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High Efficient Solid-liquid Separation Technology

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Abstract

Steel industry uses large quantities of water, generally requiring approximately 190 ton of water to make 1 ton of steel. There is a variety of use, such as indirect cooling of machinery, collecting particles and pollutants from gas streams, and direct cooling of steel. In the process of continuous casting, hot rolling, and plate rolling, direct cooling water is not only essential to remove iron oxide scale from surface of slab and steel sheet, but also control steel structure. Therefore, facility maintenance plays an important role to prevent a blockage of spray nozzles and small pipes in factory. We were successful in developing a water treatment chemical, efficiently removing SS and oil in circulated water of direct cooling. It enables the drastic improvement of circulated water quality to supply factory, and moreover both energy saving and compact process of water treatment plant are expected.

1. Introduction

The steel industry uses large quantities of water, most of which is used as cooling water. Cooling water is broadly divided into two types: Indirect cooling water to be used to indirectly cool furnace bodies and equipment; and direct cooling water that is directly sprayed onto steel products and production facilities. Both types of water are used cyclically. The wastewater treatment flow generally used for direct cooling water is briefly described in this report (**Fig. 1**).

Direct cooling water used for facilities of continuous casting and hot rolling passes through scale sluices immediately below the manufacturing lines, and goes into scale pits together with iron oxide scale that has separated from the surfaces of steel materials and rolling oil. In the general wastewater treatment process, coarse suspended solids (SS) with grain sizes of 100 μm or more (hereinafter referred to as “coarse grains”) are removed by sedimentation in a scale pit; and fine SS with a grain size smaller than 100 μm (hereinafter referred to as “particulates”) that cannot be removed in the scale pit is removed using a sedimentation basin, filter, etc. in the later process. As most of the oil contained in the circulated water attaches to the surfaces of particulates, such oil is also removed from the circulated water at the same time as when SS is removed. Lastly, a cooling tower is used for releasing the heat from the circulated water, and then the treated water is supplied to plants.

Given the current ability of water treatment by the conventional treatment flow as described above, we have worked on the development of a new wastewater treatment technology, and succeeded in making the technology named New Clear Stream Technology (NCST) available. NCST can significantly improve the quality of

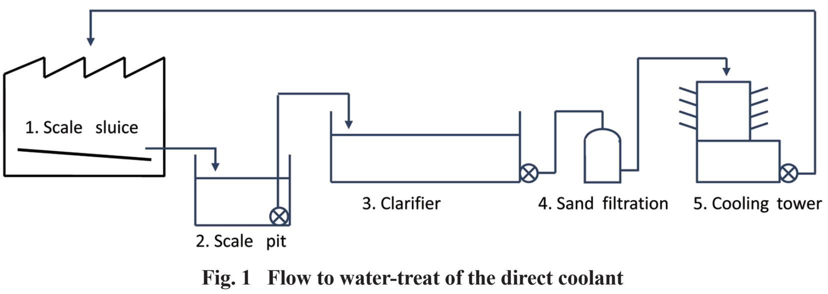

Fig. 1 Flow to water-treat of the direct coolant

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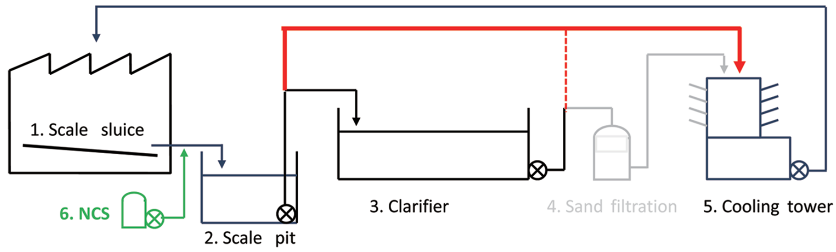

Fig. 2 Flow to water-treat of the direct coolant after the NCST application

water to be supplied to plants, compared with the conventional wastewater treatment. It also allows wastewater treatment facilities to omit some of the processes, as well as to consume less energy.

NCST involves adding a new water treatment chemical called NCS to wastewater that contains a large quantity of SS and oil under the condition of water strongly agitated in a scale sluice, etc. This makes particulates that exist in the wastewater adhere to coarse grains, enabling the major part of the particulates to be settled and separated in a scale pit together with coarse grains. Most of the SS and oil, which have been treated in sedimentation basins and filters in the conventional wastewater treatment process, can be settled and separated in scale pits, allowing simplification of wastewater treatment processes.

In addition, application of NCST to existing wastewater treatment processes will significantly improve the quality of direct cooling water to be supplied to continuous casting and hot rolling facilities, by which the clogging of small pipes and spray nozzles in plants is expected to be reduced. This enables steel production facilities to control the cooling systems of steel materials, etc., in a manner that closely resembles the design values. Moreover, the quality of steel products and yield rate are expected to be improved.

In this paper, we present an outline of NCST. Furthermore, we report NCST's effects for improving water quality that we have confirmed using actual equipment, and discuss the possibility of a reduction in the number of processes and energy saving in water treatment facilities by using NCST.

2. Solutions Offered by NCST

2.1 Effects of the introduction of NCST

From the viewpoint of maintenance and management of water treatment facilities, it is preferable to reduce the amount of equipment to be maintained and managed as much as possible. However, as water treatment equipment becomes simpler, the quality of treated water is degraded, thereby making it difficult to maintain the quality of water to a level that a plant requires. Given this, we pursued development of a technology that allowed for balancing the simplification of water treatment equipment and maintaining favorable water quality. After devising a way for particulates and oil to adhere to coarse grains in order to be settled and separated from water in a scale pit together with the coarse grains to which they adhere, we successfully developed NCS, which can realize our goal.

In the process of conventional coagulation treatment, an inorganic flocculant (e.g., poly aluminum chloride [PAC]) is added to the water to be treated. Then the polymer flocculant is added to settle and separate SS from the water in a sedimentation basin. This method requires a rapid mixing tank in which PAC is made to react, a slow mixing tank in which polymer flocculant is made to react, a sedimentation basin, and equipment for injecting various chemicals. Meanwhile, for NCST, which requires adding a single solution (NCS) alone to a scale sluice, necessary devices are a tank used for the injection of the chemical and pumps.

The NCS added to a scale sluice reacts with SS (consisting of particulates and coarse grains) in the target water very quickly, and forms aggregates that are coarse grains to which particulates adhere. These aggregates are quickly settled and separated from the water in the scale pit, completing the treatment of SS when the water reaches the outlet of the scale pit. The water treatment flow using NCST is shown in **Fig. 2**.

2.2 NCST treatment mechanism

NCST is a technology that makes particulates adhere to coarse grains using NCS. NCS is also capable of making coexisting oil adhere to coarse grains. This NCS is a type of polymer flocculant (copolymers of monomers with acrylamide and a cationic group). NCS's unique feature is its high capability of making particulates adhere to coarse grains, compared with general polymer flocculants. We compared NCS's ability with that of general polymer flocculants using a test method as shown in **Fig. 3**. The differences in ability (characteristics) found in the test are shown in **Fig. 4**.

First, we compared the ionic character. A cationic polymer flocculant and NCS showed higher ability to treat SS than anionic and nonionic polymer flocculants (Fig. 4). This is probably because cationic chemicals neutralize electrostatic repulsion on the surfaces of particulates, which are usually negatively charged, prompting aggregation.

Next, we compared the cationic chemicals. When NCS was used, the concentration of SS in the supernatant water did not exceed 10 mg/L. On the other hand, the concentration of SS of the same did not drop to 20 mg/L, when the cationic polymer flocculant was used. Although not shown in the figure, even when the injection ratio of the cationic polymer flocculant was increased, the concentration did not drop to 20 mg/L. At this time, aggregates of particulates were observed among the particulates remaining in the supernatant water. This implies that a difference in the ability for treating SS between the cationic polymer flocculant and NCS affected the formation of aggregates of particulates. Therefore, we conducted an SEM observation of precipitates obtained as a result of the treatment with each chemical.

During the observation, in the precipitate obtained from the water for which the cationic polymer flocculant was used, particulates formed aggregates ranging in size from 20 to 50 μm. While some of these aggregates adhered to coarse grains, others existed separately from coarse grains (**Fig. 5**). Meanwhile, in the precipitate obtained as a result of the treatment with NCS, the sizes of aggregates of particulates were smaller than those of the cationic polymer flocculant in the range of 5 to 20 μm; such aggregates sparsely adhering to coarse grains were observed (**Fig. 6**). In view of these observation results, NCS has the ability to make particulates adhere to coarse grains, and the NCS's flocculation ability to the particulates is lower

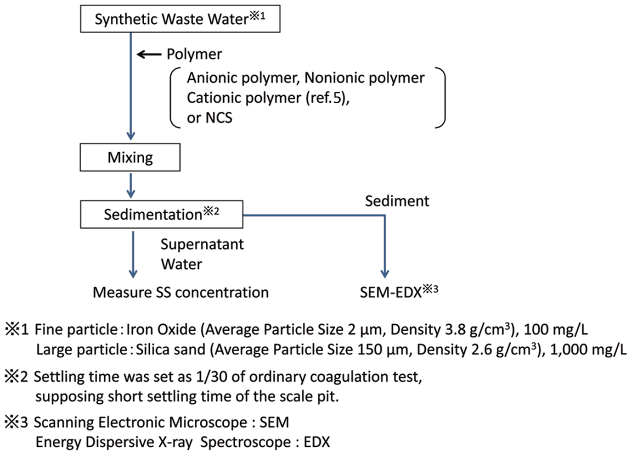

Fig. 3 Test method

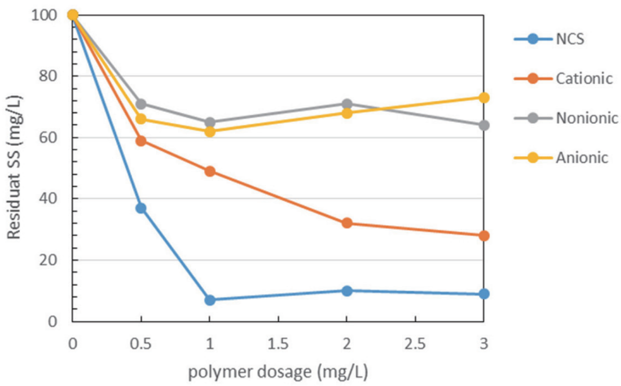

Fig. 4 SS treatability of various polymers

than that of cationic polymer flocculant. These characteristics of NCS enables the particulates to adhere to coarse grains without the formation of excessively flocculated particulates.

In the following section, we consider the aggregation mechanisms that are produced by NCS and the cationic polymer flocculant, and that are involved in the difference in aggregation properties of particulates between NCS and the cationic polymer flocculant. Although a large part of the aggregation mechanism of particulates of cationic polymer flocculants has yet to be clarified, a charge neutralization effect[1)] and cross-linking effect[2)] are proposed for the aggregation mechanism (**Fig. 7**).[3, 4)]

A study under test conditions that were similar to our test conditions has reported that a charge neutralization effect is mainly responsible for the aggregation.[5)] When the main factor of aggregation is the charge neutralization, the optimum injection ratio of a flocculant in an aggregation test usually corresponds with the flocculant injection ratio required for neutralizing the negative charge of particulates. By measuring the zeta potential, we checked the changes in the negative charges of particulates when the NCS was injected. As a result, the optimum injection ratio (1 mg/L) was remarkably lower than the injection ratio (3 mg/L) required to completely neutralize electric charges (**Fig. 8**). This indicates that the charge neutralization is unlikely to be the main factor of aggregation that occurs when NCS is used; rather the cross-linking function contributes to it largely.

In addition, we conducted another test, in which the concentration of coarse grains was increased to 2 000 and 5 000 mg/L, under conditions similar to those used in the test described above. The obtained results show that as the concentration of coarse grains is higher, the optimum flocculant injection ratio becomes smaller (**Fig. 9**). Considering that the surfaces of coarse grains are also negatively charged, the required concentration of a cationic polymer flocculant should be higher in order to cause aggregation by charge neutralization in an environment in which coarse grains exist in high concen-

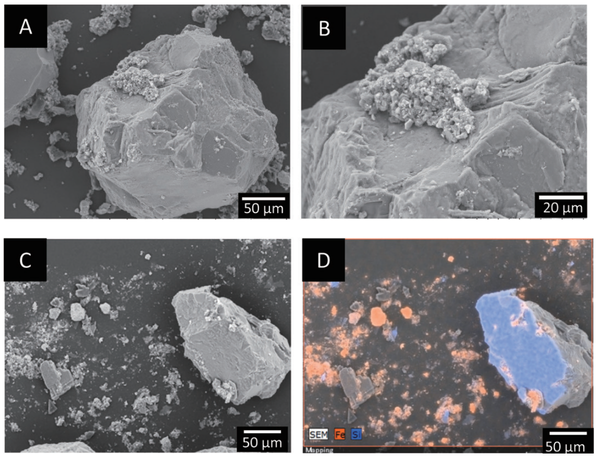

Fig. 5 SEM images of precipitates obtained with conventional cationic polymer

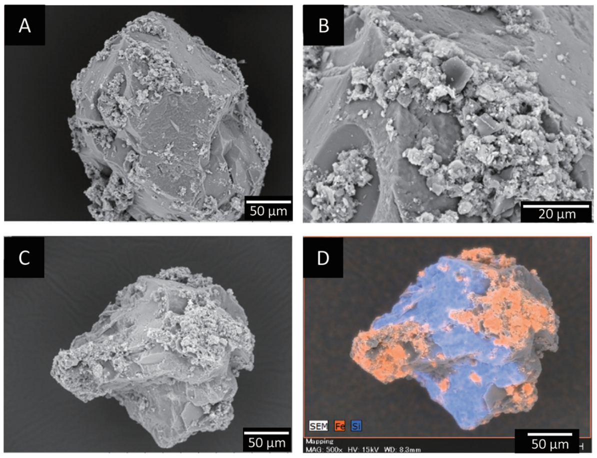

Fig. 6 SEM images of precipitates obtained with NCS

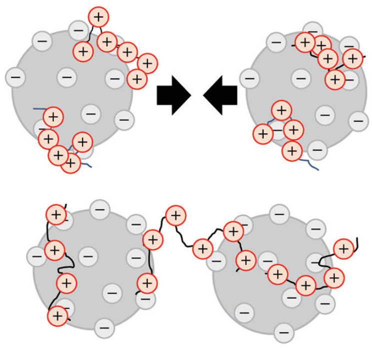

Fig. 7 Schematic representation of flocculation mechanisms

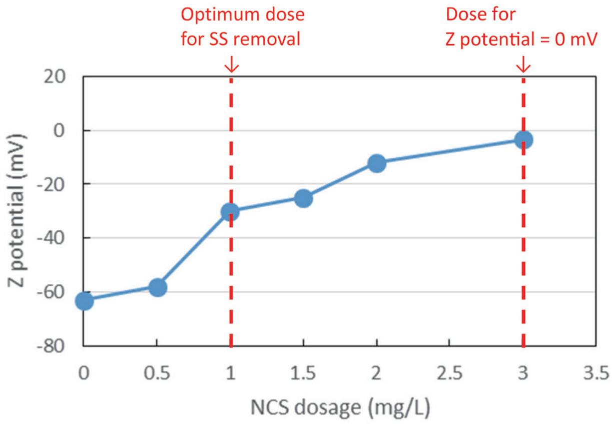

Fig. 8 Zeta potential of particle against NCS dose

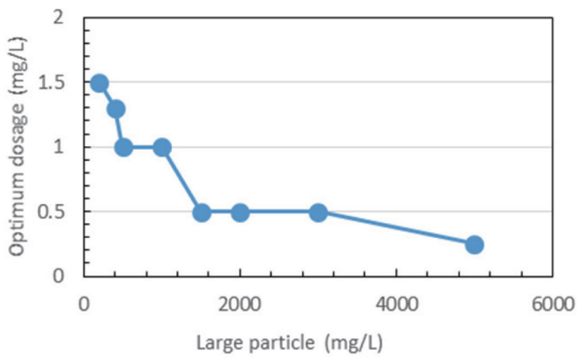

Fig. 9 Optimum dosage of NCS on various large particle concentration

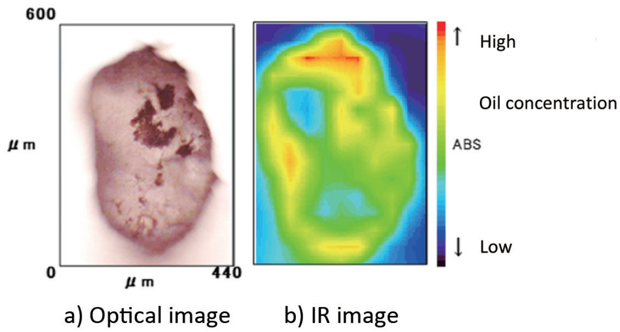

Fig. 10 Images of a large particle attached with small particles and oil

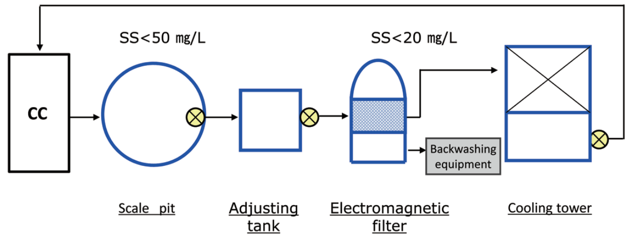

Fig. 11 Flow of water treatment process for CC (before applying NCST)

tration. However, the obtained result is contrary to that. This can be interpreted as an indication of another factor different from the charge neutralization effect—the cross-linking effect—that contributes more in the case of NCS.

Given these results, the characteristics of NCS can be summarized as follows.

- NCS is a new chemical that can efficiently make particulates adhere to coarse grains.
- The aggregation mechanism of the cross-linking model is more likely than that of the charge neutralization model in the case of NCS.
- In other words, NCS is a polymer flocculant that has an ability to selectively make particulates adhere to coarse grains.

The above is a description of the effect of NCS for making particulates adhere to coarse grains. Then, the following is the result of a test in which adhesion of oil to coarse grains was inspected. The test used simulated wastewater that was added with oil taken out from direct cooling water and concentrated, and with the particulates and coarse grains described above. We processed the wastewater with NCS, and sampled the precipitate. Next, we visualized the oil adhering to the precipitate extracted using infrared absorption in the microscopic field of vision as an index (**Fig. 10**). We confirmed that oil existed on the surfaces of coarse grains. Furthermore, the part to which a large quantity of oil adhered generally corresponded with the brown areas to which particulates adhered. This indicates the possibility that NCS made oil adhere to coarse grains together with particulates.

3. Application Example: CC Water Recirculation Station

3.1 Characteristics of the CC water treatment facility before NCST was introduced

About 30 years have passed since the CC (continuous casting) water recirculation station concerned (hereinafter referred to as the "CC facility") was constructed in 1986. In the facility, water used for direct cooling in the continuous casting process passes through a scale sluice and goes into a scale pit. Then it passes through an adjustment tank and is processed with an electromagnetic filter (**Fig. 11**). Back in those days when this CC facility was constructed, the effect of electromagnetic filters for removing SS was high, and the criteria for water to be supplied to the plant (SS: 20 mg/L or less, oil: 5 mg/L or less) was sufficiently satisfied. However, in recent years, the removal rates of SS and oil have declined, because the function of the electromagnetic filter used had deteriorated due to aging, and properties of wastewater changed from those when the CC facility was designed. At the CC facility, along with an increase in the concentration of SS and oil in the circulated water, problems such as clogging of strainers and spray nozzles occurred, and the need for a prompt improvement of the quality of circulated water began to increase.

3.2 Results of the application of NCST

In June 2012, NCST was applied to the CC facility for the first time. Before NCST was applied, the concentration of SS in the water treated using the electromagnetic filter was 19 mg/L, which was reduced to 6 mg/L after NCST was applied even under the condition in which the electromagnetic filter was not operated. In addition, while the concentration of oil was 7 mg/L before NCST application, it declined to 1 mg/L after the application. The water in the scale pit was muddy and brownish before NCST was applied, but after the application, it became very clear (**Fig. 12**). This means the quality of water was significantly improved. **Table 1** shows the results of analysis of the quality of circulated water before and after the appli-

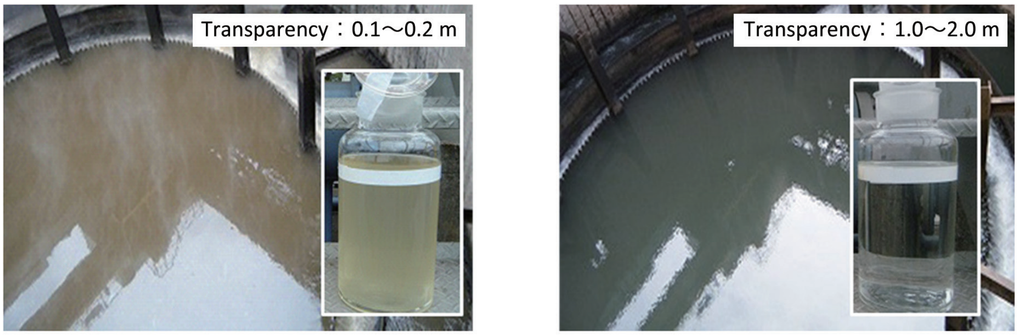

Fig. 12 Appearance comparison of the scale pit and the treated water
Left: Before applying NCST, Right: After applying NCST

Table 1 Comparison of water quality (electromagnetic filter vs NCST)

Item of analysis	Before applying NCST (electromagnetic filter run)		After applying NCST (electromagnetic filter stop)	
	Treated water from scalepit	Supply water to mill	Treated water from scalepit	Supply water to mill
SS (mg/L)	37	19	9	6
n-hex (mg/L)	10	7	2	1

* Before applying NCST data is the average of the 2011 fiscal year (number of experiments 35 times).
* After applying NCST data is the average of the 2013–2015 fiscal year (number of experiments 105 times).

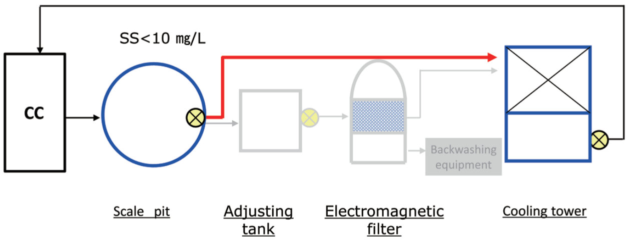

Fig. 13 Flow of water treatment process for CC (after applying NCST)

cation of NCST.

Approximately four years have passed since the use of the electromagnetic filter in the CC facility was stopped in September in the same year. Even now, the sedimentation of SS and oil is completed within the scale pit alone (**Fig. 13**), allowing for a simple treatment procedure in which the water recirculation station is used only for cooling water.

4. Effects of NCST and Future Prospects

4.1 Expected effects of NCST

When the treatment of SS and oil is completed in a scale pit, the sedimentation basin, filters, and accompanying backwash drainage facilities in the processes following the scale pit treatment become obsolete. Even with a sedimentation basin kept as a spare facility, NCST significantly reduces the quantity of accumulated sludge, facilitating periodic maintenance further. Furthermore, the treated water becomes clearer than that prior to the application of NCST, which prevents filling materials for cooling towers from clogging equipment, improving the cooling efficiency.

In addition, the use of clearer circulated water stabilizes the plant operation by reducing the number of cases in which deteriorated plant water quality forces the rolling lines to be paused, or the production to be slowed down. Moreover, as well as the maintenance cost reduction for pumps, valves, looper rolls, and other parts, the elimination of clogging of spray nozzles contributes to uniform cooling of steel materials, thereby the yield rate of products can be expected to improve.

4.2 Application to lines other than the CC line

Since confirming the effects of NCST through the application to the water treatment in the CC line, we have been testing the possibility of applying NCST to water treatment in other actual steel manufacturing lines. NCST has been showing successful results in improving the quality of water in all tests at the water treatment facilities of these lines. Currently, NCST is in full-scale operation at water treatment facilities in the CC and rolling lines.

As NCST can be applied as long as the water contains both coarse grains and particulates, we will continuously strive to expand its application to water treatment facilities in manufacturing lines other than those of the CC and rolling mills.

5. Conclusion

This paper described NCST's treatment mechanism using experimental data, and presented an example case in which the quality of water was improved by applying NCST to a facility in actual steel manufacturing lines. NCST uses a very simple water treatment method in which NCS with high ability to make particulates adhere to coarse grains is added to the scale pit. After applying NCST to the CC line, the operation of the existing electromagnetic filter was stopped, but the quality of water, which had been improved from the condition before the application of NCST, was maintained. We are currently promoting the application of NCST to water treatment in rolling mills in addition to CC water treatment, and the water quality improvement has been achieved in all these lines. Therefore, NCST is a useful means to secure desirable water quality without large investment in equipment.

Note: NCST is a registered trademark owned by Nippon Steel &

Sumikin Eco-Tech Corporation.

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