

# Control of mercury in flue gas emissions from coal fired plants with MerControl technology

Lukas Pilar and Lionel Barré

To be compliant with the Industrial Emissions Directive (IED) (Directive 2010/75/EU) or aligned with sustainability objectives, large combustion plants are using Best Available Techniques (BAT) or innovative solutions to reduce mercury concentration in their gas emissions.

However, when using wet flue gas desulfurisation (FGD), plants are often limited by a phenomenon that reduces the mercury capture in the liquid phase and increases the mercury concentration in the gas phase: Re-emission. This can lead to a higher risk of non-compliance in the gas emissions or additional costs of treatment upstream the wet scrubber.

Nalco Water, an Ecolab Company has developed an innovative chemistry solution to improve mercury retention in the liquid phase at wet flue gas desulfurization plants, achieving

efficient and cost-effective compliance with emissions limits. This chemistry has several advantages compared to typical commodities, including better efficiency on mercury capture and a better environmental safety profile.

The technology has been in place for over a decade in large combustion plants in the US and is now available in Europe.

A successful trial was run in a coal fired plant burning lignite in eastern Europe in 2024. During this trial, the target emission limit ( $7 \mu\text{g}/\text{Nm}^3$ ) was achieved when applying a dose of 5 l/h of the reagent solution, with an average concentration of mercury in the emission of  $5.2 \mu\text{g}/\text{Nm}^3$ .

## Background

From the hazard perspective, mercury is a neurotoxin that impacts our health system by causing insomnia, weakness, psychological disorders, and tingling and burning sensations, among other issues. It can also cause blood pressure problems. This heavy metal is introduced into our bodies through methylmercury (mostly in water) and elemental mercury (mostly in air). In addition to impacts on human health, mercury also damages wildlife and ecosystems, especially aquatic life, which eventually impacts human health again due to the food chain.

Mercury is a heavy metal that can be found naturally in the earth's crust. However, anthropogenic activities such as fuel combustion may increase its presence in the envi-

ronment. Mercury emissions are not zone-limited, as mercury can travel thousands of miles in the atmosphere before it is eventually deposited back to the earth.

Due to this situation, the European Commission deemed it necessary to regulate its use and emissions to the environment, thereby moving towards a more sustainable future. This was done in through the Industrial Emissions Directive (IED, Directive 2010/75/EU) and the establishment of the Best Available Techniques (BAT) for large combustion plants in 2017, which set mercury emission limits to apply beginning in 2021 (Table 1).

Due to a legal challenge in some countries, the EU General Court annulled the original document on procedural grounds but kept the stricter limits in place with a new compliance date. Certain plants were granted derogations, allowing up to four extra years (until August 2025) for compliance.

Coal combustion releases mercury in three different forms. This phenomenon is called Flue Gas Mercury Speciation.

The degree to which speciation occurs can substantially affect mercury control approaches:

- Particulate-bound mercury (HgP) is relatively easy to capture in particulate control devices like bag filters (BF) or electrostatic precipitators (ESP). High levels of carbon in the fly ash enhance mercury sorption onto particulate matter which will help its capture in this stage.

Tab. 1. BAT-associated emission levels (BAT-AELs) for mercury emissions to air from the combustion of coal and lignite.

Combustion plant total rated thermal input ( $\text{MW}_{\text{th}}$ )	BAT-AELs ( $\mu\text{g}/\text{Nm}^3$ )			
	Yearly average or average of samples obtained during one year			
	New plant		Existing plant <sup>(1)</sup>	
	Coal	Lignite	Coal	Lignite
< 300	< 1-3	< 1-5	< 1-9	< 1-10
$\geq$ 300	< 1-2	< 1-4	< 1-4	< 1-7

<sup>(1)</sup> The lower end of the BAT-AEL range can be achieved with specific mercury abatement techniques.

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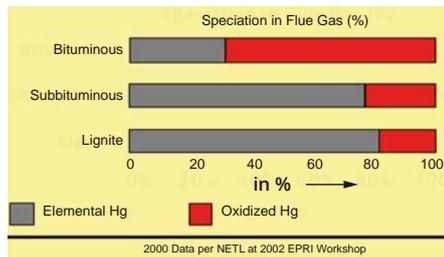
- Oxidised mercury ( $\text{Hg}^{2+}$ ) is prevalent in the flue-gas from coal combustion, and being water-soluble, is relatively easy to capture using  $\text{SO}_2$  controls such as wet limestone scrubbers at flue-gas desulfurization plants (FGD). This will be the one we will be focusing on. Sulfur dioxide ( $\text{SO}_2$ ) in flue-gas can act as a reducing agent to convert  $\text{Hg}^{2+}$  to  $\text{Hg}^0$ , which is more challenging to collect.
- Elemental mercury ( $\text{Hg}^0$ ) is not water-soluble, so difficult to capture. There is a significant link between the level of mercury speciation in flue gas and the type of coal used at a power plant. Especially important is the chlorine content.

$$[\text{Hg}^1] = [\text{Hg}]_{\text{particulate}} + [\text{Hg}^{2+}]_{\text{gas}} + [\text{Hg}^0]_{\text{gas}}$$



Coals with higher chlorine content, such as bituminous coal, tend to produce more oxidized mercury ( $\text{Hg}^{2+}$ ) while coals with lower chlorine content, like lignite, typically result in higher levels of elemental mercury ( $\text{Hg}^0$ ), which is more challenging to capture (Table 2).

Tab. 2. Speciation of mercury in flue gas for different types of coal.



Achieving the emission level limits requires mercury capturing rates of 80–95% at lignite-fired power plants.

The Best Available Techniques Reference Documents (BREFs) describe the BAT for specific industrial sectors, including large combustion plants. BREFs are developed through an exchange of information among EU Member States, industry experts, and environmental organizations, and they provide detailed guidance on the techniques considered to be the most effective in

achieving high environmental protection standards.

The capture of mercury in coal-fired power plants (CFPP) occurs ‘unintentionally’ through the flue-gas cleaning process. This type of emission reduction is called native techniques, which means: the selective catalytic reductor (SCR) system for  $\text{NO}_x$  control, followed by an electrostatic precipitator (ESP) for particulate control, and finally by the flue-gas desulfurization (FGD) for acid gas removal (Figure 1).

In addition to these techniques, non-native techniques are often considered to enhance the mercury capture. Non-native techniques include carbon sorbent injection, use of halogen additives, and fuel pre-treatment and cleaning.

Wet scrubber FGD systems are an effective method for reducing emissions of certain metals and particularly mercury in oxidized form. This is mostly because the flue-gas temperature is reduced to about 50–60 °C by passing through the absorber, which allows many of the more volatile metals to condense from the vapour phase and allows them to be removed from the flue-gas.

The condensed metals are then mainly transferred to the wastewater from the wet FGD system. The Hg can then be removed from the wastewater stream using reduction, volatilisation, condensation and Hg separation processes.

In theory, FGDs can capture more than 90% of oxidized mercury ( $\text{Hg}^{2+}$  is soluble in water up to 4.8 g/l). However, a range of 50–80% capture is typically observed because under some conditions oxidised mercury may be reduced to elemental mercury in wet FGD units, and this could be re-emitted. When gaseous compounds of oxidised mercury ( $\text{Hg}^{2+}$ ) are absorbed in the liquid slurry of a wet FGD system, the dissolved species are believed to react with dissolved sulfides from the flue-gas to form mercuric sulfide ( $\text{HgS}$ ), which precipitates from the liquid solution as sludge. In the absence of a sufficient concentration of sulfides in the liquid solution, a competing reaction with sulfites that reduces dissolved  $\text{Hg}^{2+}$  to elemental mercury ( $\text{Hg}^0$ ) is believed to take place. Once this reduction occurs, the newly formed  $\text{Hg}^0$  is transferred to the flue-gas and

increases the concentration of  $\text{Hg}^0$  in the flue-gas passing through the wet FGD.  $\text{Hg}^{2+}$  reduction and subsequent  $\text{Hg}^0$  re-emission may be more significant in magnesium-enhanced limestone scrubbers, which operate with a much higher sulfite concentration than limestone systems.

The wet FGD redox potential also plays an important role in the possible reduction of  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  and the consequent re-emission of Hg. In some cases, the reduction of  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  and subsequent re-emission are abated with the help of sulfide-donating liquid reagent. In addition, transition metals in the slurry (originating from fly ash in the flue-gas) are believed to play an active role in the conversion reaction, since they can act as catalysts and/or reactants for reducing oxidised species. There also appears to be increased potential for re-emission of mercury in wet FGD systems with appreciable concentrations in the liquor phase.

Due to re-emission, the level of mercury in gas emissions exceeds the limits set by the Industrial Emissions Directive (IED) in some cases.

## Solution

As explained above, a reconversion of  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  is likely to occur in the FGD. One of the main techniques to avoid this is the addition of various chemicals in the FGD that do not allow this conversion to occur since  $\text{Hg}^{2+}$  is easy to capture. The chemicals used are typically organic or inorganic sulfides (well-known at industrial level) or strong ligands like bromide (limited to lab-scale and few full-scale tests). These techniques are usually perceived as compliance security techniques. One of the main advantages of this technique is its low investment, especially important in a decarbonization context where some coal power plants will face reduced production in the coming years, making them more willing to invest in OPEX rather than CAPEX.

However, these chemicals have drawbacks when applied. They include safety and environmental concerns for some of them as well as limits in their efficiency in specific conditions. The amount of chemicals necessary for the treatment may also be challenging for the storage and dosing.

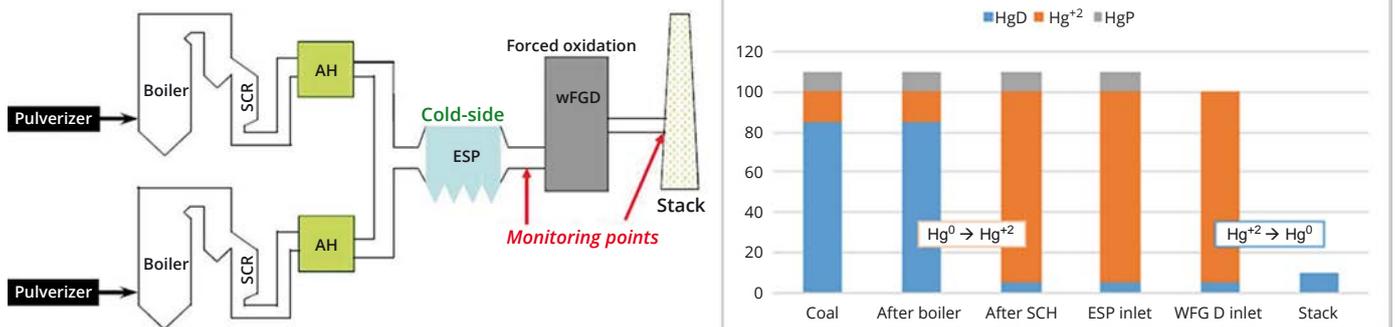


Fig. 1. Capture of mercury in coal-fired power plants.

To overcome the challenges of these drawbacks, Nalco Water developed an alternative approach called Nalco MerControl technology.

Nalco MerControl technology is a family of patented chemicals based on a water-soluble dithiocarbamate copolymer used to enhance mercury removal in wet flue-gas desulfurization (wFGD) scrubbers through binding with mercury in water to form large, insoluble precipitates. The effectiveness of the MerControl product line is directly related to the level of oxidation achieved. The oxidation can come from many sources: natural chlorides in the fuel, the additional of a halogen to oxidize the mercury, or a catalyst found in specific equipment. Nalco MerControl can achieve greater than 95% capture rate of oxidized mercury, preventing both stack emissions and re-emission of elemental mercury.

Nalco MerControl technology has been used extensively in North America since the early 2010's, with continued advancements in the formulation to provide a cost effective and reliable mercury capture product. Over the past decade, regulation of coal fired power industry has been highly on metals capture in North America, and many customers have come to the realization that compliance with all regulations is very challenging. They want a technical partner in Nalco to take on compliance challenges and drive operational savings. Nalco MerControl technology was implemented more recently in Europe.

Compared to other chemicals used for mercury capture in the FGD, Nalco MerControl technology has several advantages:

- Improved performance (based on tests) allowing significantly lower dosages (up to ten times compared to inorganic sulfides), which implies a reduced need for storage capacity, reduced safety and environmental risks, and reduced number of deliveries.
- “Practically non-toxic” as defined by US EPA (Environmental Protection Agency). Low Toxicity translates into Safer Handling, and a lowered risk for storage and delivery. This allows greater flexibility in managing raw material and supply chain issues.
- Patented Technology (composition, application, and manufacture).
- Improved Product Stability (>1 year).
- No Chlorides added with the dosage of product and no contribution to the corrosion of the wet flue gas desulfurization (closed plant friendly).
- Low capital cost feed systems with a small footprint and compatible with plant control systems. Liquid additive simplifies application, distribution, and control. Nalco MerControl feed systems require very little maintenance compared to some technology used such as halogenated active carbon.

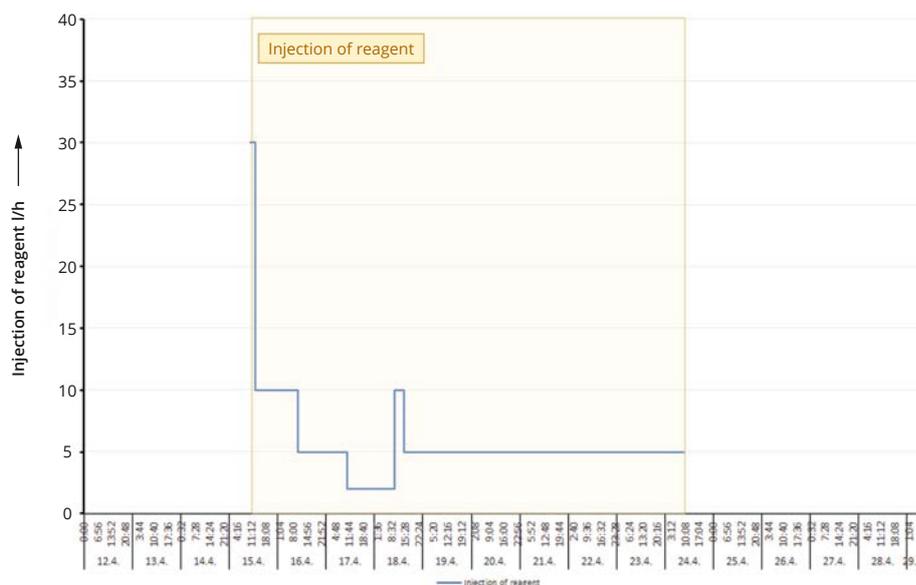


Fig. 2. Dosage of MerControl 8034 PLUS (l/h) in absorber 2 during the trial.

- No impact on emission particulate matter: New standards will be lowered and will be increasingly hard to achieve.
- Potential co-benefits in removing heavy metals like Selenium and Cadmium and preparing their removal from liquid effluents in the wastewater treatment plant.

## Case history

The 7 µg/Nm<sup>3</sup> limit in gas emission set by the Industrial Emissions Directive applied on a 12-month average to a power plant burning lignite located in Eastern Europe. The composition of the lignite burnt varies in time and so does its concentration in mercury. This leads to peaks of mercury in the gas emissions, with the risk to exceed the annual limit of 7 µg/Nm<sup>3</sup>.

For this reason, this plant was looking for techniques to improve the capture of mercury in the flue gas treatment process and to work on the safe side.

Ing. Lukas Pilar, Ph.D. from the Czech Technical University of Prague was approached to supervise a trial of Nalco MerControl technology in this plant.

This power plant has six (6) units with a capacity of production of 60 MW for each unit. The flue gases of three (3) units are directed to absorber and the flue gas of the three remaining units to another unit.

Flue gas desulfurization is based on the principle of wet limestone scrubbing technology. Each absorber has a shower zone with three shower floors – each floor has its own recirculation pump, and an important part of the absorber is the internal technological built-in TRAY and a three-stage droplet separator system. Finely ground limestone is added to the absorber according to the pH value of the sorption suspension. The system of extraction, dewatering and transport of gypsum from each absorber consists of exhaust pumps, hydro-cyclone sta-

tions, belt vacuum filters and a system of conveyors to storage silos. The filtrate is returned to the absorbers. Flue gases from two desulfurization lines are led to a wet chimney.

A trial was done on two scrubbers for 11 days. We are describing hereunder the results for the absorber No. 2, but results were similar for the second absorber.

The test was based on initial and continuous dosage. An initial dosage of Nalco MerControl was slug fed into the scrubber (into a stream sent to the basin). Then, a continuous dosage was applied to the suction of the recirculation pump of the scrubber, to allow a rapid mixing and to get a maximum concentration of active where the liquid gets in contact with the flue gas.

A dosage of 30 l/h was applied initially, progressively decreased to 2 l/h and stabilized finally at 5 l/h (Figure 2).

At the same time, a continuous monitoring of key parameters was done. It included:

- Energy output
- The concentration of total mercury in gas effluent at the inlet and the outlet of the scrubber
- pH
- ORP

The main results from the trial follow and are based on the graphs hereunder (Figure 3).

Based on the evaluation of the results obtained during the test, the dosing of Nalco MerControl increased the efficiency of Hg capture by 20%, from an average of 69% to an average of more than 89%.

During this specific test, the emission limit (7 µg/Nm<sup>3</sup>) was achieved when applying a dose of 5 l/h of the reagent solution, with an average concentration of mercury in the emission of 5.2 µg/Nm<sup>3</sup>. Each plant will have its own dosage based on several factors (ORP, MW loading and fluctuation, pH, etc.)

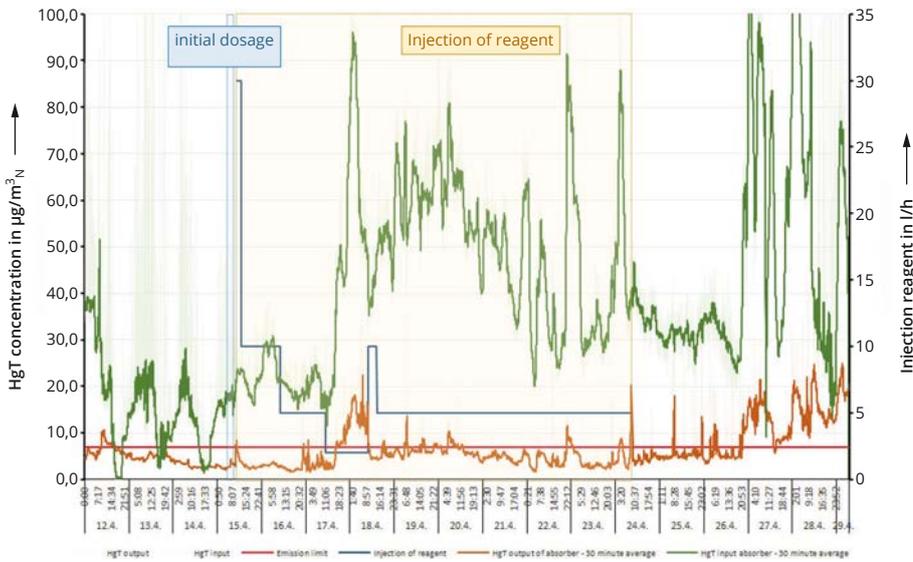


Fig. 3. Mercury concentrations in flue gas at the inlet (green) and outlet (orange) of the scrubber No. 2. The period of the trial is highlighted in light orange and the dosages applied are indicated.

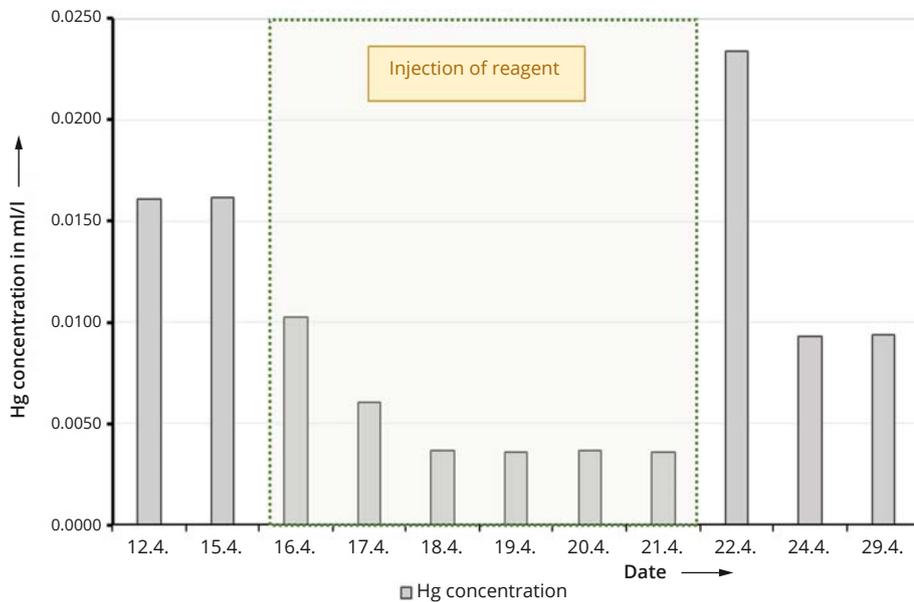


Fig. 4. Gypsum suspension – Overflow from ABS hydro-cyclone No. 2 – Liquid phase – .Hg.

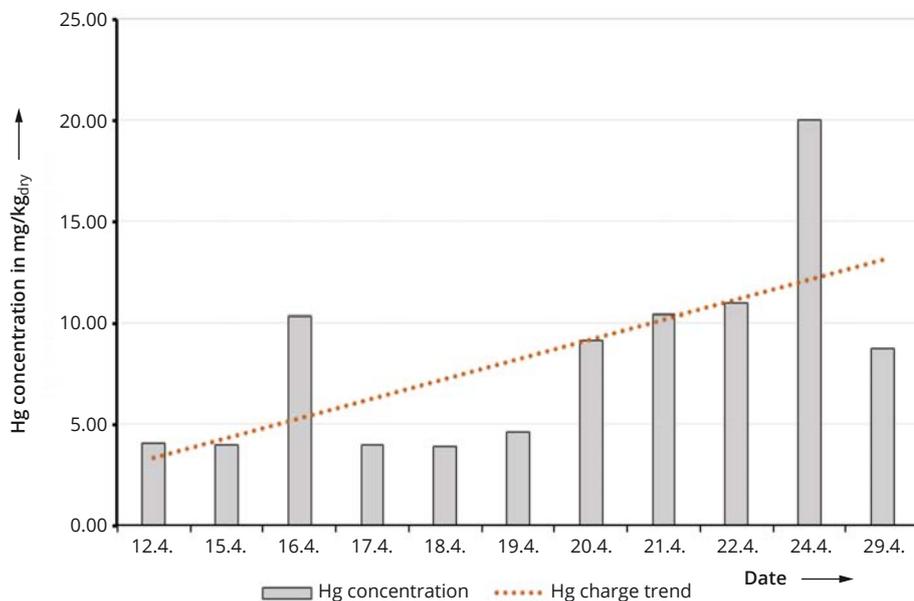


Fig. 5. Gypsum suspension – Overflow from ABS hydro-cyclone No. 2 – Solid phase – Hg.

and a chemistry trial should be conducted to show the dosage range.

During the test, the mercury content of the fuel changed significantly between 0.21 mg/kg dry as a minimum and 0.59 mg/kg dry as a maximum. There was a large spike of mercury at the inlet of the absorber during test. Nevertheless, the efficiency of mercury capture remained above 80 %, with the gas mercury concentration only slightly exceeding  $10 \mu\text{g}/\text{m}^3_{\text{N}}$  during peaks.

After the end of dosing and saturation of the absorber, the average concentration of mercury in gas emissions increased to  $14.5 \mu\text{g}/\text{Nm}^3_{\text{N}}$ , then above the limit expected.

The effect of the fuel change on the increase in the concentration of gas mercury at the outlet of the absorber was much more pronounced than during the dosing. The efficiency of gas mercury capture in the absorber dropped below 60 % (Figure 3).

The concentration of mercury was also checked in several sampling points over time: burned fuels, gypsum suspension taken from the exhaust of the absorber sump, the upper overflow of the hydro-cyclone, gypsum and filtrate.

The positive effect of Nalco MerControl on the mercury capture was also visible with the samples, for example the upper overflow of the hydro-cyclone. A higher metal content is expected in this location because of the content of fine fly ash particles on which metals are adsorbed.

The liquid and solid phases of the samples from absorber sump were separated and then analysed: A decrease of the mercury concentration was observed in the liquid phase, whereas the mercury concentration increased on the solid phase, showing that more mercury is captured in the scrubber (or less is re-emitted) (Figure 4 and Figure 5).

## Summary

Due to the risks for human health and environment related to industrial mercury gas emissions, the Industrial Emissions Directive (IED, Directive 2010/75/EU) is applicable in European Community to large combustion plants.

To be compliant with this directive, large combustion plants are using Best Available Techniques (BAT) or innovative solutions to reduce mercury concentration in their gas emissions.

However, when a wet flue gas desulfurization is in place, the mercury capture in the liquid phase can be limited by a phenomenon called re-emission. Part of the oxidized mercury in the liquid phase is reduced, generating elemental mercury and increasing the mercury concentration in the gas phase. Subsequently there is a higher risk of non-compliance in the gas emissions released by the plant.

Nalco Water has developed an innovative chemistry called Nalco MerControl, based on polymeric organo-sulfides. This technology improves mercury retention in the liquid phase at wet flue gas desulfurization plants, achieving efficient and cost-effective compliance with emissions limits. This chemistry has several advantages compared to commodities used in some cases, including a better efficiency on mercury capture and a better environmental safety profile.

The technology has been in place for over a decade in large combustion plants in the US and is now available in Europe.

A successful trial was run in a coal fired plant burning lignite in eastern Europe in 2024: The effectiveness of Nalco Water's scrubber additive MerControl has been demonstrated in controlling mercury re-emission in Wet Flue Gas Desulfurization (WFGD). During this specific test, the emission limit ( $7\mu\text{g}/\text{Nm}^3$ ) was achieved when applying a dose of 5 l/h of the reagent solution, with an average concentration of mercury in the emission of  $5.2\mu\text{g}/\text{Nm}^3$ .

The positive effect of Nalco MerControl on the mercury capture was also visible with samples taken from the scrubber: A decrease of the mercury concentration was observed in the liquid phase, whereas the mercury concentration increased on the solid phase, showing that more mercury was captured in the scrubber (or less is re-emitted).

After the dosage of Nalco MerControl was interrupted, the level of mercury in gas emissions immediately increased above the limit expected.

## Authors

Ing. Lukas Pilar is a member of the Czech Technical University in Prague, Faculty of mechanical engineering, Department of energy.

Main area of research:

- Reduction of emissions from combustion of solid fossil and alternative fuels, particularly mercury and other pollutants in accordance with BAT requirements, including applied research on full-scale combustion units.
- Research on solid sorbents for reduction of  $\text{CO}_2$ , total mercury (HgT), and other heavy metal emissions.
- Research on liquid reagents for reduction of HgT and other metals and their application on industrial-scale equipment,
- Development and research of flue gas cleaning technologies after solid fuel combustion.

The Department of Energy Engineering is an agency who trains experts for jobs in a wide range of energy engineering fields. Education is focused on issues of production of

electricity and heat from fossil, nuclear and renewable sources and energy consumption in industry and in the housing and municipal sphere. Special attention is paid to heat pumps, cooling technology and gas compression. Exceptional emphasis is laid on the economics of gaining and transformation of energy and its effective use. The Department also deals with ecological aspects of the operation of energy engineering equipment aimed at reduction of negative impacts of energy engineering on the environment.

Lionel Barré is an Industry Technical Consultant at Nalco Water, an Ecolab Company. A global leader in water and process management solutions, Nalco Water works with customers across a wide range of industries to help them address their business goals. With a global presence in more than 170 countries, Nalco Water combines innovative products with digital innovation and extensive expertise to help maximize performance while addressing water and energy targets. The network of 30,000 water performance management systems helps fuel insights that lead to fast, proactive action for customers.

## Kurzfassung

Überwachung von Quecksilber in Rauchgasemissionen aus Kohlekraftwerken mit MerControl-Technologie

Um die Industrieemissionsrichtlinie (IED, Richtlinie 2010/75/EU) einzuhalten oder Nachhaltigkeitsziele zu erreichen, setzen große Verbrennungsanlagen beste verfügbare Techniken (BVT) oder innovative Lösungen ein, um die Quecksilberkonzentration in ihren Emissionen zu reduzieren.

Bei der Verwendung von nasser Rauchgasentschwefelung (FGD) sind Anlagen jedoch häufig durch ein Phänomen eingeschränkt, das die Quecksilberabscheidung in der flüssigen Phase verringert und die Quecksilberkonzentration in der Gasphase erhöht: die Reemission. Dies kann zu einem höheren Risiko der Nichteinhaltung der Gasemissionsgrenzwerte oder zu zusätzlichen Kosten für die Behandlung vor dem Nasswäsher führen.

Nalco Water, ein Unternehmen von Ecolab, hat eine innovative chemische Lösung entwickelt, um die Quecksilberrückhaltung in der flüssigen Phase in Nassreinigungsanlagen zu verbessern und so eine effiziente und kostengünstige Einhaltung der Emissionsgrenzwerte zu erreichen. Diese Chemie hat gegenüber herkömmlichen Produkten mehrere Vorteile, darunter eine bessere Effizienz bei der Quecksilberabscheidung und ein besseres Umweltsicherheitsprofil.

Die Technologie wird seit über einem Jahrzehnt in großen Verbrennungsanlagen in den USA eingesetzt und ist nun auch in Europa verfügbar.

Im Jahr 2024 wurde ein erfolgreicher Versuch in einem Braunkohlekraftwerk in Osteuropa durchgeführt. Während des Versuchs wurde der angestrebte Emissionsgrenzwert ( $7\mu\text{g}/\text{Nm}^3$ ) bei einer Dosierung von 5 l/h der Reagenzlösung erreicht, wobei die durchschnittliche Quecksilberkonzentration in den Emissionen  $5,2\mu\text{g}/\text{Nm}^3$  betrug.

be energised  
be inspired  
be connected  
be informed

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ENERGY IS US