater leakage, the amount of leakage and the area of contamination increase, elevating the risk of the aforementioned failures and equipment

damage. Once the equipment is broken, repair is needed. Cleaning is also needed to remove the contaminants remaining in the system. Such work and lost opportunity of power generation due to plant shutdown for the work incur a huge economic loss. Therefore, cation conductivity in the steam-water circuit of a thermal power plant is measured to detect seawater leakage at an early stage and minimize the damage.

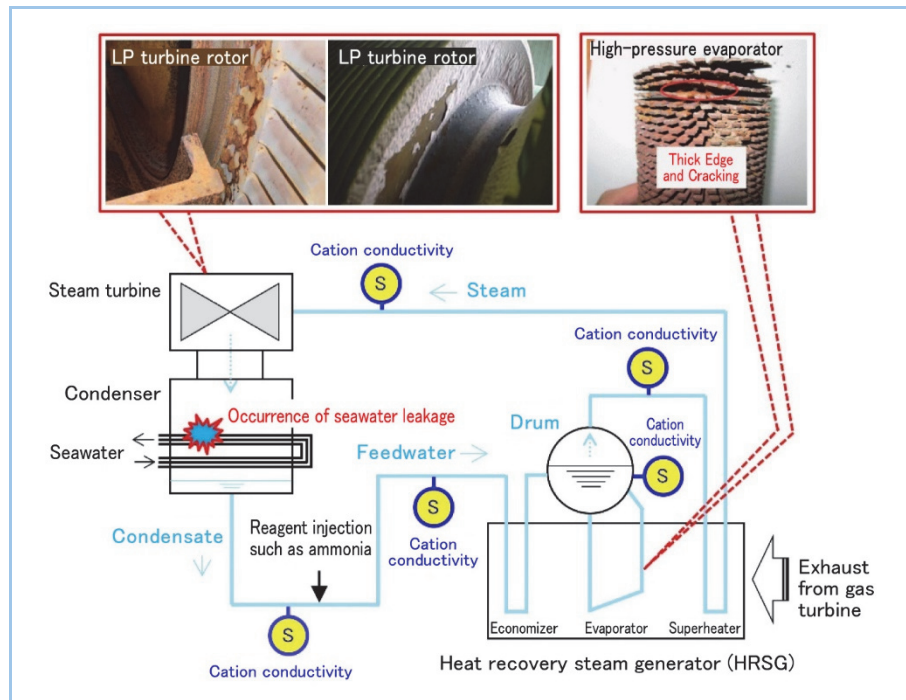


Figure 3 Schematic diagram of steam-water circuit system of combined-cycle power plant⁽⁴⁾⁻⁽⁶⁾

4. Cation conductivity overview and its issues

Cation conductivity is an indicator to show if there is contamination of soluble salts (as an electrolyte) containing anions other than hydroxide ions⁽³⁾. Figure 4 illustrates the principle of cation conductivity measurement. Cation conductivity is obtained by measuring the electrical conductivity after removing cations from the collected sample water. Leakage of seawater into the steam-water circuit can be detected as an increase of cation conductivity associated with the increase in the concentration of anions such as chloride ions.

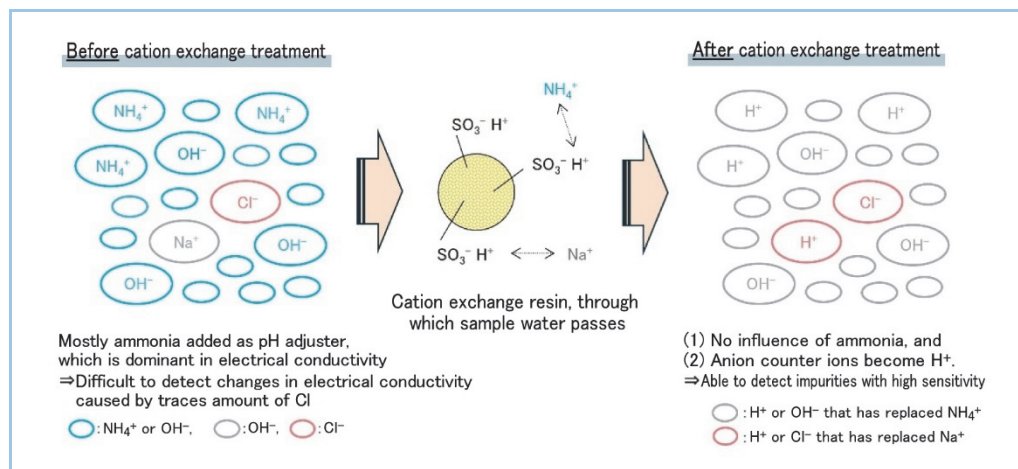


Figure 4 Principle of cation conductivity measurement







On the other hand, there is the problem of carbon dioxide interfering with the measurement of cation conductivity. After the plant is shut down, and especially when a vacuum in the condenser is broken, carbon dioxide from the air dissolves in the condensate. When the plant is started again, cation conductivity increases because of carbonate ions and bicarbonate ions, making it difficult to

detect seawater leakage based on cation conductivity in a timely manner. As more renewable energies are introduced, thermal power plants will become subject to frequent startups and shutdowns as part of the electric power conditioning. The time spent for starting up will account for more of the total plant operation time, raising concerns about increased risk of delay in detecting seawater leakage. It is therefore necessary for seawater leakage to become detectable easily and inexpensively even with the presence of carbon dioxide.

5. Seawater contamination amount identification model based on chemical equilibrium calculation

Table 1 summarizes how water quality changes when the steam-water circuit of a thermal power plant is contaminated with carbon dioxide or trace seawater. With either carbon dioxide or seawater contaminant in the steam-water circuit, cation conductivity is elevated, making it impossible to determine which contaminant is present based only on cation conductivity. However, upon dissolving in water, carbon dioxide acts as an acid. As seawater is nearly neutral, how the pH level changes at the time of contamination differs between carbon dioxide and seawater. Moreover, as carbon dioxide and seawater show different levels of electrical conductivity per unit concentration, the behavior of electrical conductivity at the time of contamination also differs. Focusing on this difference, we built a model to identify the amount of seawater contamination based on not only the conventional cation conductivity but also pH and electrical conductivity.

Table 1 Change in water quality in leakage of carbon dioxide or trace seawater into steam-water circuit

Case	Behavior of change associated with increase in contaminant		
	Cation conductivity	pH	Electrical conductivity
Leakage of carbon dioxide			
Leakage of seawater			

*Different levels of electrical conductivity per unit concentration

This model supposes the application of High-AVT (LO) which is applied especially at a high feedwater pH range (approximately 9.8 to 10.3) among High-All Volatile Treatment (Low Oxidizing) AVT(LO) as the steam-water circuit water treatment. High-AVT (LO) is a water treatment method with ammonia as the only chemical in use throughout the system and has been increasingly used in combined cycle power plants in recent years. It does not involve the use of hydrazine, whose effect on human health is a concern, or sodium phosphate, which may cause phosphate corrosion. It is also possible to prevent flow accelerated corrosion, shorten the plant starting up or shutting down process, produce labor saving effects, and reduce costs⁽⁷⁾⁽⁸⁾. When the steam-water circuit is contaminated with carbon dioxide and seawater while High-AVT(LO) is in operation, the chemical components that are present in the system are ammonia, carbon dioxide and seawater. By arranging the equations defining the chemical equilibrium state such as dissociation equilibrium of each component, mass balance and charge balance, an identification model has been developed to allow separate calculations of carbon dioxide and seawater contamination⁽⁹⁾. **Figure 5** is a schematic diagram of this novel identification model. The amount of seawater contamination can be estimated in real time even in the presence of carbon dioxide by inputting pH, electrical conductivity and cation conductivity measured at an actual plant.

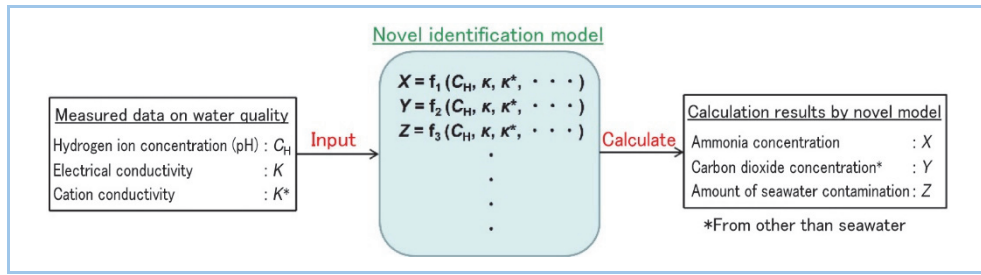


Figure 5 Schematic diagram of novel identification model

6. Verification of novel identification model

6.1 Verification results using chemical equilibrium calculation software

The calculation results by the novel identification model were verified using the chemical equilibrium calculation software OLI Analyzer ver. 11.0 (OLI Systems, Inc.). The expected values of ammonia concentration (X), carbon dioxide concentration (Y) and seawater contamination (Z) in an actual plant were first preset. OLI Analyzer used these X , Y and Z to calculate cation conductivity, pH and electrical conductivity. The calculated values were then used as the input to the novel model, to calculate X , Y and Z backwards and compare with the preset values (true values). The results are shown in Figure 6, which indicates that the error between the true value and the calculated value is sufficiently small in ammonia, carbon dioxide and seawater. In the case of a low level of carbon dioxide concentration or seawater contamination, the calculation error is from several to a dozen percent, which is equivalent to 0.01 to 0.05 $\mu\text{S}/\text{cm}$ when converted to cation conductivity. The absolute value of error is therefore small. In addition, there were cases where the cation conductivity of feed water and steam in actual plants has been confirmed to be up to 5 mg/L and the scope of this model application includes this value. Moreover, when also the minimum determination limit of seawater contamination $1 \times 10^{-6} \text{ m}^3/\text{m}^3$ is converted to cation conductivity, it is 0.26 $\mu\text{S}/\text{cm}$ and below the level prescribed by JIS B 8233 for feedwater control reference value (i.e., 0.5 $\mu\text{S}/\text{cm}$). Based on the above, either trace seawater contaminant can be detected before reaching this control reference value, indicating that the novel identification model has practically no problems with regard to accuracy and sensitivity.

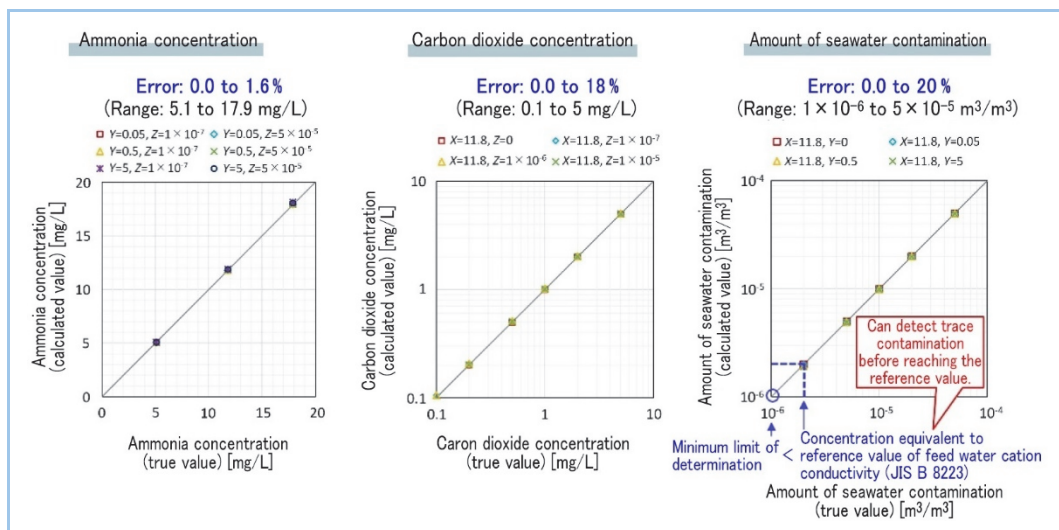


Figure 6 Verification results of novel identification mode using chemical equilibrium calculation software

6.2 Results of verification using the actual unit data

The validity of the novel identification model was verified using this novel model to calculate the carbon dioxide concentration and the amount of seawater contamination based on the water quality data measured in an actual plant. Figure 7 shows the identification results of feedwater which carbon dioxide contaminated at the time of plant startup. While doing the verification, we also measured the plant's chloride ion concentration and confirmed that there was no seawater leakage.

As shown in the figure, the amount of seawater contamination is below the minimum determination limit throughout the identification period, while the carbon dioxide concentration behaves in consistent with the cation conductivity. **Figure 8** shows the identification results of drum water from an operating plant, which has been in steady operation, where seawater leakage has occurred. The carbon dioxide concentration is below the limit of quantification (< 0.1 mg/L) throughout the identification period, while the change in the amount of seawater contamination corresponds to the cation conductivity. It is confirmed from the above that the novel identification model can produce calculation results that are in agreement with the behavior expected from the plant conditions based on the actual unit's data, thereby indicating the validity of identification with the new model.

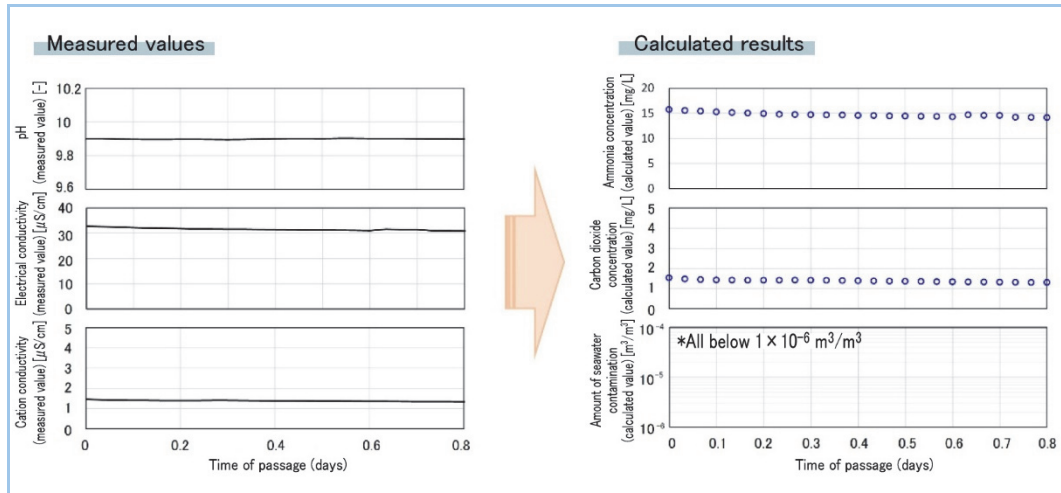


Figure 7 Verification results of novel identification model using water quality data from actual unit (contaminated with carbon dioxide, feedwater)

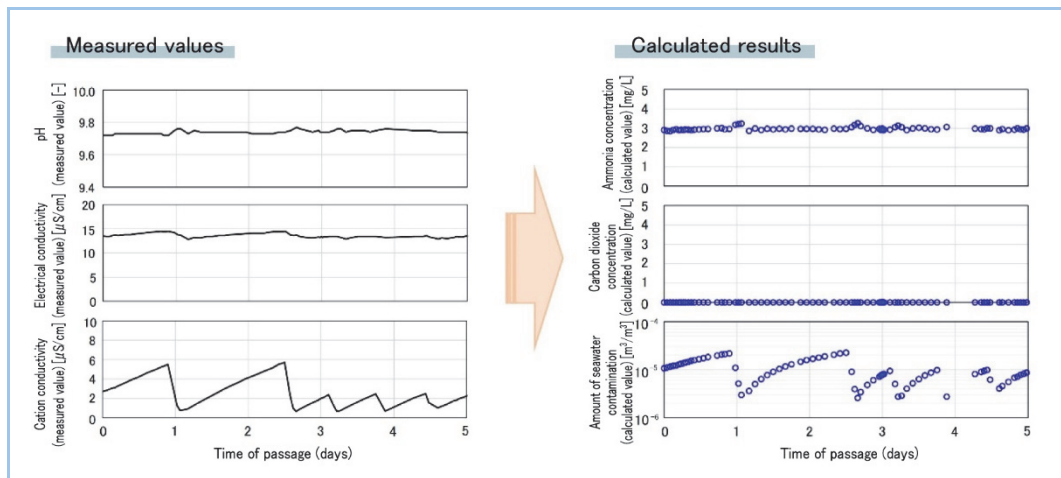


Figure 8 Verification results of novel identification model using water quality data from actual unit (contaminated with seawater, drum water)

7. Conclusion

Cation conductivity is measured as an indicator of impurity contamination in steam-water circuits of thermal power plants. However, as carbon dioxide interferes with the measurement, a novel identification method was studied to solve this problem. Because cation conductivity is elevated by contamination of either carbon dioxide or seawater, it is impossible to determine which contaminant is present based only on cation conductivity. However, pH and electrical conductivity behave differently depending on the contaminant. Focusing on this difference, we devised a novel model for identifying seawater contamination based on chemical equilibrium calculation considering not only cation conductivity but also pH and electrical conductivity. The results of verification using the chemical equilibrium calculation software and the data from actual units show that the novel identification model has good accuracy with an error of 0 to 20 % compared to chemical equilibrium calculation software. It has also been confirmed that trace seawater leaks can be detected before

reaching the limit value prescribed by JIS B 8233 for feedwater control (i.e., cation conductivity of 0.5 $\mu\text{S}/\text{cm}$). Looking forward, we will further verify the validity and improve the accuracy by, for example, examining the case of simultaneous contamination of carbon dioxide and seawater using data from actual units, and evaluating the impact of the actual unit's measurement error on the calculation results.

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