

A STUDY ON DEVELOPMENT OF EFFICIENT COLUMN DETECTION SYSTEM IN WASTEWATER TREATMENT OF THERMAL POWER PLANTS

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Abstract

This study deals with the development of a column capable of analysing the regeneration exchange cycle of ion exchange resin or the state of ion exchange resin in water treatment of thermal power plant. This is to obtain reliable water treatment results with scientific and efficient monitoring. It is also intended to develop an ion exchange resin detection system capable of reducing the cost savings due to maintenance. Generally, thermal power plants use high purity water to obtain steam, and keeping water quality of plant water at a high purity level in a water circulation system is an essential element for stable operation of a power plant. To obtain high purity water using ion exchange resins is one of the methods currently used today. So far, only the water quality of the system has been measured, but the condition of the column and other factors are theoretically and largely excluded. Therefore, it is very important to analyze the changes in the water quality while observing the reactions in the column as the phytoremediation passes through the column. In addition, it is necessary to observe the exact condition of the system water as well as the exchange cycle and maintenance of the ion exchange resin. Thus, it is necessary to develop column sensing sensors and measuring devices with smart functions. This study aims to ensure stable operation of thermal power plants by maintaining an objective and reliable high-purity system numbers at the site.

Keywords: ion exchange resin, water purity, detection system.

Introduction

Ion exchange resin is a polymer substance that combines a functional group of tiny three-dimensional structures, and it exchanges to refine ionic substances dissolved in polar and non-polar solution.

The use of these ion exchange balances is due to the introduction of impurities into the system water, which can cause corrosion of the facility and cause fatal damage to the main machinery. Although impurities may flow into the plant system, heat exchangers, such as condenser, can flow through cooling water containing highly corrosive ions between the thin outer walls of the heat tube, making it easy for large quantities of impurities to enter the system through holes due to corrosion or erosion [1,2].

Theoretical Problems in Current System of Measuring Instruments

In practice, systematic measurement is not easy

The general measurement items for each point of the current thermal power plant are as follows [3]:

- Sodium ion concentration can be measured at the points before and after ion exchange resin passes to determine the desalination efficiency and resin saturation.

• pH and electrical conductivity can be measured as part of the ion exchange resin regeneration cycle.

• The efficiency of the ion exchange resin, water treatment system, and reverse osmosis system can be determined by measuring the specific conductivity and the non-conductivity at various points.

• The ORP can also be monitored as a control variable for monitoring the presence of some compounds in the chlorinated / dechlorinated form in the influent or protecting the facility such as reverse osmosis filters or deionized resins (chlorine can damage the ion exchange resin).

Several instruments are installed near heat exchangers such as the steam condenser in the plant to monitor the inflow of impurities at all times. Among these instruments, conductivity is most commonly used due to its price and ease of operation.

In addition, since the pH of the system is adjusted by the plant to suppress corrosion and scale of the system, the pH of the system water is used to monitor the inflow of impurities by measuring the electrical conductivity, excluding the effects of these drugs, and increasing detection sensitivity, the positive conductivity measurement method is used to measure the electrical conductivity by passing a portion of the system water through the system.

However, this method is not easy to detect impurities in power plants that use cooling water, such as Cl^- or SO_4^{2-} in large quantities, even if small amounts of coolant are introduced into the system water, but contain less chlorine ions or sulfuric acid ions while relatively high amounts of HCO_3^- are used as cooling water.

It is not easy to detect impurities in plants that use this much-contained fresh water as a cooling water. In fact, the electrolyte solution's electrical challenge depends on the type and concentration of ions present in the solution; the cation impurities introduced into the system can be replaced with H^+ using a hydrogen cation exchange resin and the anion impurities with a chlorine anion exchange resin to improve detection sensitivity.

The reversible decomposition of a compound into an atom or smaller molecule of its constituent is called electrolytic dissociation, and most of the substances that occur form an ion through chemical bonds with the solvent and the degree of ionization is called dissociation constant [4].

Diversity assets such as carbonic acid and sulfuric acid exist primarily in the form of HCO_3^- or HSO_4^- among the receptors, as shown by the dissociation constant (K_a) as the primary nautical constant is much higher than the secondary nautical constant. In the case of bicarbonate ions, the higher the pH of the water solution, the higher the degree of nautical chart, and the lower the pH, the lower the pH, the greater the CO_2 molecular state. Therefore, the higher the pH of the solution, the higher the rate of nitric acid ion, and the higher the electrical conductivity can be obtained if replaced with chlorine ion using chlorine anion resin.

River water, lake water, and seawater contain various ionic components and generally contain cations such as Na^+ , Ca^{2+} , Mg^{2+} and anions such as Cl^- , SO_4^{2-} , and CO_3^{2-} . The concentration of each ion differs greatly depending on the type of water.

In the seawater, the anions are in the order $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$, and in the fresh water $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$. In the cationic electro-conductivity method, the sample water passes through a small number of cation columns. Therefore, since the chloride ion and the sulfate ion become hydrochloric acid and sulfuric acid having high dissociation, almost all of them are dissociated and contribute to increase the electric conductivity. However, so that the electrical conductivity is lowered. The effect of bicarbonate ion can be neglected when the concentration of chlorine ion or sulfate ion is extremely higher than the concentration of bicarbonate ion such as seawater. However, when chlorine ion or sulfate ion is less than bicarbonate ion like fresh water, it is difficult to detect it because the sensitivity is low. Therefore, it is necessary to increase the dissociation degree of the bicarbonate ion and to convert it to another ion having a larger electric conductivity [5-7].

Conductivity and pH form a very complex relationship

In general, when the conductivity of pure water is less than $1\mu\text{S}/\text{cm}$ ($100\text{M}\Omega\cdot\text{cm}$), it is not necessary to carry out pH control. However, the pure water has a different pH from the measured value in many cases described as follows.

- When measuring pH in the laboratory by sampling:
 - $\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}^+ + \text{HCO}_3^-$
 - Since CO_2 in the atmosphere dissolves in pure water, pH continues to degrade during pH measurement.
- pH meter is installed in the line:
 - In general, only the pH electrode is selected when attempting to install a pH measurement system, but this is incorrect and the use of pH meters for raw water and pure water (especially ultrapure water) is quite different. Since the pH of the pH electrode is different from that of the glass diaphragm, the circuit and algorithm of the pH meter must be different. However, it is usually used by calibrating with a general pH meter.
 - Even if the pH meter for pure water is very low, the measurement value of the pH meter is out of the theoretical value, so the measurement value of the system number cannot be regarded as accurate.

Conductivity and pH form a very complex relationship

If the electrical conductivity is less than $0.1\mu\text{S}/\text{cm}$, it is generally referred to as a pH non-measurement zone. Water with an electrical conductivity of less than $0.1\mu\text{S}/\text{cm}$ theoretically exists between 6.2 and 7.6 pH. However, measurements usually exist beyond this range at the site, all of which are unreliable, and as electrical conductivity decreases, the reliable pH range becomes smaller. PH measurements of pure water with extremely low ion concentration are extremely difficult and can be cited for several reasons:

- Although the glass of the pH electrode is very small, it is strongly influenced by dissolved ions in the case of pure water whose buffering effect is low because it dissolves in pure water. For example, even if the pH of the same pure water is measured at the same temperature, the reason why the measured pH value differs depending on the type of glass of the pH electrode to be measured is different.
- Although it is a trace amount from the comparative electrode, since the potassium chloride solution flows out, it can sufficiently receive the influence of potassium chloride and its impurities.
 - Since the carbon dioxide in the air (about 3% of the atmosphere) dissolves in pure water, the pH changes with time.
 - The contamination of containers such as the beaker used in the measurement and the liquid measured before the electrode attached to the electrode is very small, but it is a major cause of pH change in pure water (especially ultrapure water).
- When measuring the pH of flowing pure water, since the conductivity of pure water is extremely small, the pH measurement is affected by leakage current or induced current from the outside.

Therefore, it is difficult to measure the exact pH of pure water due to lack of buffering action or conductivity of pure water itself. For this reason, the pH value of pure water measured in phytoremediation is unreliable.

Theoretical Difficulty of High Purity Measurement

Since high purity is literally pure, it immediately absorbs as soon as it comes into contact with impurities like a dry sponge. When high purity water is exposed to air, carbon dioxide is absorbed instantaneously, and the conductivity rises to about $2 \sim 3 \mu\text{S}/\text{cm}$. If you calibrate high

purity water in an open container, you will face a similar problem unlike when you calibrate a sample that flows through a process line even with the same sample.

The reason why the measurement of conductivity of pure water is very difficult is because the water itself must be ionized and the ionization must also detect a trace amount of ion impurities while being highly dependent on the temperature. In order to remove or reduce impurities in very small amounts, it is necessary to cope with the installation and calibration of measurement equipment. The trace impurities in the pure water itself are also variable in temperature coefficient and can reach up to about 7% per °C in severe cases.

For example, even a small amount of NaOH can result in a negative conductivity (lower than the theoretical conductivity of pure water) because OH⁻ ions overwhelm H⁺ ions (OH⁻ ion conductivity is lower than H⁺ ion conductivity).

Ultrapure water is the result of ionization of H⁺ and OH⁻ ions in the water itself because of the fact that conductivity is measured in the field even though there is no impurity (other than water). The ultrapure water conductivity value at 25°C is 0.055 µS/cm (resistance value is 18.18 mΩ·cm). In order to know the conductivity or resistance of ultrapure water, it is difficult in reality to be able to accurately perform temperature compensation under low conductivity conditions (for example, less than 10 µS/cm).

If the pH sensor and the sample line are used together, the conductivity sensor must be in front and the pH sensor should be behind. This is because the KCl flows out from the pH sensor reference electrode and consequently the conductivity rises. For conductivity, the sensor and receiver should be installed as close as possible. This is to minimize electrical interference. In case of pure water, it is preferable to use stainless steel for sample line in order to ensure consistency. The flow rate is almost irrelevant, but iron oxide residue tends to accumulate the least at around 2m per second.

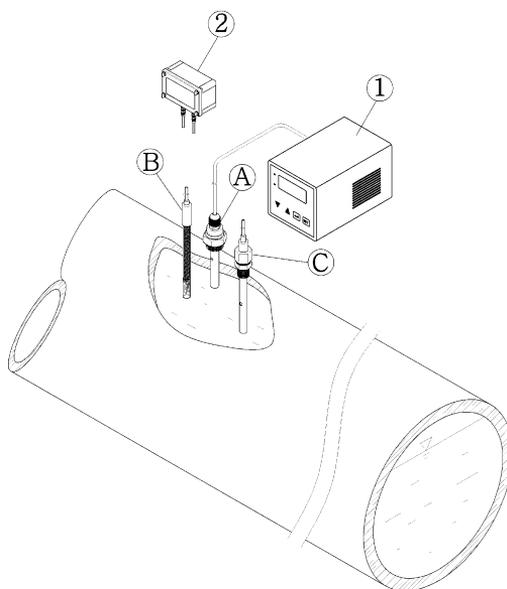


Fig. 1. Measuring instruments (1, 2) and sensors (A, B, C) for water quality measurement

If resin is used for desalination, the inside of the resin tank is a cation or anion environment. Therefore, when the cation exchange resin saturates, the pH value rises. On the other hand, when the anion exchange resin saturates, the pH value decreases. To check whether the chemical treatment is effectively performed in the desalination apparatus, it is necessary to measure the pH after passing through the desalination apparatus. However, since the electrolyte

does not remain in the water immediately after the desalination unit, it is not easy to measure the pH.

When the resin exchange capacity reaches the limit, not only the conductivity of the water but also the pH value changes, and the anion resin / cation resin of the mixed ion exchanger. There is a high probability that the pH value has dropped due to the ratio imbalance.

Objective Measures Needed to Solve the Problem

It is important to compensate the temperature of the actual system water

The self-ionization phenomenon of water is greatly affected by temperature. To ensure temperature compensation, conductivity of the pure solvent must be subtracted from the conductivity of the solution. This is because the conductivity of the electrolyte can be known. In the case of high purity water such as the general electric conductivity meter of the current system, accurate temperature compensation cannot be performed by adding a linear value in a few degrees per °C. Therefore, more effective temperature compensation is required.

Ion exchange resin beads should also be studied to determine if the color is directly related to the performance of the resin

This is often mentioned, but the color can vary depending on the ion exchange resin production lot. Apparent color differences are almost independent of resin performance. In the case of cation exchange resins, slight deterioration occurs rarely during storage and may turn orange. Even so, you can return to the original color by rinsing it with water or using a regeneration process before use.

Ion exchange resins are sometimes mixed with dark beads, but the thermal environment cannot be completely constant during the production of ion exchange resins. As a result, some beads have a lighter or darker color than the average. Mixed resin has cation exchange resin and anion exchange resin. Cation exchange resin usually has a dark color and anion exchange resin tends to have a bright color. In other words, it is not directly related to judging the relationship between the performance of the resin and the tree number only by the bead color. Therefore, a measurement system capable of objectively detecting this phylogenetic tree is needed.

Reliable sizing criteria is needed

When the solution ion replaces most of the resin ions, it is regarded as resin saturation. Normally, an electric conductivity cell is installed at the outlet of the desalination unit (ion exchange resin) and it is judged whether or not it is saturated based on the measurement result. If the resin is neutralized and the conductivity value is high, it can be automatically entered into the resin regeneration cycle. When the value is low, it is also possible to measure the pH from the anion exchange resin portion of the hybrid cartridge. If the cartridge is transparent and looks invisible, it may be observed that the cartridge has salt on the wall because the anion exchange resin is (neutral) deteriorated (neutral) and eventually reaches saturation.

When the ion exchange capacity is lost (saturates), the resin that has discolored (usually blue and discolored to saturate), it is possible to know when to replace the cartridge due to the color change, but it is possible to increase the reliability more by automation control using the measuring instrument.

The condition of the regenerated ion exchange balance should be known

Regenerative work is important. Reducing the concentration of regenerative agents result in some of the ions that need to be filtered out without exchange, thereby reducing the water quality. In the case of a mixed desalination device, if the cation exchange resin regeneration operation is incomplete (unless enough to replace the jagged ion with hydrogen) the sodium ion can still flow into the anion exchange resin tank (sodium capture is the most difficult among the

cations that are commonly contained by the source, because of its low affinity with the resin). If the anion exchange balance is passed, sodium hydroxide is generated, resulting in a base solution of 8-9 pH. However, they do not place excessive amounts of regenerative curer in the goal of full regeneration, and actually recover only 2/3 of the resin treatment capacity. In most cases, however, it does not require a complete clean up. For example, boiler water furnaces have a good alkaline property, but the 8-9 pH above is perfect.

Some impurities, such as silica, can only be removed with a strong base resin. Most of the water contains dissolved silica as a main component. Silica is usually present as a neutral polymer but has a negative charge when the pH is high. That is, silica can be replaced or removed in the form of a hydroxyl group only in a strong basic environment of a strong base resin. If the instrument is used, the data can be detected before and after the regeneration so that the state of the regenerated ion exchange resin can be grasped.

There is a need to know about the cycle chemistry of thermal power plants

If copper alloy is used in the power plant's water supply section, the concentration of dissolved oxygen is kept very low to prevent corrosion. Usually, the concentration of dissolved oxygen is lowered by using a reducing agent or deoxidizing agent (hydrazine or amine reducing agent). Often, the DO meter is used to monitor dissolved oxygen, but in practice it is appropriate to measure the ORP (which better reflects the environment affecting the metal oxide passivation layer in the actual water supply train). In addition, the ORP is sensitive to the overloading of the reducing agent (accelerating corrosion by overloading the reducing agent).

It is known that it is possible to supply reducing agent based on ORP in the reduction cycle chemical control. The ORP measurement for the reducing environment is approximately -100mV to -350mV, although this may vary depending on plant characteristics or other cyclic chemical parameters. Set points should be based on long-term operation to minimize iron and copper corrosion product concentrations. If the ORP is too high, an oxidizing environment is created and copper is affected. If the ORP is too low, it will contribute to accelerated flow corrosion of the iron pipe.

Drawing the appropriate curve of the ORP with the ORP versus hydrazine supply at the plant will form a similar shape to the dechlorination curve described earlier. However, the ORP range moves downward from 500mV to 600mV.

The Importance of Quality Control for Water Treatment Process in Power Plants

A common utility water system is affected by a variety of variables. The quality of the supplemental water supplied to any system can change over time depending on its properties. Depending on where the raw water comes from, the fluctuation of the water quality of the raw water may be large or small. Changes in the amount of water reused, changes in product yields, and chemical feed rates all contribute to the operation of the plant. Other factors that can affect utility water system are as follows:

- Water temperature
- Process temperature, surface temperature
- Water quality (SS, hardness pH fluctuation, etc.)
- Flow/speed
- Throughput
- Evaporation rate
- Quality of processed products
- Driver's skills and proficiency

These parameters are considered in the test process or application process of the pilot plant to develop water treatment of various water systems. However, it is not easy to simulate the factors affecting actual operation in this process. It is said that all water systems are unique

because the water sources and operating methods of each water system applied to the industry are different and the factors mentioned above are different. In order to properly treat inflow water, boiler, cooling water or effluent water, steady water treatment chemical processes should be controlled and adjusted for sudden disturbances. Although the water treatment system should be well designed for proper water treatment, in practice, it is necessary to control the chemical process for water treatment and to control the problem without exceeding the standard value. In order to successfully solve the problems in the water treatment system, the knowledge, skill, skill and logic of the worker are needed. In order to improve the operation of the water treatment plant, it is necessary to recognize the importance of getting accustomed to the facility, acquiring the operation procedures of the plant, and continuously improving the facility based on continuous efforts. Reliable and appropriate data are needed to measure and reduce plant operation variability.

In recent years, it has become much easier to manage, collect, and utilize these data through computerized control systems. The operation data of the control system is stored in the database and can be recalled and re-processed and analyzed in various forms. Thus, operators can easily use these analytical materials to solve problems in the control system without spending a lot of time.

Necessity of Column Meter Development for Thermal Power Plant

Column meters for thermal power plants are highly needed. For this purpose, it can be solved by the measurement method using selective ion sensing using minute current in water. This can solve various problems caused by the method of measuring the system water with the conventional water quality measuring instrument. For example, the column is monitored to analyse the regeneration exchange cycle and various states of the ion exchange resin. In addition, more reliable water treatment can be obtained by comparative analysis with measuring instruments installed in the line.

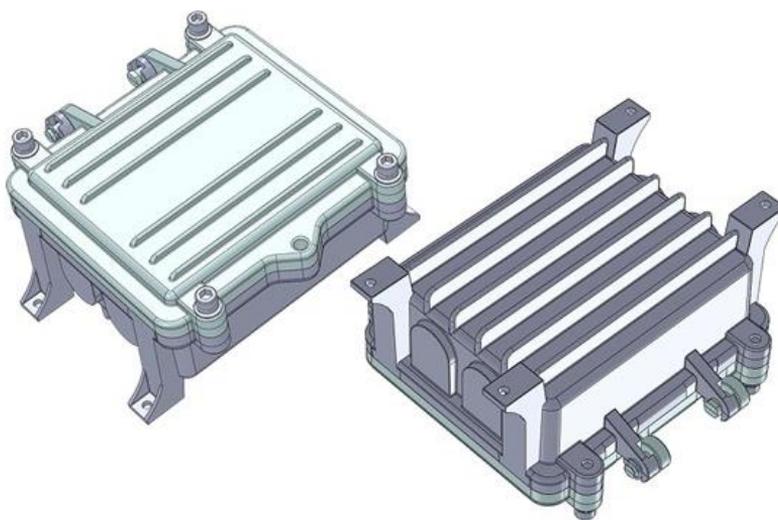


Fig. 2. Outer appearance of column meter

At various points around the column of the thermal power plant, the ion exchange resin efficiency is determined by measuring the specific conductivity and the ion conductivity, or the pH or conductivity is measured as part of the ion exchange resin regeneration cycle. It is also possible to determine the desalting efficiency and the saturation of the resin by measuring the

sodium ion concentration before and after the passage of the ion exchange resin. However, the problems of general measuring instruments measured in these trees are as follows:

- If pH sensor and electric conductivity sensor are used together in the sample line, the conductivity sensor must come in front and the pH sensor should follow in order.
- Limitations of the inability to measure the pH range as the electrical conductivity decreases.
- The trace impurities in the pure water itself are also variable, and if they are severe, they can rise to about 7% per °C. In general, the number of thermometers is fixed.
- The water itself is ionized and its ionization is also highly dependent on the temperature, and there is a limit to detecting trace ion impurities.
- For mixed-bed ion exchange resins in desalting systems in some cases, it is necessary to change the resin cartridge in every cycle. When the resin exchange capacity reaches the limit, not only the conductivity of water but also the pH value is changed.
- It is theoretically unreliable because pH is not easy to measure because there is almost no electrolyte left in water right after desalination.
- If the regeneration process is incomplete, sodium ions can flow into the anion exchange tank as it is. Among the cations contained in the raw water, sodium capturing is the most difficult and this can also be affected by the electrical conductivity.
- Currently, the system for analyzing the water quality of water in the system does not compensate the temperature due to the self-ionization phenomenon of water, but compensates by measuring the water temperature.
- It is important to take action before the resin completely degrades through fouling, and there are limitations to the general instruments used to periodically monitor and control the resin.
- If the solution ion replaces most of the resin ions, it is regarded as resin saturation. Normally, the conductivity cell is installed at the outlet of the desalination unit (ion exchange resin) and the saturation is judged based on the measurement result. In many cases.
- Boiler water treatment during pause is often overlooked. The main obstacles of the boiler during the rest period are corrosion trouble. In case of rest, calibration or transient, most of the time, the instrument keeps the previous figures and most of the time, the risk of fortune exhibition may occur.



Fig. 3. Power plant's on-site photo of the column

Since the above-mentioned risk that can occur in such a site is much higher than that, it is difficult to accurately determine the condition of water quality only by the water quality

measuring device of the water system line. Therefore, it is necessary to research and develop a column dedicated meter to further objectify have.

Function of Column Meter in Thermal Power Plant

- The ion exchange resin saturation state is identified step by step (1 ~ 5 steps). This signal can be calculated by the CPU to know the predicted saturation level.
- The exchanged resin automatically detects and informs the regeneration cycle of the resin according to the information input at first, so it can always be prepared in advance.
- Early diagnosis of the fouling progression of the resin and possible predictive fouling alarms are possible.
- Even during pause, two column sensors measure before and after the column and transmit signals in real time.
- The built-in temperature sensor of two column sensors analyzes the temperature difference before and after the column, thus it can perform precise temperature measurement by automatically compensating the variable temperature coefficient.

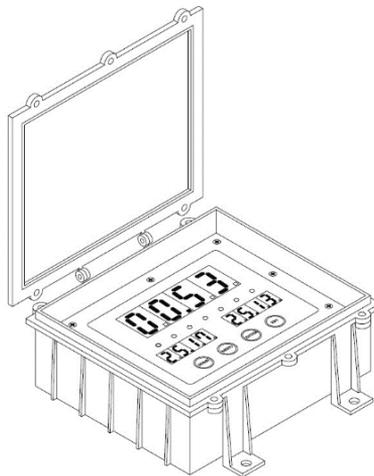


Fig.4. Perspective view of the column meter

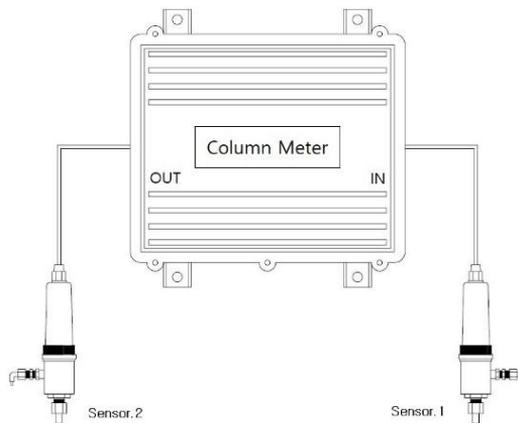


Fig. 4. Overall structure of column meter

Basic Specifications for Column Meter Development

- Measurement method: Selective ion detection method using micro-current.
- Usage: Detecting column of power plant and analyzing post-flow tree.
- System configuration: 1 main body, 2 sensors (can be multi-installed in some cases).
- Temperature Compensation: automatic temperature compensation according to the tree water temperature coefficient.
 - Body material: Aluminum die casting.
 - Calibration: Automatic calibration by artificial intelligence (manual).

As shown in Fig. 5, the selective ion mass detected by the micro-current is measured in the two column sensors. This can be seen by the signal difference between Sensor 1 and Sensor 2, and these two signals are calculated by the Column Meter's CPU.

In addition, the temperature sensor inside the sensor can measure the temperature before and after the column to perform precise temperature compensation. This is possible because, unlike conventional automatic temperature compensation, it calculates the comparative temperature before and after the column measured at both sensors, which is temperature compensated by the absolute temperature coefficient of the system.

Conclusion

All waters in nature contain salts that are dissociated in the form of ions. Positively charged cation and negatively charged anion are dissolved in water. These ionic materials can cause problems in the reliability and efficiency of the operation in the boiler or process system. As an example of these problems, tube damage such as catastrophic tube overheating due to a scale formed locally in the heat exchanger can occur, resulting in increased operating costs and loss due to unplanned outages.

Hardness components such as calcium and magnesium must be removed prior to being fed into the boiler feed-water system. In the boiler feed-water system of high temperature and high pressure, almost all kinds of ions including silicon and carbon dioxide should be removed. In this case, an ion exchange resin system is applied to remove ions dissolved in the water to effectively remove ions.

In an ion exchange resin, one ion can be changed to another ion, and the ion exchanged in the raw water is temporarily stored in the ion exchange resin. Then, the ion exchanged resin is released in the regeneration step. In an ion exchange resin, this process exchanges unwanted ions contained in raw water with more acceptable ions.

The column meter study presented in this paper can scientifically analyse and measure the regeneration exchange cycle of the ion exchange resin or the state of the ion exchange resin by continuously monitoring the columns of the thermal power plant. Therefore, it is essential to develop a column sensor and measuring instrument to obtain a reliable water treatment result and to reduce cost reduction by maintenance.

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