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Biological Treatment Process of Steelmaking Wastewater Treatment

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Abstract

The biological treatment methods have been widely applied to the treatment of various industrial wastewater and sewage. The coke oven wastewater generated from blast furnace coke plant has been treated by using the activated sludge process. Biological wastewater treatment process utilizes the metabolic function of microorganism to purify wastewater. If COD components and reductive inorganic compounds could be oxidized by bacteria efficiently, the energy and the cost for wastewater treatment would become lower. Therefore, Nippon Steel & Sumitomo Metal Corporation has been working on improving the biological steelmaking wastewater treatment methods. The typical trials in Nippon Steel & Sumitomo Metal are reported in this paper.

1. Introduction

The steelmaking industry deals with a lot of water. Nippon Steel & Sumitomo Metal Corporation uses 186 m^3 of water per ton of steel, approx. 90% of which is recovered and cyclically used.[1)] Types of wastewater differ in accordance with the manufacturing process in which water is used and discharged. For example, the coke manufacturing process releases gas liquor (coke oven wastewater) from a coke oven that contains components distilled from coking coal; the processes of a blast furnace and converter furnace discharge wastewater containing dust as a result of the cleaning of the blast furnace and converter gases; the rolling process releases wastewater containing steel powder (rolling wastewater); and the cold rolling and plating processes discharge oil-containing wastewater, acidic wastewater, alkaline wastewater, and plating wastewater. We have introduced various water treatment technologies to treat various wastewater types, and have been using them in our steelworks.

Among the various wastewater treatment technologies used to treat wastewater generated in steelmaking processes, this report focuses on biological treatment that is characteristic of the steelmaking wastewater treatment. We describe the characteristics of the biological treatment, and report its development status.

2. Adoption of Biological Treatment for Steelmaking Wastewater Treatment

Wastewater treatment involves various processes such as coagulation settling, floatation, filtration, adsorption, membrane separation, neutralization, and oxidation-reduction. Most of the wastewater treatment technologies used by the steelmaking industry are those generally used: Coagulation settling and filtration are used to remove SS (suspended solids) that contains coke dust, ore powder, and iron oxide; coagulation pressure floatation to remove oil contents; neutralization for acidic or alkaline wastewater; and chemical oxidation-reduction for soluble iron and metals.

Biological treatment technologies using microorganisms are high-efficient water treatment technologies with low environmental burden, low energy consumption, and low cost. In the fields of sewage and industrial wastewater treatment, biological treatment is used to reduce loads of the BOD (biochemical oxygen demand) and COD (chemical oxygen demand), and to remove nitrogen and phosphorus as activated sludge methods and biological methods for removing nitrogen and phosphorus. Biological treatment used for sewage treatment is a technology that mainly degrades and removes dissolved organic matter in the water and removes eutrophication substances such as nitrogen and phosphorus. In the steel industry using

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the blast-furnace pig iron-making process, as wastewater to be discharged from coke ovens contains dissolved organic matter (e.g., phenol), the activated sludge method has been conventionally used to treat it. Given this, we considered that suitable use of oxidation-reduction reactions involved in the metabolism of microorganisms would allow the existing chemical oxidation-reduction treatment to consume less energy and to be cost-effective. Since then, we have been developing biological treatment technology focusing on reductive inorganic compounds contained in steelmaking wastewater.

To adopt biological treatment into steelmaking wastewater treatment, it is important to identify microorganisms that can retain high activity and grow in the peculiar environment of steelmaking wastewater to establish a highly efficient biological treatment method. Moreover, it is important to establish treatment conditions under which the method can exert the ability in a stable manner; even the quantity and quality of wastewater change depending on the operation status in a manufacturing line. In view of this, we have been working on the adoption of biological treatment technology to wastewater that contains reductive inorganic compounds, and stabilization of the effects of existing biological treatment processes. In the following chapter, among the researches that we have worked on to date, we focus on typical cases and describe them in detail: Separation and recovery technology for metal compositions in plating wastewater using iron-oxidizing bacteria; wastewater treatment technology for alkaline wastewater containing reductive sulfur compounds using sulfur-oxidizing bacteria; and the study in pursuit of sophistication of the activated sludge method for treating wastewater discharged from coke ovens.

3. Main Subject

3.1 Steelmaking wastewater treatment using iron-oxidizing bacteria

3.1.1 Concept of the treatment

Electroplating wastewater contains metal elements including iron (mainly Fe^{2+}), zinc, nickel, and chromium. Usually for such wastewater that contains metals, Fe^{2+} is oxidized by aeration at neutral pH and made into a metal hydroxide. Then, it is removed by coagulation settling (neutralizing coagulation and sedimentation method in **Fig. 1**).[2] This treatment method is based on the principle that the solubility of many metal ions declines at high pH as shown in **Fig. 2**.[3] This neutralizing coagulation and sedimentation method, which has advantages of low treatment costs and stable quality of treated water, has been widely used. However, during the process of the treatment using this method, iron, zinc, nickel, and other various metals coexisting in wastewater are mixed into sludge, making the reuse of such sludge difficult.

However, separating iron from other metals and collecting them may expose the course of reuse. The solubility (properties) of Fe^{2+} and Fe^{3+} significantly differs as shown in Fig. 2. If Fe^{2+} can be oxidized into Fe^{3+}, Fe^{3+} can be separated from other metal ions of nickel and zinc, etc. to be recovered in principle; therefore, we have continued the development of a treatment process consisting of an iron oxidation and separation process (first step) and a valuable metal recovery process (second step) as shown in **Fig. 3**.

Fe^{2+}, which is difficult to oxidize in air under acidic conditions, can be easily oxidized by the electrolytic oxidation method, and the chemical oxidation method using hydrogen peroxide, ozone, etc. However, such methods have hardly been used for actual wastewater treatment from the viewpoint of cost.[4] On the other hand, methods using iron-oxidizing bacteria that have activity to oxidize Fe^{2+} under acidic conditions (about pH 2 to 3) have reportedly been used in the fields of mine wastewater treatment and bioleaching.[5] Iron-oxidizing bacteria, as typified by *Acidithiobacillus ferrooxidans*, are autotrophic bacteria that use energy produced during the iron oxidation reaction process for carbon assimilation. The use of iron-oxidizing bacteria facilitates Fe^{2+} oxidation under acidic conditions, as long as oxygen is supplied. We expected the method using iron-oxidizing bacteria to have an advantage over the electrolytic oxidation method and chemical oxidation method in terms of the running cost.

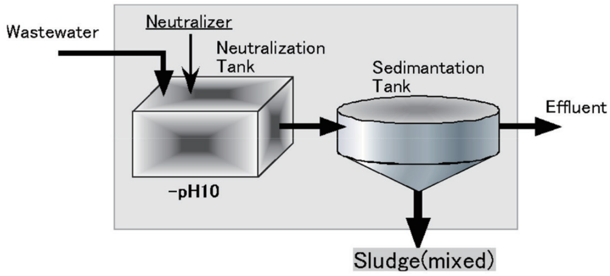

Fig. 1 Conventional process flow of neutralizing coagulation and sedimentation

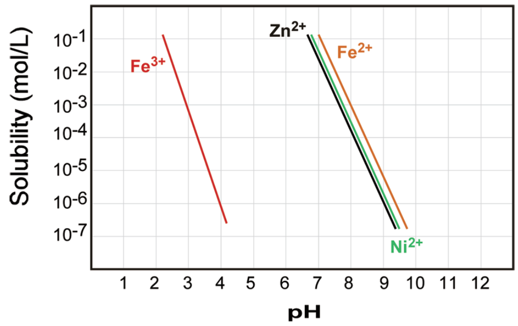

Fig. 2 Relationship between pH and solubility of metallic ions

3.1.2 Basic experiment using simulated wastewater

To date, using iron-oxidizing bacteria that we have collected from activated sludge at urban sewage treatment plants and have domesticated, we examined their practicality for plating wastewater treatment.[6–9] **Photo 1** shows an example of the experimental equipment.

After domesticating iron-oxidizing bacteria in a batch reactor, we fed simulated wastewater (Fe^{2+}: 350 to 450 mg/L, NH_4-N: 5 mg/L, PO_4-P: 1 mg/L) into the reactor such that the HRT (hydraulic retention time) of the reactor was 24 hours. At this time, we adjusted the pH in the reactor to be 2 to 3. We supplied oxygen to the wastewater and stirred it by aeration. The temporal change in the concentration of Fe^{2+} for three months from the start of the experiment (the HRT was gradually reduced from 24 to six hours) is shown in **Fig. 4**. At first, the oxidation rate of Fe^{2+} was low at around 10%. However, in about two weeks from the start of continuous water feeding, a drop in the concentration of Fe^{2+} in the treated water was observed. An increase of the quantity of introduced water together with reduction of the HRT did not affect the oxidation rate of Fe^{2+}, which remained at approx. 90% or more.

After that, we reduced the HRT gradually at regular intervals, and continued the operation, which did not affect the bacteria's ability for oxidizing Fe^{2+}. As domestication progressed, MLSS (mixed liquor suspended solids) rapidly increased due to the accumulation of ferric hydroxide formed in the reactor. After about six months

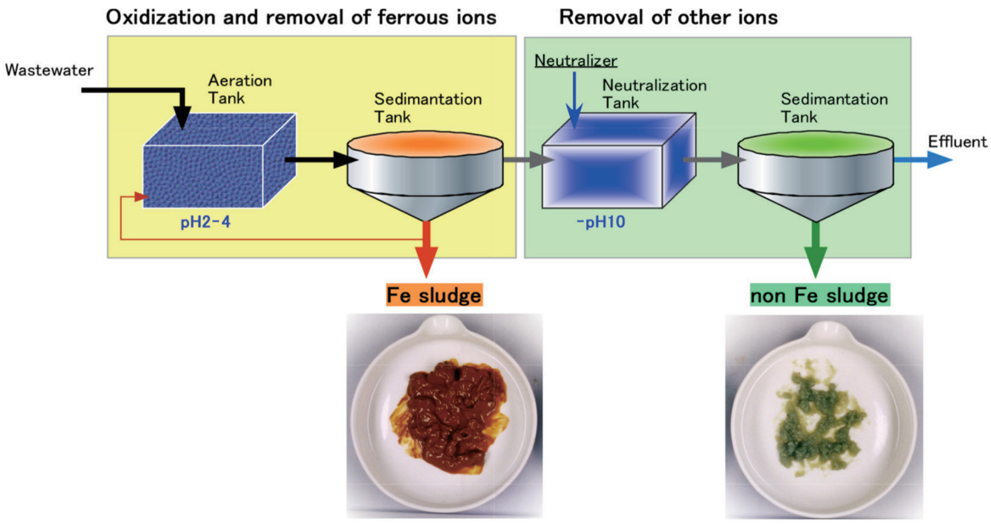

Fig. 3 Process flow of metal recovery from electroplating wastewater using iron-oxidizing bacteria

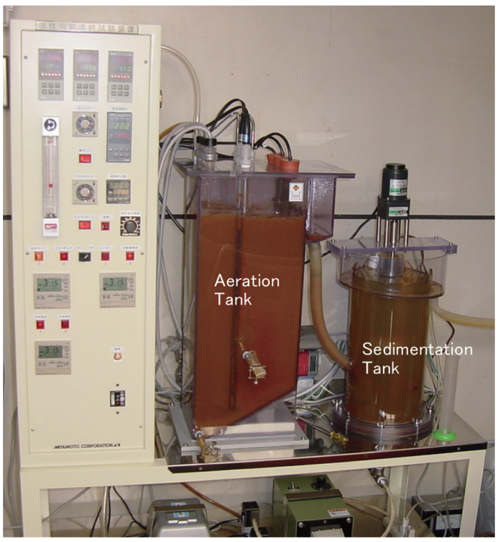

Photo 1 Experimental reactor for iron-oxidizing bacteria

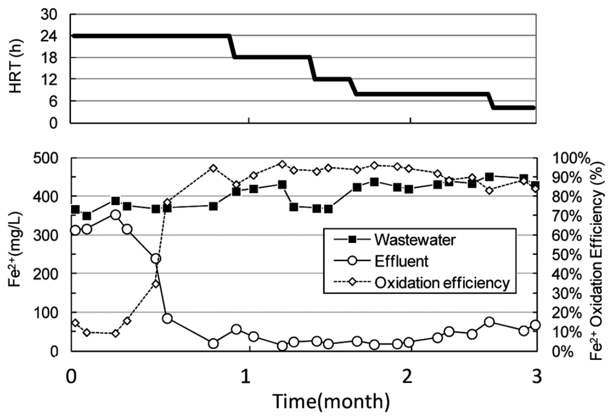

Fig. 4 Time course changes of Fe^{2+} and oxidation efficiency of artificial wastewater and effluent

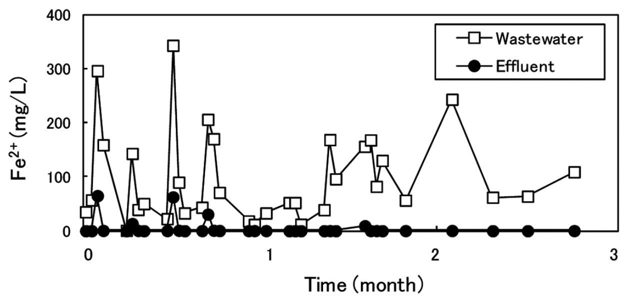

Fig. 5 Time course changes of Fe^{2+} of actual wastewater and effluent

had passed from the start of the experiment, when the HRT was two hours, MLSS exceeded 10000 mg/L, and the oxidation rate of Fe^{2+} was stable at 95% or more. In addition, as a result of molecular biological analysis of the increased sludge, we found *Acidithiobacillus ferrooxidans*, iron-oxidizing bacteria, existing in the sludge. The activity of *A. ferrooxidans* is inhibited by chloride ions, which has made it difficult to use the bacterium for wastewater discharged from plating plants that contains hydrochloric acid chemicals. For this reason, we took activated sludge from the coke oven wastewater treatment facilities at a steelworks, and tried to domesticate iron-oxidizing bacteria capable of oxidizing Fe^{2+} contained in plating wastewater to Fe^{3+} even in an environment with high-concentration chloride ions. To date, we have obtained an iron-oxidizing bacterium that is closely related to *Acidithiobacillus prosperus* and resistant to chloride ions.[9)]

3.1.3 Demonstration experiment using actual wastewater

The temporal change in the concentration of Fe^{2+} contained in wastewater and treated effluent when electroplating wastewater from a steelwork was continuously treated is shown in **Fig. 5**. The HRT was two hours, and the concentration of MLSS was approx. 12000 to 31000 mg/L. The concentration of Fe^{2+} in the treated effluent was maintained at 0.5 mg/L or less, with the exception of increases that occurred when the concentration of Fe^{2+} in the wastewater significantly increased. When the concentration of Fe^{2+} in the wastewater significantly increased to 300 mg/L or more, the ability for oxidizing Fe^{2+} was temporarily decreased. From the viewpoint of stability of treatment, it is desired that such change in the concentration (quality) of wastewater be made as small as possible and lev-

Photo 2 Pilot-scale reactor for iron-oxidizing bacteria

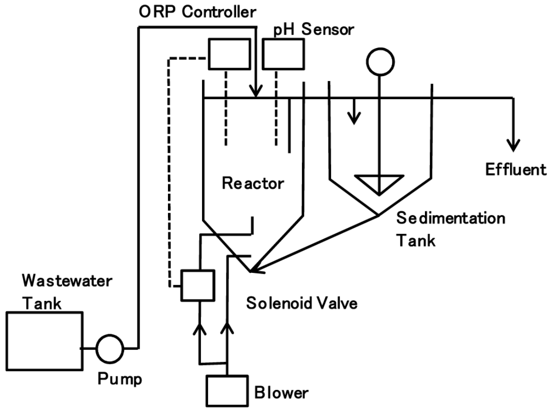

Fig. 6 Bench-scale experimental reactor

elled. However, it has been confirmed that the ability of iron oxidation can recover in a short period of time even when it is influenced by load change. Therefore, this technology is adequate for practical use.

Furthermore, we have completed a demonstration experiment of this technology using a demonstration plant set for the experiment as shown in **Photo 2**.

3.1.4 Verification in the demonstration plant

Using actual plating wastewater and a demonstration plant with a 5700-L reactor, we conducted a continuous water feeding test. First, we started domestication of iron-oxidizing bacteria using a domestication solution (Fe^{2+}: 28 g/L; NH_4-N: 4 mg/L; PO_4-P: 1 mg/L) prepared from 35 L of seed activated sludge that was retained to incubate iron-oxidizing bacteria in a laboratory in advance, and for which the existence of iron-oxidizing bacteria was confirmed. The iron-oxidizing bacteria in the domestication solution increased to approx. 150 times in about one month, and the MLSS could be maintained at approx. 60 g/L. Then, we started continuous treatment of actual plating wastewater for about five months (pH: 3.8 to 4.2; aeration rate: 900 L/min; temperature of the water: 20 to 30°C; HRT: two hours). As a result, the oxidation rate of Fe^{2+} of the raw wastewater became high at 95 to 99%. The ratios of Ni and Zn (Ni: < 0.05%; Zn: < 0.05%) in the sludge were small, compared with those resulting from the neutralizing coagulation and sedimentation method (Ni: 0.75%, Zn: 0.97%). We succeeded in obtaining highly recyclable sludge through the selective separation of iron.[10)]

As described above, through the initiatives in pursuit of a biological treatment technology using iron-oxidizing bacteria starting from the laboratory experiments, we have demonstrated a sufficient oxidation rate of Fe^{2+} and metal recovery rate also in a pilot-scale test in which a large quantity of cultivated iron-oxidizing bacteria was used.

3.2 Steelmaking wastewater treatment using sulfur-oxidizing bacteria

3.2.1 Biological treatment of high-pH wastewater containing sulfur compounds

As the COD of alkaline wastewater containing sulfides and thiosulfuric acid compounds is high due to reductive sulfur compounds, discharge of alkaline wastewater into a public water area (sea, a river, a lake, a port/harbor, coastal sea, a waterway for public use, etc.) is not allowed without being treated. Usually, a large quantity of sodium hypochlorite is injected into alkaline wastewater for oxidation, and then the pH of the alkaline wastewater is neutralized using counteractives. However, as chemicals used in this treatment method are extremely costly, development of more inexpensive treatment technology has been demanded.

Table 1 Compositions of artificial wastewater

$Na_2S_2O_3 \cdot 5H_2O$	1 g *	NH_4Cl	0.02 g
$Ca(H_2PO_4)_2 \cdot H_2O$	0.6 g	$CaCl_2$	0.05 g
$MgCl_2$	0.02 g	Distilled water	1 L

* $S_2O_3^{2-}$ = 452 mg/L

The oxidation of sulfur compounds in water, which is difficult by aeration alone, can be performed using sulfur-oxidizing bacteria that inhabit sulfur springs and other similar environments. For example, it is *Acidithiobacillus thiooxidans* oxidizes inorganic sulfur compounds in an environment with air. The following formulas show the reaction.

$$4S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 2S_4O_6^{2-} + 4OH^- \quad (1)$$
$$+)\ 2S_4O_6^{2-} + 7O_2 + 6H_2O \rightarrow 8SO_4^{2-} + 12H^+ \quad (2)$$
$$4S_2O_3^{2-} + 8O_2 + 4H_2O \rightarrow 8SO_4^{2-} + 8H^+ \quad (3)$$

This type of bacteria, which has the ability to assimilate carbon dioxide by using energy that is produced when sulfur compounds are oxidized, grows under the condition in which no organic matter exists in the wastewater. In view of this, we thought that sulfur-oxidizing bacteria could be used to treat such alkaline wastewater. However, these bacteria are active in the acidic conditions of pH 2 to 3.5, and they become extremely less active when the pH is 4 or higher. Therefore, use of sulfur-oxidizing bacteria that are highly active in a neutral or alkaline environment was desired.

After we considered the use of sulfur-oxidizing bacteria that inhabited sewage activated sludge with neutral pH, we conducted a domestication test using a bench-scale experimental reactor shown in **Fig. 6**. Sewage sludge that contained ≈1500 mg/L of MLSS was put in the reactor. The pH of the simulated wastewater shown in **Table 1** was adjusted to be around 12. Then the simulated wastewater was fed such that it was retained in the aeration tank for eight hours. We set the pH of the aeration tank to be 5 to 7, the aeration rate 5.4 L/min, and the water temperature 20°C. As a result, as shown in **Fig. 7**, almost all thiosulfuric acid ions had been oxidized in 12 days. We thus confirmed that sulfur-oxidizing bacteria that are highly active around neutral pH can be taken from sewage activated sludge for domestication. In addition, we conducted another bench-scale experiment during which we continuously fed simulated

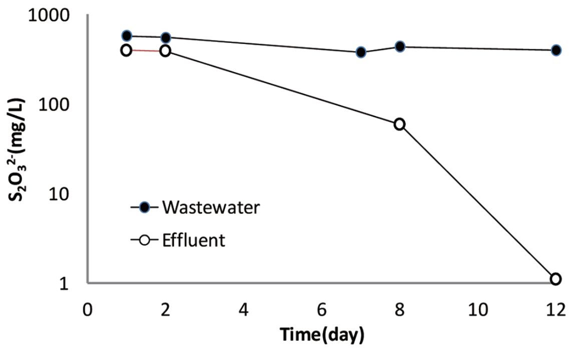

Fig. 7 Time course changes of $S_2O_3^{2-}$ during acclimation in bench-scale reactor

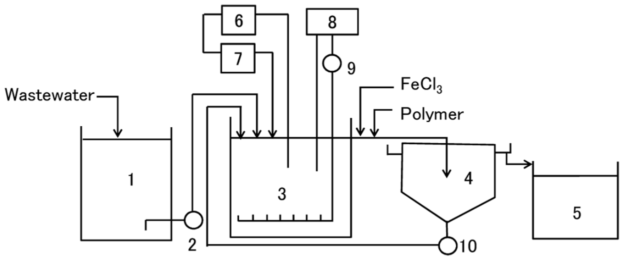

Fig. 8 Flow sheet of pilot-scale experimental plant
1. Wastewater tank, 2. Pump, 3. Reactor (1 m × 1 m × 2 mh), 4. Sedimentation tank (1.2 mφ × 1.6 mh), 5. Effluenet tank, 6. pH sensor/controller, 7. H_2SO_4 dosing, 8. ORP controller, 9. Blower, 10. Sludge return pump

wastewater with 400 to 500 mg/L of thiosulfuric acid ion concentration, and reduced the HRT gradually from eight hours to six, four, three, and two hours. As a result, we confirmed that when the HRT was three hours or more, the treatment of wastewater with a thiosulfuric acid ion concentration as above could produce treated effluent with a COD of 20 mg/L or less.

Following the confirmation of the high possibility of practical use of these bacteria obtained in view of the results of the bench-scale experiments, we started a pilot plant experiment. An outline of the test equipment is shown in **Fig. 8**. The test conditions are shown in **Table 2**.

As a result of the pilot test that took about one year, we confirmed that the COD of the treated effluent could be stably maintained at 20 mg/L or less. Based on the test results, we further constructed a wastewater treatment facility with the treatment capacity of 720 m^3 per day.[11)]

As described above, we found that alkaline wastewater containing sulfides and thiosulfuric acid compounds can be treated at a low cost by the activated sludge method in which domesticated sulfur-oxidizing bacteria originally inhabiting sewage sludge are used. These findings have led to the construction of wastewater treatment facilities, for which we have been working on further enhancement of the efficiency.

3.2.2 Development of a contact oxidation method using sulfur-oxidizing bacteria

To install a sedimentation tank required in the activated sludge method, a large area is required in the facility site. For this reason, we have been working to reduce the footprints of wastewater treatment facilities. As a measure to reduce the footprint of a wastewater treatment facility, we selected the use of a contact oxidation method, and conducted a demonstration experiment using actual wastewater;

Table 2 Test conditions of pilot-scale plant

Wastewater quality (average)				
	pH	12.4	$S_2O_3^{2-}$	197 mg/L
	COD	158 mg/L	S^{2-}	29 mg/L
Seed sludge	Sewage sludge			
Reactor conditions	HRT		3–30 h	
	ORP*		+100 mV	
	pH		6–7	
	Return sludge ratio		Around 25% of wastewater flow rate	
	Temperature		3–15 °C	
Nutrients dosing	Ammonium sulfate		5 mg-N/L	
	Phosphoric acid		1 mg-P/L	
Coagulant dosing	$FeCl_3$		5 mg/L	
	Polymer		0.5 mg/L	

* ORP: Oxidation-reduction potential

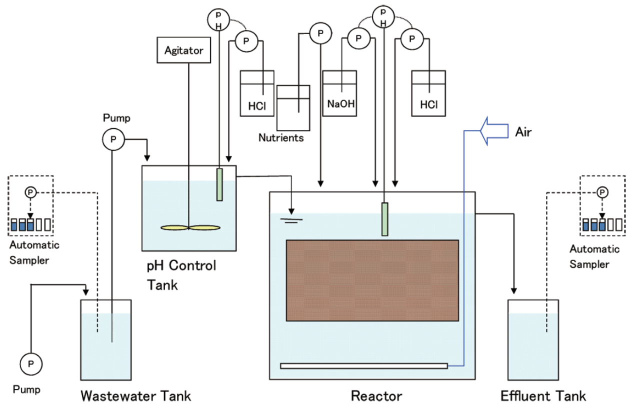

Fig. 9 Flow of experimental reactor

Contact oxidation is a method in which contact filter media are immersed under wastewater in a biological treatment tank, followed by aeration, thereby treating the wastewater with sulfur-oxidizing bacteria colonizing on the surfaces of such contact filter media. A block diagram of the process flow among the entire experiment equipment is shown in **Fig. 9**. The test conditions are shown in **Table 3**. Plastic honeycomb contact filter media were used. In addition, sludge taken from an aeration tank in operation under the activated sludge method was used as seed sludge for the startup. The seed sludge was added such that the MLSS in the reactor became approx. 500 mg/L. The COD and SS in the treated effluent are shown in **Fig. 10** and **Fig. 11**, respectively. As a result of the stepwise HRT reduction from six hours to four, three, two, and 1.5 hours, treated effluent with favorable COD smaller than 15 mg/L was produced when the HRT was two hours or more. Furthermore, the SS of the treated effluent, which was high at the start, was confirmed to become stable at 20 mg/ L or less on the fourth day and after since the wastewater feeding was started. Thus we confirmed that favorable treatment capacity can be obtained even when no sedimentation tank is used.

Moreover, we sampled some from the sludge that adhered to the honeycomb contact filter media used in this experiment, and analyzed the microbial flora. As a result, the SAB-1 strain (accession number: NITE P-1543) of a sulfur-oxidizing bacterium that belongs to *Halothiobacillus* (genus), inhabited the sample.

Table 3 Test conditions

		Condition-1	Condition-2	Condition-3	Condition-4	Condition-5
Wastewater	Flow rate	1.4 L/min	2.2 L/min	2.9 L/min	4.3 L/min	5.3 L/min
pH control tank	Capacity	24 L				
	pH condition	pH 11				
Reactor	Capacity	520 L				
	Media	60% volume of reactor				
	HRT	6 h	4 h	3 h	2 h	1.5 h
	COD loading rate	0.2 kg/m³/day	0.3 kg/m³/day	0.4 kg/m³/day	0.6 kg/m³/day	0.8 kg/m³/day

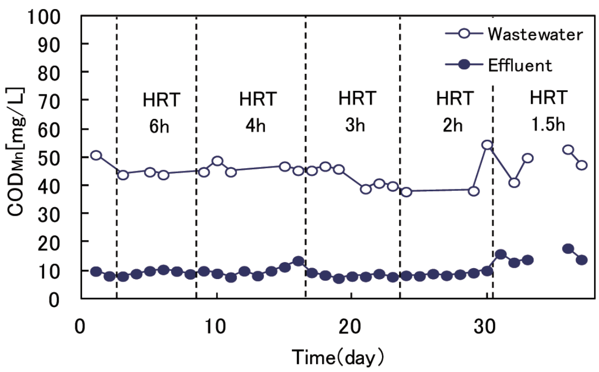

Fig. 10 Time course change of COD_{Mn} of actual wastewater and effluent

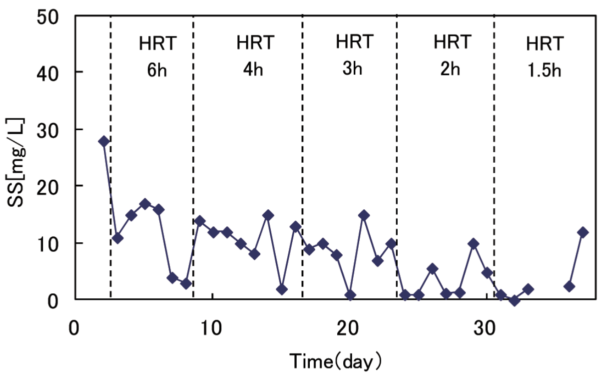

Fig. 11 Time course change of SS of effluent

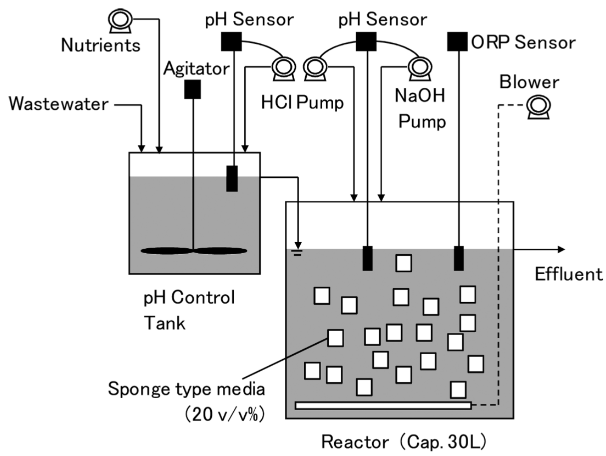

Fig. 12 Flow of experimental reactor

3.2.3 Development of an activated sludge method using floating carriers to which sulfur-oxidizing bacteria colonize

Recently, research of the activated sludge method with carriers floating in the wastewater to be treated (moving bed bio-film reactor, "MBBR") has gathered much attention. In the method, carriers are floated in the wastewater in an aeration tank under the activated sludge method so that microbial films are formed on the surface of the carriers that are moved in the wastewater to increase the concentration of microorganisms in the aeration tank, thereby improving the reaction efficiency. As only putting carriers in the wastewater in an aeration tank to float the carriers in the water will allow for higher treatment capacity than that of existing methods, we considered the introduction of the MBBR method in pursuit of the enhancement of efficiency of existing sulfur-oxidizing bacteria reactors.

For the examination of the MBBR method, a test was conducted by feeding actual wastewater into an aeration tank in the test equipment shown in **Fig. 12**, into which sludge containing the SAB-1 strain that belongs to *Halothiobacillus* (genus) and carriers are to be floated. Since the actual wastewater contained calcium, there was concern that deposited calcium might adhere to the surfaces of the carriers, interfering with the floating of the carriers. Given this, we used polyurethane resin carriers in an amount of approx. 20% of the volume of the aeration tank to continuously feed wastewater. As a result, there was no problem with the floating of the carriers, and the treatment of the actual wastewater (COD: 88 mg/L [average]; Ca^{2+}: 436 mg/L [average]) had the effect of reducing the COD to 20 mg/L or less with two-hour HRT. Moreover, we compared the treatment capacities of several types of carriers using actual wastewater. The microorganisms most readily adhered to polyurethane resin carriers as shown in **Table 4**.

As described above, through the research in preparation for the introduction of the contact oxidation method and MBBR method to our biological treatment technologies using sulfur-oxidizing bacteria, we confirmed that these methods can improve the treatment efficiency.

3.3 Application of an activated sludge model to activated sludge treatment for coke oven wastewater

3.3.1 Background of development of our own activated sludge model for coke oven wastewater treatment

Ammonia contained in coke oven wastewater discharged during the coke oven process is treated by ammonia stripping. The remaining COD components (phenol, thiosulfuric acid, and thiocyanic acid) are treated by biodegradation using the standard activated sludge method. To date, coke oven wastewater treatment has been managed empirically based on management indexes. However, recently, as the operation environment changes, for example, the growing number of types of raw fuel and changes in the operation

Table 4 SS attached on various media

Materials of media	Polyurethane	Polyester	Polypropylene	Polyethylene
Size of media	10 mm × 10 mm × 10 mm			
Average COD of effluent (mg/L)	9	13	13	11
SS attached on media (kg-SS/m^3)	6.3	6.7	6.8	6.3
Inorganic component in attached SS (kg-SS/m^3)	1.2	2.3	3.1	1.8
Organic component in attached SS (kg-SS/m^3)	5.1	4.4	3.7	4.5

rate, variations of properties and quantity of raw wastewater are becoming larger than before, requiring more accurate management and operation of treatment facilities.

In the field of sewage, the activated sludge model[12] has been proposed, and various application cases have already been reported. The activated sludge model mainly consists of the following procedures.

(1) The COD concentration in influent of wastewater is fractionated in accordance with the properties of components such as dissolved inactive organic matter, easily degradable organic matter, suspended inactive organic matter, and slowly degradable organic matter. A variable for each component is determined based on the COD concentration.

(2) For each process related to heterotrophs such as growth and autolysis, the stoichiometry between variables and the rate equation of the process are determined.

(3) Stoichiometric factors and parameters of the rate equation constants are determined by calibration using data actually measured in a test for the oxygen consumption rate and the quality of water.

(4) The COD concentration, etc. in a biological treatment tank and in the treated effluent and others are calculated by simulation.

This activated sludge model is useful as a management tool, and sewage treatment management systems using such activated sludge model have been proposed. Although biological treatment processes are used to treat industrial wastewater that contains components different from those of sewage, no activated sludge model has been applied yet to simulating methods for the water quality. In particular, wastewater discharged from coke ovens contains mainly phenol, thiosulfuric acid, and thiocyanic acid, which are substances not contained in sewage. For this reason, the applicability of an activated sludge model to industrial wastewater has not been studied.

Against this background, we considered that if the activated sludge model could be applied to the treatment of coke oven wastewater using activated sludge, and if the quality of treated effluent could be predicted from the properties of raw wastewater by simulating the decomposition of components in the coke oven wastewater, then we would be able to perform the treatment and management of coke oven wastewater more accurately. The next step was the start of development of our activated sludge model for coke oven wastewater treatment.

3.3.2 Outline of the activated sludge model for coke oven wastewater treatment

When the activated sludge model is applied to coke oven wastewater activated sludge treatment, the following issues arise.

(1) The activated sludge model only predicts the COD concentrations of wastewater that flows in and treated effluent when the wastewater containing multiple components in a mixed manner (e.g., sewage) is processed by aerobic biological treatment, not capable of predicting the concentrations of biodegradable compound components. For example, regarding coke oven wastewater discharged from coke ovens, phenol concentration in coke oven wastewater, for which the effluent standard is set together with other substances, needs to be predicted through simulation. However, it is difficult to predict using the activated sludge model the concentration of phenol in treated effluent produced after wastewater containing multiple components, like coke oven wastewater in particular, is processed by means of aerobic biological treatment. Therefore, applying the activated sludge model to industrial wastewater including that discharged from plants is not worthwhile.

(2) Industrial wastewater including that discharged from plants contains dissolved slowly biodegradable organic matter (surface-active agents, e.g., linear alkylbenzenesulfonate) or inorganic matter (e.g., thiosulfuric acid and thiocyanic acid). However, as urban sewage to which the activated sludge model has been applied contains little dissolved slowly biodegradable components, which decompose very slowly, their influence on the oxygen balance in the model has not been taken into account. The activated sludge model does not have dissolved slowly biodegradable components in the first place, making it difficult to apply the activated sludge model to industrial wastewater including that discharged from plants.

Given the situation, as our own activated sludge model applied to coke oven wastewater treatment, we have built a new activated sludge model for the process in which wastewater containing biodegradable compound components (e.g., industrial wastewater including that discharged from plants) is aerobic biologically-treated in a bioreactor tank. The purpose of the new model is to simulate how the concentrations of such biodegradable compounds in the wastewater change after the aerobic biological treatment. Specifically, each component in wastewater is fractionated, and the type of the bacterium that degrades the component, variables, and reaction processes are determined for each component, so that the activated sludge model can simulate aerobic biological treatment processes, thereby allowing the concentrations of components in the treated effluent to be calculated. In addition, even for wastewater that contains dissolved slowly biodegradable components, each component is fractionated as well, which allows for the simulation of aerobic biological treatment processes using the activated sludge model without using the dissolved slowly biodegradable components.

Based on the activated sludge model, the activated sludge model for coke oven wastewater treatment is defined as the following Eq. (4),

$$\frac{dC_i}{dt} = \sum P_{ij} \cdot \rho_j \tag{4}$$

where

C_i : Concentration of each component
i : Serial number indicating each component
P_{ij} : Stoichiometric parameter
j : Serial number indicating each process
ρ_j : Process rate

Table 5 Stoichiometric and kinetic parameters

Items		Definition	Unit
Component concentration	S_{Phe}	Phenol concentration	mgCOD/L
	S_{S2O3}	Thiosulphate concentration	mgCOD/L
	S_{SCN}	Thiocyanate concentration	mgCOD/L
	S_{O2}	Dissolved oxygen concentration	mgCOD/L
	X_{Phe}	Phenol degrading biomass concentration	mgCOD/L
	X_{S2O3}	Thiosulphate degrading biomass concentration	mgCOD/L
	X_{SCN}	Thiocyanate degrading biomass concentration	mgCOD/L
Stoichiometric parameter	Y_{Phe}	Yield of phenol degrading biomass	mgCOD/mgCOD
	Y_{S2O3}	Yield of thiosulphate degrading biomass	mgCOD/mgCOD
	Y_{SCN}	Yield of thiocyanate degrading biomass	mgCOD/mgCOD
Reaction rate parameter	μ_{Phe}	Growth rate of phenol degrading biomass	1/day
	μ_{S2O3}	Growth rate of thiosulphate degrading biomass	1/day
	μ_{SCN}	Growth rate of thiocyanate degrading biomass	1/day
	K_{Phe}	Saturation constant for S_{Phe}	mgCOD/L
	K_{S2O3}	Saturation constant for S_{S2O3}	mgCOD/L
	K_{SCN}	Saturation constant for S_{SCN}	mgCOD/L
	K_{O2}	Saturation constant for S_{O2}	mgCOD/L

Table 6 Stoichiometric matrix and kinetic rate expressions ρ_j

Process ρ_j	Component i	S_{Phe}	S_{S2O3}	S_{SCN}	S_{O2}	X_{Phe}	X_{S2O3}	X_{SCN}	Process rate equation ρ_j
ρ_1	Growth of phenol degrading biomass	$-1/Y_{Phe}$	–	–	$-(1-Y_{Phe})/Y_{Phe}$	1	–	–	$\mu_{Phe} \cdot \frac{S_{O2}}{K_{O2}+S_{O2}} \cdot \frac{S_{Phe}}{K_{Phe}+S_{Phe}} \cdot X_{Phe}$
ρ_2	Growth of thiosulphate degrading biomass	–	$-1/Y_{S2O3}$	–	$-(1-Y_{S2O3})/Y_{S2O3}$	–	1	–	$\mu_{S2O3} \cdot \frac{S_{O2}}{K_{O2}+S_{O2}} \cdot \frac{S_{S2O3}}{K_{S2O3}+S_{S2O3}} \cdot X_{S2O3}$
ρ_3	Growth of thiocyanate degrading biomass	–	–	$-1/Y_{SCN}$	$-(1-Y_{SCN})/Y_{SCN}$	–	–	1	$\mu_{SCN} \cdot \frac{S_{O2}}{K_{O2}+S_{O2}} \cdot \frac{S_{SCN}}{K_{SCN}+S_{SCN}} \cdot X_{SCN}$

As the concentration of each component is handled as an equivalent to COD, then phenol, thiosulfuric acid, and thiocyanic acid are converted into COD. The following equations (5) to (7) were used to calculate the theoretical oxygen consumption for COD conversion.

$$C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O \quad (5)$$

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \quad (6)$$

$$SCN^- + 2O_2 + 2H_2O \rightarrow SO_4^{2-} + NH_4^+ + CO_2 \quad (7)$$

As a result, the COD conversion factors of phenol, thiosulfuric acid, and thiocyanic acid are 2.38, 0.57, and 1.1, respectively.

Table 5 shows the stoichiometric and reaction kinetic parameters. **Table 6** shows the stoichiometric and reaction kinetic matrix of each process.

3.3.3 Simulation of biodegradable of components in coke oven wastewater

We used the activated sludge model for coke oven wastewater treatment to simulate the decomposition of phenol, thiosulfuric acid, and thiocyanic acid. Data on the decomposition of components in coke oven wastewater was obtained through a test using OUR (oxygen uptake rate) equipment as shown in **Fig. 13**. In the test, we put the target components in a 1-L reactor vessel such that the phenol concentration was 100 mg/L, thiosulfuric acid concentration was 100 mg/L, and thiocyanic acid concentration was 10 mg/L. The MLSS concentration was 5000 mg/L. During the test, we measured the concentration of dissolved oxygen using a dissolved oxygen meter, and measured the pH as well using a pH meter. In addition, we made adjustments such that the concentration of dissolved oxygen was 3.25 mg/L, and the pH was 7.5.

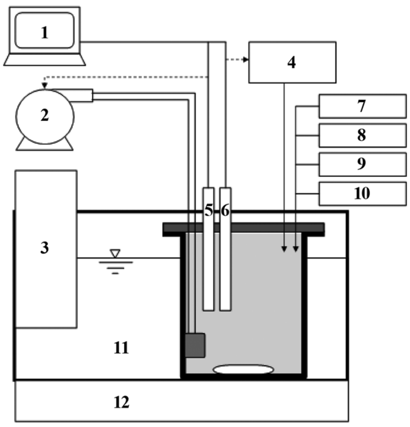

Fig. 13 OUR test apparatus
1. Data logger, 2. Air pump, 3. Heater, 4. Acid/alkali feeder, 5. DO sensor, 6. pH sensor, 7. Activated sludge, 8. BOD dilution water, 9. Nitrification inhibitor, 10. Component, 11. Water bath, 12. Stirrer

We calculated the growth yield and specific growth rate from the test results. Then we simulated the decomposition of each component using Eq. (4), and compared the simulation results with the test data. The simulation results are shown in **Fig. 14**. As described above, we have made it possible to predict the quality of treated ef-

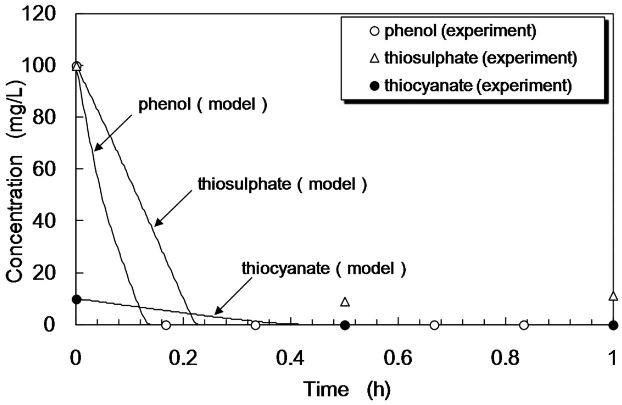

Fig. 14 Time course of components biodegradation in coke oven wastewater and model simulation

fluent by fractionating each component in coke oven wastewater and by defining the degrading bacterium and reaction processes for each component based on the activated sludge model used in the field of sewage.

4. Conclusion

Recently, the importance of initiatives for environmental cleanup have been growing in pursuit of natural ecosystem protection. The usefulness of low-cost biological treatment technologies that impose less burden on the environment and that consume less energy is likely to further increase. Going forward, adopting microbial flora analysis technologies and applying various highly-efficient biological reactors to the field of steelmaking wastewater treatment will allow for further advancement of biological treatment technologies in the steelmaking industry. In view of this, we will strive to continue working on the development of practical biological treatment technologies, in pursuit of the improvement of steelmaking wastewater treatment technologies.

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