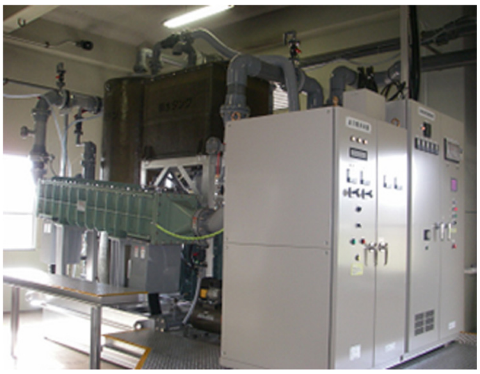
Application of Electrolytic Denitrification System to Treatment of Waste Water from Power Plants



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Hydrazine has been used at thermal power plants as a water treatment agent. There is a trend, however, toward banning the use of hydrazine mainly in Europe. As an alternative option, the adoption of “high-pH treatment (high-AVT)” is suggested.

The use of high-AVT results in an increase in ammoniacal nitrogen levels in waste water from power plants. As the discharge of nitrogen is regulated in many countries, appropriate measures should be taken. This report introduces an electrolytic denitrification system that is useful for abiding by the regulations on nitrogen discharge and is a proprietary technology of Mitsubishi Heavy Industries Environmental & Chemical Engineering Co., Ltd.

1. Background of emerging need for denitrification technology

When “high-pH treatment (high-AVT)” is adopted for water treatment at thermal power plants instead of hydrazine, ammoniacal nitrogen levels in waste water increase, necessitating that suitable measures be undertaken.

(1) High-AVT-induced change in waste water qualities

The use of high-AVT results in an increase in ammoniacal nitrogen levels in boiler waste water (**Table 1**).

Table 1 High-AVT-induced change in the quality of waste water

Adopted method	Hydrazine treatment	High-AVT
Ammoniacal nitrogen level in boiler water	30 mg N/L	100 mg N/L
Ammoniacal nitrogen level in the storage tank	15 mg N/L or less	50 mg N/L

(2) Trend of nitrogen regulations

As many countries have regulations on nitrogen in effluent, ammoniacal nitrogen treatment is needed for waste water that is discharged from boilers with high-AVT (**Table 2**).

Table 2 Nitrogen regulations by country (Surveyed in 2012)

Item	Effluent criteria	
	Total nitrogen T-N	Ammoniacal nitrogen NH_4-N
World Bank		10 mg/L or less
Japan	120 mg/L (Daily average: 60 mg/L)	
Saudi Arabia		1 mg/L (30-day average)
Indonesia		1 mg/L (30-day average)
Vietnam	15 mg/L	5 mg/L
China		15 mg/L
Brazil		5 mg/L
South Korea	60 mg/L	

2. Principle of electrolytic denitrification system

A chloride ion-containing solution such as seawater is electrolyzed to produce hypochlorous acid. Ammoniacal nitrogen is oxidized by the hypochlorous acid and is released as harmless N_2 gas into the air.

(1) Chlorine formation

Chlorine (Cl_2) is produced at the anode. Chlorine is then instantaneously subjected to disproportionation decomposition near the electrode to form hypochlorous acid (HClO).

Anode	$2Cl^-$	→	$Cl_2 + 2e^-$
	$Cl_2 + H_2O$	→	$HClO + HCl$
Cathode	$2H_2O + 2e^-$	→	$2OH^- + H_2$
	$2NaOH$	→	$2Na^+ + 2OH^-$

(2) Nitrogen removal

Ammoniacal nitrogen in water reacts with the hypochlorous acid (HClO) produced as a result of the chlorine formation reaction and is converted into harmless N_2 gas.

$$2NH_3 + 3HClO \rightarrow N_2 \uparrow + 3HCl + 3H_2O$$

3. Ammonia removal from boiler waste water

(1) Verification of the effect on waste water from an actual power plant (boiler effluent)

The waste water from an actual power plant facility (boiler effluent) is mixed with an electrolytic hypochlorous acid solution to evaluate the ammonia removal performance. It has been confirmed that the ammoniacal nitrogen levels in the treated water meet the discharge regulations (i.e., 10 mg/l or less), thus demonstrating that the treatment is sufficiently effective for power plant waste water.

(2) How to control/detect the end point

Ammoniacal nitrogen-containing waste water from power plants is oxidized by mixing with an electrolytic hypochlorous acid solution. In batch processing, as the ammoniacal nitrogen contained in the mixture solution is removed, pH levels will change as shown in **Figure 1**. Therefore, measured pH levels can be an indicator of the reaction end point in the oxidation treatment.

The necessary amount of hypochlorous acid is determined based on the ammoniacal nitrogen level or the quantity of waste water. The supply of hypochlorous acid can be regulated by controlling electrolytic currents, making it possible to keep up with changes in the quality of waste water, etc.

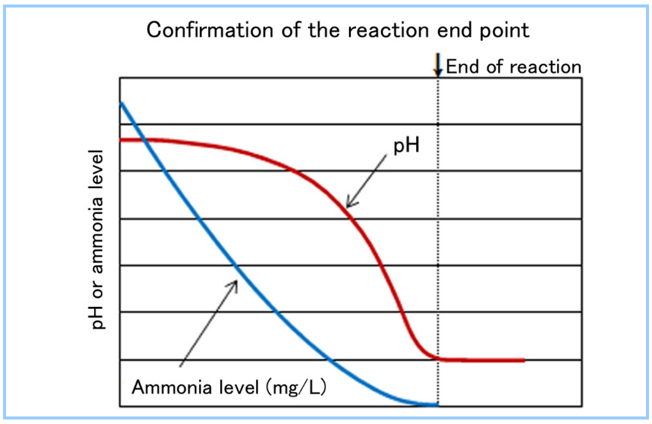

Figure 1 Confirmation of the reaction end point in the oxidation treatment

4. Application to the waste water process of power plants

Figure 2 shows the waste water treatment process of power plants, while the design specifications for ammonia treatment are given in **Table 3**. Hypochlorous acid solution, which is formed as a result of the electrolysis of seawater or other solutions, is mixed in the mixing tank with the power plant waste water (boiler effluent) collected in the storage tank, whereby ammoniacal nitrogen in the solution decomposed through oxidation. Once the ammoniacal nitrogen level in the treated water is confirmed to be at or below the regulation limit (i.e., 10 mg/l), it can be discharged.

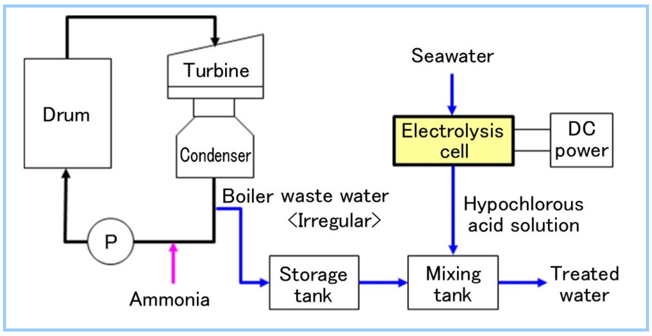

Figure 2 Flow diagram of waste water treatment process at power plants

Table 3 An example of the design specifications for ammonia treatment

Item	Capacity
Boiler capacity	500,000 kW/unit
Nitrogen level in the waste water of storage tank	50 mg N/L (After being diluted at reduced temperature)
Flow rate	1,000 m^3/week (After being diluted at reduced temperature)
Treated amount of ammoniacal nitrogen	50 kg N/week
Capacity of electrolytic formation of chlorine	405 kg Cl_2/week

5. Comparison with other ammonia treatment methods

Our ammonia treatment method using the electrolytic denitrification system is superior to other treatment methods such as ion exchange and ammonia stripping (**Table 4**).

Table 4 Comparison of our electrolysis method with other ammonia treatment methods

	Ion exchange	Ammonia stripping	Electrolysis	Rating
Treatment time	Short	Long	Short	Good
Area for installation	Intermediate	Large	Small	Good
Operability	No special operating procedures. Unexpectedly increased concentrations may make the ion exchange capacity insufficient.	Uses steam and NaOH solution in large quantities. Low treatment efficiency at low concentrations.	Change in concentration can be immediately handled by modulating the currents.	Good
Maintenance	Resin regeneration and replacement	Large-scale maintenance, because of many auxiliary facilities	Acid cleaning of the electrolysis cell Electrode replacement	Good
Construction period	Short	Long, because of many auxiliary facilities.	Short	Good
Necessary operational costs	Resin regeneration and replacement Concentrated ammonia solution treatment (as an extra)	Steam and pH adjusters Ammonia gas treatment (as an extra)	Electricity Electrolysis cell maintenance	Good
Waste	Used ion exchange resins Concentrated ammonia solution (desorption)	Ammonia gas Alkaline waste water	Seawater Acid effluent	Good
Issues to be addressed	Regeneration Treatment of regeneration waste water Lack of ion selectivity	Measures against ammonia gas diffusion Recovery and treatment	Necessity of chloride ion-containing solutions such as seawater	Good
OPEX (operating expenditure)	1040%	385%	100%	Good
CAPEX (capital expenditure)	187%	103%	100%	Good