Highly-Efficient Removal of Toxic Trace Elements and Particulate Matter in Flue Gas Emitted from Coal-fired Power Plants by Air Quality Control System (AQCS)

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Both at home and abroad, over the years, Mitsubishi Hitachi Power Systems, Ltd. (MHPS) has provided technologies to eliminate nitrogen oxides, sulfur oxides, etc., in flue gas from thermal power plants and is in recent years enthusiastic for the technical development of AQCS to upgrade such technologies, as well as to remove toxic trace components. This technology totally and efficiently operates high-functioning NOx reduction catalysts, heat exchangers, dry electrostatic precipitators and wet flue gas desulfurization equipment. We have so far examined for demonstration actual coal-fired emissions with the 1.5MW pilot test plant (combustion and flue gas treatment test facility) of Kure Works (Akitsu District), a 5-MW pilot plant in the U.S. (at Crist Power Station) and a 720-MW commercial power plant in the U.S. (at Miller Power Station), finding toxic trace elements (mainly mercury and selenium), particulate matter and blue plume-/acid rain-causing SO_3 *to be removed to a significant extent.*

1. Introduction

Regulations over emissions from thermal power plants have continued to intensify globally and, in particular, mercury control under the MATS (Mercury and Air Toxics Standards) of the U.S. is nearly too stringent to allow new coal-fired thermal power plants to be built. Particulate matter (PM) control is also being strengthened in each country and there is growing demand for technologies to remove it from flue gas to a significant extent.

Figure 1 shows the conceptual flow of AQCS-based mercury removal from flue gas at MHPS. Mercury (Hg) in coal is discharged mainly as reduced-form metallic mercury vapor from high-temperature boiler furnaces, but as exhaust gas cools down, combined with gasses such as chlorine (Cl) to become oxidized mercury, it induces adsorption onto ash particles or dissolution into the liquid phase within wet flue gas desulfurization equipment (FGD) to be removed from flue gas.

The three key technologies for this process are the following: (1) an SCR (selective catalytic reduction) catalyst for NOx removal (TRAC®: triple action catalyst) developed by making both mutually opposing functions of high mercury oxidation and low SO_2-to-SO_3 conversion activity compatible, (2) a high-performance PM removal system where a non-leak fin tube-type gas cooler is installed in the fore stage of the dry electrostatic precipitator (ESP) to lower flue gas temperature

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to around 90°C to 100°C and promote the adsorption of gaseous oxidized mercury and SO_3 onto ash particles, thereby enhancing the removal across a dry ESP, and (3) successful inhibition of mercury re-emission achieved by controlling the oxidation load (air flow for oxidation) at FGD so that the oxidation-reduction potential (ORP) may fall within a certain range. At the high-performance PM removal system of (2), even the oxidized mercury remaining unremoved through a dry ESP dissolves into the absorbent liquid in the wet FGD to be efficiently removed. Moreover, other than mercury, high-volatility trace components such as selenium can also be removed to a significant extent. The ORP control of (3) is also effective, since it controls the oxidative status of the absorbent, in inhibiting scale occurrence due to the oxidation of manganese, as well as in removal of selenium in waste water through the suppression of selenium peroxidation.

In addition to these technologies, when the Cl content of coal is low and the mercury oxidation activity of a conventional SCR is poor, ammonium chloride (NH_4Cl) instead of ammonia (NH_3) as a NOx reduction agent can be injected into the upstream side of the SCR to improve the mercury oxidation while maintaining the NOx reduction performance.

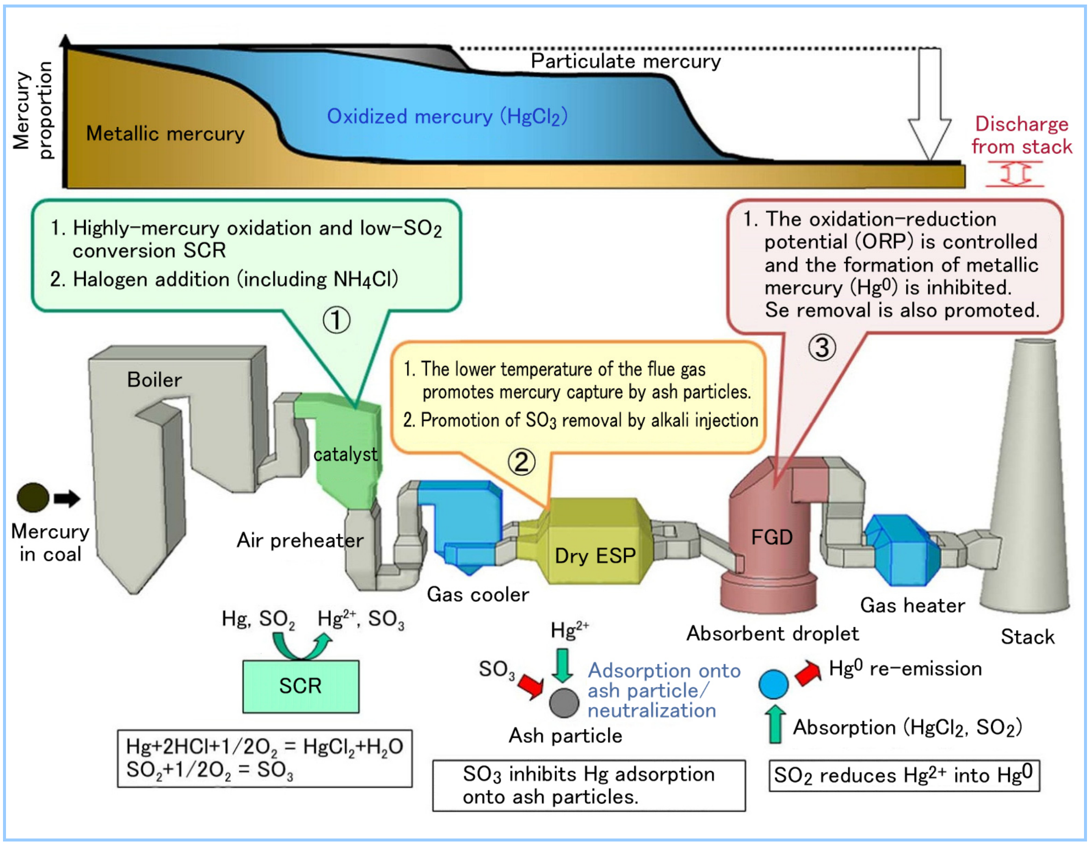


Figure 1 Mercury behavior in flue gas and conceptual flow of MHPS' AQCS

2. History of AQCS development

As shown in **Table 1**, since 1998 MHPS has been engaged in a variety of R&D activities for the commercialization of technologies to evaluate the behavior of and remove toxic trace substances such as mercury contained in flue gas from coal-fired power plants. In the 1.5-MW pilot test plant (combustion and flue gas treatment test facility) in Kure Works (Akitsu District), which is equipped with a series of furnace-through-stack systems just like at an actual coal-fired power plant, a wide variety of tests are now being conducted continuously to take advantage of its operational flexibility.[1]

Furthermore, in cooperation with customers in the U.S., in addition to element technologies, a total system was also tested for demonstration, successfully proving their effectiveness and practicality in 2007 and 2009 with 5-MW pilot equipment and in 2011 with 720-MW commercial plant.[2]

Table 1 Outline of AQCS demonstration tests at MHPS

1.5-MW captive pilot test	5-MW pilot test in U.S	720-MW commercial plant test in U.S.
1998 -	2007, 2009	2011
 Combustion/flue gas treatment test facility in Kure Works (Akitsu District)	 Crist Unit 5, MRC (Mercury Research Center)	 Miller Unit 1 (Southern Company Service)
- Evaluation of mercury behavior in detail - Verification of the effectiveness to reduce PM/mercury/SO_3 through the total operation of TRAC$^{®}$, gas cooler, low-low temperature ESP, and wet FGD - Evaluation of various additives - Evaluation of selenium behavior	- Demonstration of mercury re-emission prevention based on ORP control through wet FGD - Demonstration of mercury oxidation/removal performance improvement through HCl/NH_4Cl injection upstream the SCR	- Demonstration of the NH_4Cl injection system - Total system (SCR-FGD)-based performance of NOx/mercury removal

Since the late 1990s, MHPS has continued experiments and research on advanced technology to treat toxic components, mainly mercury in coal-fired flue gas, using its own or customer's equipment of various scales.

3. AQCS development using MHPS' own pilot test plant

3.1 Outline of pilot test plant

Figure 2 shows the appearance of the 1.5-MW pilot test plant and **Figure 3** shows its system flow. It is provided with a set of furnace equipped with a low-NOx burner, heat exchanger, SCR system, gas cooler, gas heater, dry ESP (fabric filter is also available as PM removal equipment if by-passed), and wet FGD just like at an actual coal-fired power plant, making a variety of experiments possible due to the great flexibility of each piece of equipment in terms of its operating conditions. In addition, at a significant point for the evaluation of performance throughout the AQCS flue gas, ash particle, FGD liquid, etc., can now be sampled, making detailed examination possible. Mainly conducted with this test plant was a behavior evaluation of toxic substances in flue gas including mercury, PM and SO_3, as well as -development tests of advanced removal technology using high-mercury oxidation catalyst, a gas cooler and low-low temperature ESP combination..

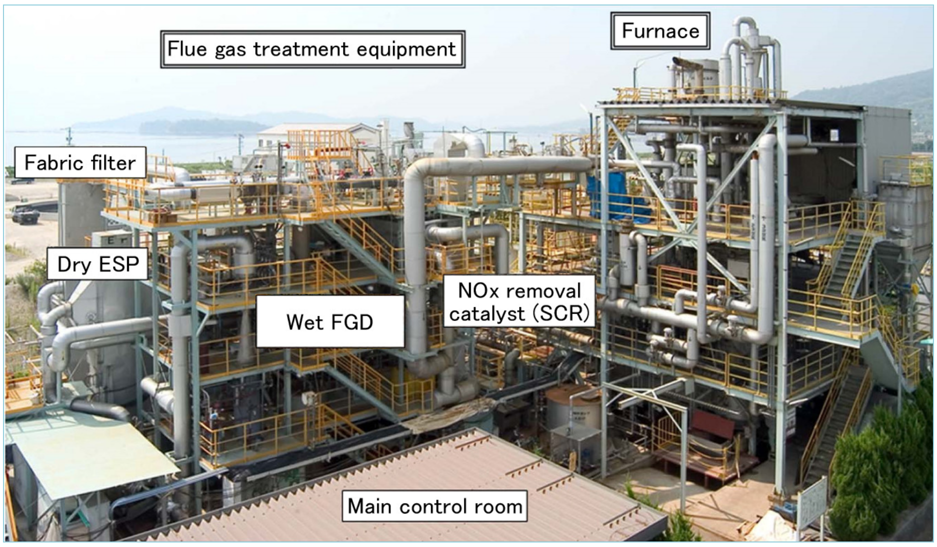


Figure 2 Appearance of 1.5-MW pilot plant

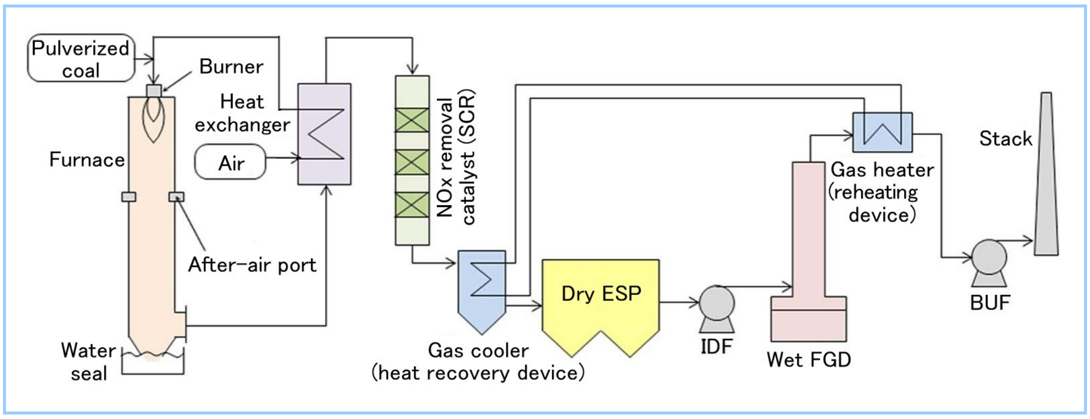


Figure 3 Flow diagram of 1.5-MW pilot test plant
The captive test plant is provided with a set of basic furnace-through-stack equipment, just like at an actual installation.

3.2 Test results

(1) Mercury removal

In recent years, it has come to be common knowledge that an SCR catalyst promotes the oxidation of metallic mercury and MHPS, early enough to focus on this fact, started to develop a high-mercury oxidation catalyst ahead its global rivals. Conventional technology had the problem that if the catalyst's activity of mercury oxidation increased, the conversion from SO_2 to SO_3 also increased (**Figure 4**). In 2008, however, MHPS successfully developed and introduced onto the market TRAC®. In this technology, the mercury oxidation activity alone was increased, with its SO_2 conversion and NOx reduction activities maintained at a level equivalent to those of the conventional catalyst (**Figure 5**), through the reaction mechanism-based optimization of catalyst composition/manufacturing method.

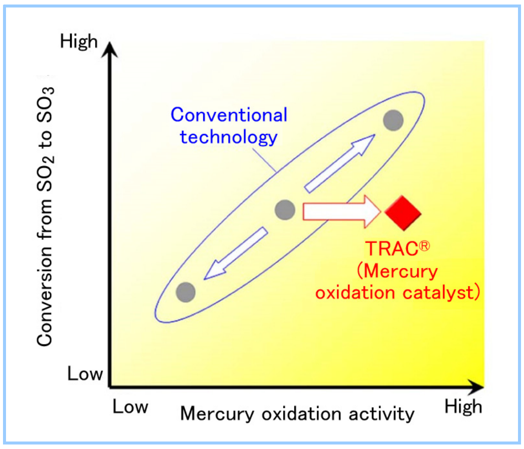


Figure 4 Concept of TRAC®
The TRAC concept of increasing the mercury oxidation activity without increasing the SO_2 to SO_3 conversion is shown

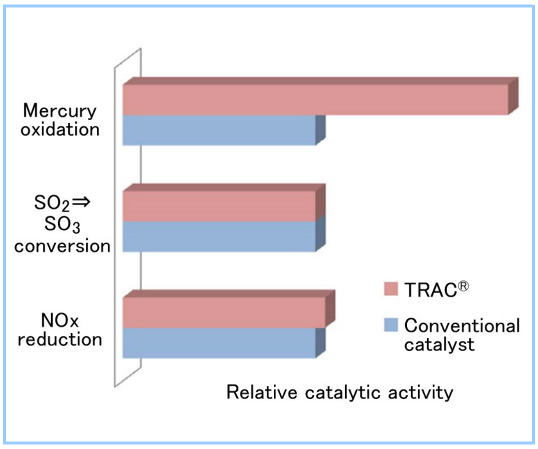


Figure 5 Characteristics of TRAC®
A comparison of TRAC® and a conventional catalyst for mercury oxidation activity, SO_2 conversion activity and NOx reduction activity is shown.

Oxidized mercury is highly adsorptive and water-soluble. The flue gas treatment system using a conventional low-temperature ESP (with operation temperature of 130 to 170°C) allows some of the oxidized mercury to be adsorbed onto ash particle and removed by an ESP, while most of the remainder dissolves into an absorbent liquid at the wet FGD to be removed. While in the AQCS of MHPS, the temperature of the flue gas leaving the catalyst is lowered below 100°C by a gas cooler and then introduced into a low-low temperature ESP so that the adsorption of oxidized mercury onto ash particle could be promoted to substantially improve the efficiency of mercury removal at ESP. Moreover, since a small amount of oxidized mercury passing ESP is efficiently absorbed and removed at the wet FGD, the decrease in removal efficiency due to mercury re-emission is moderate.

As shown in **Figure 6**, the combination of an increase in the activity of mercury oxidation due to TRAC® and an increase in the oxidized mercury removal due to the low-low temperature ESP proved to reduce the amount of system-wide mercury emission to about 1/4. Furthermore, regarding selenium in flue gas, it was also found that the low-low temperature ESP promoted condensation to improve the removal.

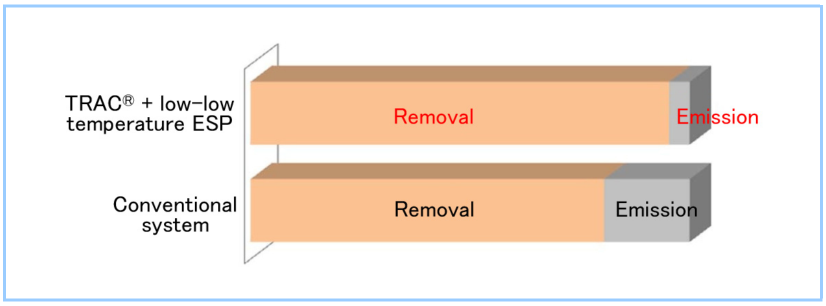


Figure 6 Mercury removal performance enhanced by a total system
By combining TRAC® and low-low temperature ESP into a total system, the mercury emission can be made smaller than that of a conventional system

(2) Particulate matter removal

At an ESP, the lower the electrical resistivity of ash particle, the higher the precipitator performance becomes in general, but as shown in **Figure 7**, the conventional low-temperature ESP's operating temperature of 140°C to 170°C is in the range where the electrical resistivity of coal ash is high.

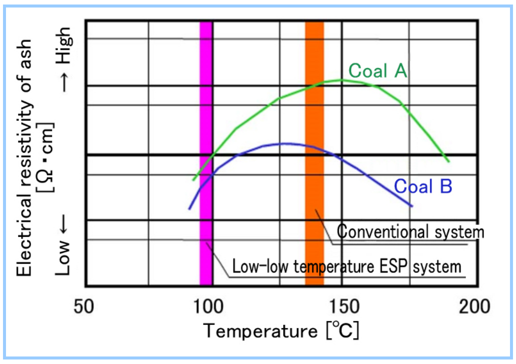


Figure 7 Relationship between flue gas temperature and electrical resistivity of ash
The electrical resistivity of coal ash differs for different temperatures of the flue gas and, within the temperature range of a low-low temperature ESP, the electrical resistivity decreases from its level in a conventional system.

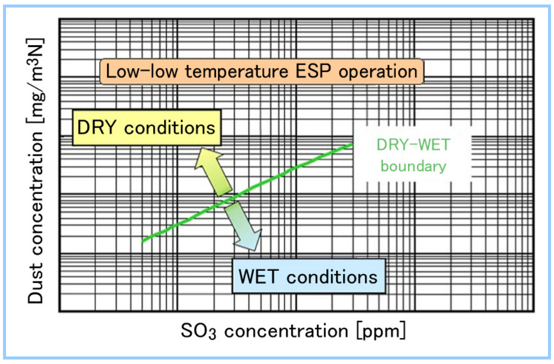


Figure 8 Conditions for dust/SO_3 within the low-low temperature ESP operating range
A low-low temperature ESP's operating range usually falls under DRY conditions of the dust-SO_3 ratio..

In contrast, at the low-low temperature ESP operating below 100°C, the electrical resistivity of ash decreases, thereby not only improving the dust collection efficiency, but also allowing ESP equipment to be downsized due to lower gas temperature. On the upstream side of ESP, the concentration of ash dust is high, but as shown in **Figure 8**, the dry conditions where SO_3 is neutralized by alkali contents of ash enable corrosion and/or blockage to be avoided. In the case of wet conditions where SO_3 outstrips ash dust in quantity, an alkaline agent such as Ca can be added to the flue gas to solve the problem. In addition, since the low-low temperature ESP reduces the amount of ash entering the desulfurization equipment, the quality (purity) of by-product gypsum also improves.

(3) SO_3 removal

A low-low temperature ESP permits not only dust, but also SO_3 removal performance to be improved substantially. **Figure 9** shows the structure of a gas cooler in the pilot plant. At this actual equipment-like non leak-type/fin tube-style installation, ash adhesion can be easily removed, using a soot blower. **Figure 10** shows the test results. Since the acid dew point of SO_3 in boiler flue gas is around 170°C, at an ESP temperature of 90°C, most of the gaseous SO_3 is condensed onto ash particle and removed through ESP, significantly reducing its concentration in gas. Moreover, since the use of TRAC® permits the conversion from SO_2 to SO_3 to be kept low, a further diminution of SO_3 is possible. In this way, the application of MHPS-developed AQCS enables the SO_3 content of the flue gas to be lowered to the utmost limits without an expensive large-size wet ESP.

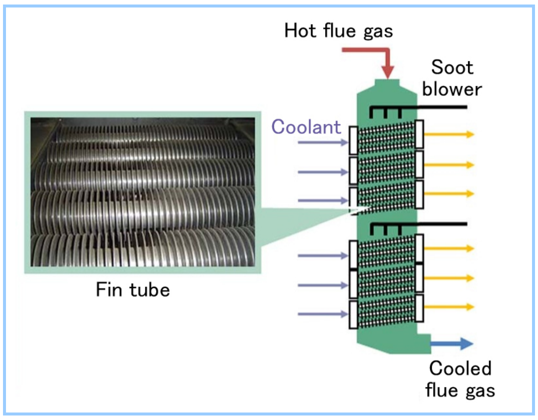


Figure 9: Structure of gas cooler
The gas cooler cools flue gas by letting coolant through the fin tubes arranged inside. Ash adhered to tubes is removed using a soot blower.

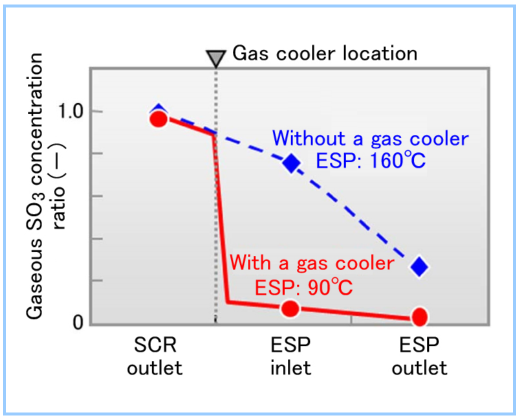
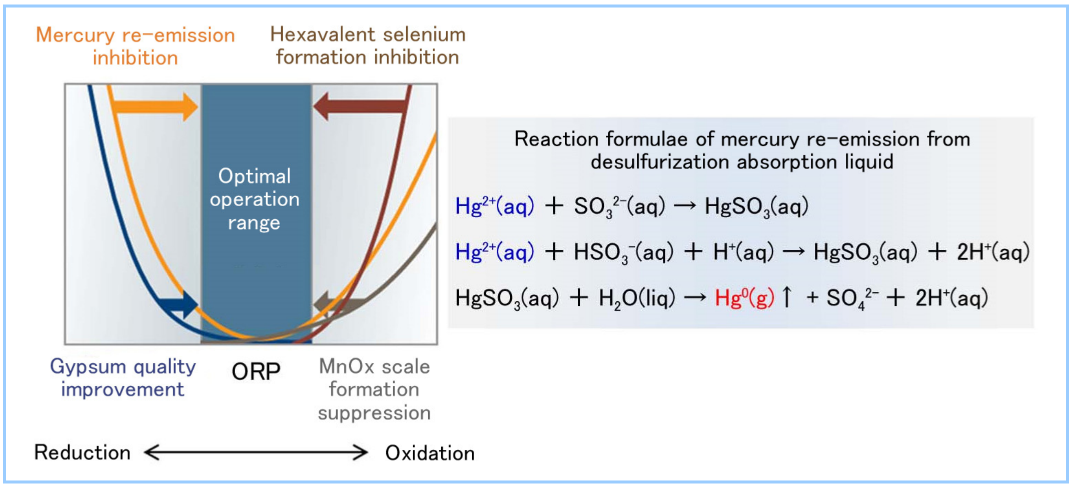


Figure 10 Effects of gas cooler to lower flue gas temperature
Using a gas cooler installed at the fore stage of ESP, flue gas temperature is lowered to 90°C, thereby condensing gaseous SO_3 into ash to be removed efficiently from flue gas.

4. Inhibition of mercury re-emission from wet FGD (ORP control) at U.S. 5-MW demonstration tests

Even if the mercury oxidation and/or the mercury removal efficiency at ESP are allowed to increase as mentioned above, if the remaining oxidized mercury flows into the wet FGD and accumulates in absorbent liquid in large quantities, it is partially reduced into metallic mercury and may sometimes be re-emitted from the wet FGD . Since re-emitted mercury is released from the stack as-is, the inhibition of re-emission at the wet FGD was an important issue. On the other hand, MHPS demonstrated through the U.S. 5-MW pilot tests that re-emission could be inhibited if the oxidation load (air flow for oxidation) at the FGD was controlled for the ORP to fall within a certain range.

As shown in **Figure 11**, if the ORP is controlled so as to fall within the optimal operation range, mercury re-emission can be inhibited while improving gypsum quality. In addition, since selenium peroxidation (tetravalent→hexavalent) is inhibited as well, it is also valid in the treatment of selenium in desulfurization wastewater and, likewise, since manganese oxide scale formation is suppressed, it may contribute to the stable operation of FGD.



Reaction formulae of mercury re-emission from desulfurization absorption liquid

$Hg^{2+}(aq) + SO_3^{2-}(aq) \rightarrow HgSO_3(aq)$

$Hg^{2+}(aq) + HSO_3^{-}(aq) + H^{+}(aq) \rightarrow HgSO_3(aq) + 2H^{+}(aq)$

$HgSO_3(aq) + H_2O(liq) \rightarrow Hg^{0}(g)\uparrow + SO_4^{2-} + 2H^{+}(aq)$

Figure 11 Concept of ORP control
Controlling the ORP of desulfurization absorption liquid so that it falls within the optimal operation range makes it possible to inhibit mercury re-emission, improve gypsum quality, prevent selenium peroxidation and limit MnOx scale formation..

5. Demonstration of NH_4Cl addition-based mercury abatement method with U.S. 720-MW commercial power plant

When Cl in coal is scarce and a conventional SCR’s mercury oxidation activity is poor, the mercury oxidation efficiency can be improved by feeding a Cl compound on the upstream side of the catalyst. MHPS has developed a technology to supply NOx reduction agent NH_3 and mercury-oxidizer HCl (hydrogen chloride) at the same time by injecting NH_4Cl aqueous solution into a flue gas duct to let it vaporize as shown in **Figure 12**.

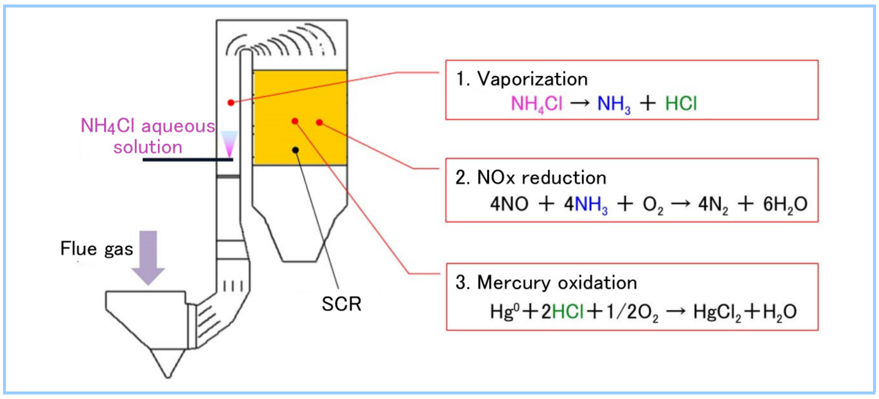


Figure 12 NH_4Cl addition-based promotion of NOx reduction and mercury oxidation
NH_3 (g) as a NOx reduction agent and HCl (g) as a mercury oxidation agent are supplied at the same time by injecting NH_4Cl aqueous solution into flue gas on the upstream side of the SCR to let it vaporize

Using this technology in the U.S., verification tests were conducted with 720-MW commercial plant based on 5-MW pilot demonstration test results. **Figure 13** outlines a test with the commercial plant. Flue gas was treated under two systems; one with conventional NH_3 injection and the other with NH_4Cl injection. **Figure 14** shows the test results, indicating that the use of NH_4Cl could (a) result in an NH_3-equivalent of NOx removal performance and (b) improve the mercury oxidation efficiency in favor of removal at downstream equipment such as an ESP and wet FGD to result in a substantial abatement of mercury emissions from stacks. NH_4Cl can be stored/carried in its solid state and, therefore, is easier to handle than liquid NH_3. It also has another advantage of less impact on the environment compared with other additives for mercury removal (including activated carbon and bromine compounds).

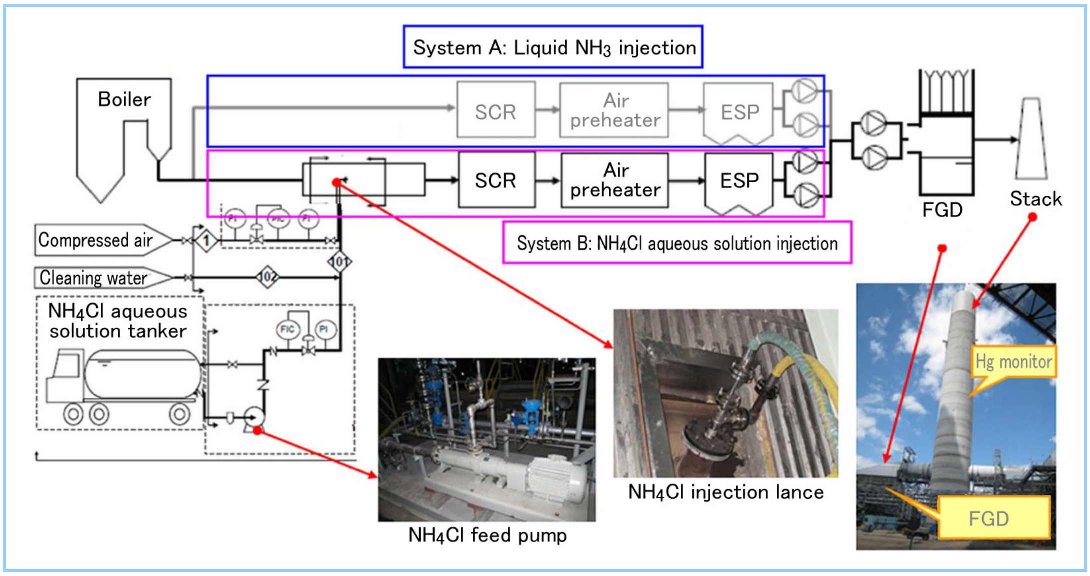


Figure 13 Outline of verification test in U.S. 720-MW commercial plant (with a flue gas amount of 3,400,000m^3/h from stack)
Using commercial power plant in the U.S., tests were conducted to compare two systems of flue gas treatment equipment for NOx reduction and mercury oxidation performances by injecting NH_3 into one system and NH_4Cl aqueous solution into the other.

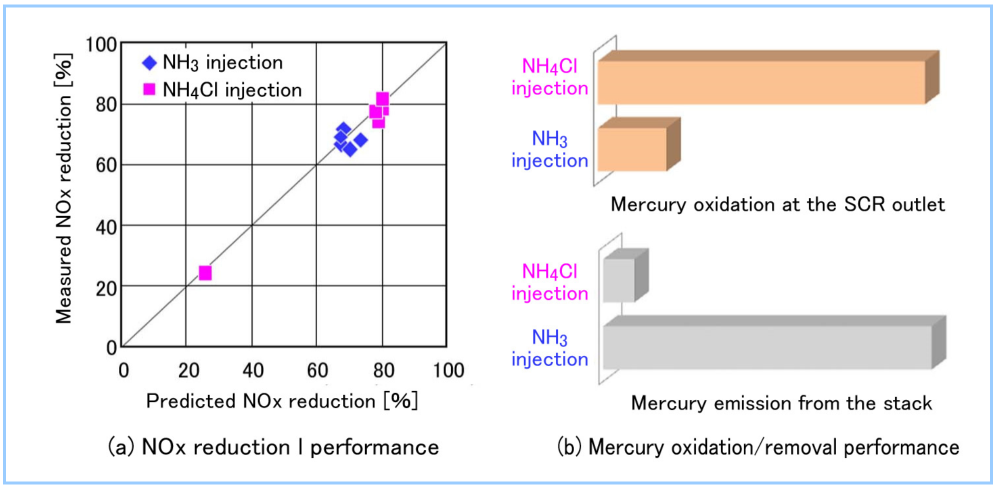


Figure 14 NH_4Cl injection test results

(a) The efficiency of NH_4Cl aqueous solution-injected NOx reduction is equivalent to that of conventional NH_3 injection.

(b) NH_4Cl aqueous solution injection improved the conventional efficiency of mercury oxidation to reduce the mercury emission

6. Conclusion

Since no country can do without coal-fired thermal power generation as one of the important sources of electric power for the time being, the importance of environmental technology is growing. MHPS developed, starting from its basic stage, AQCS capable of eliminating toxic trace components and particulate matter in flue gas to a significant extent and demonstrated its validity by way of pilot and commercial plants tests. Our captive 1.5-MW pilot test plant is provided with furnace-to-stack air quality control systems in a basic set and can be utilized for a wide variety of R&D as versatile test equipment. Toward the future, MHPS also intends to develop technologies to reduce, immobilize, and otherwise treat not only exhaust gas, but also solid waste (recovered ESP ash and FGD gypsum) and toxic substances in wastewater, thereby further contributing to thermal power plant-wide mitigation of environmental burden.

References

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