Combating the threat of mercury

Emerging legally binding action on mercury emissions highlights the importance of monitoring and quantifying emissions from gas operations

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Mercury has been elevated to the status of a pollutant of global concern owing to some of its unique toxic properties, which pose environmental and health risks. Mercury is found both naturally and as an introduced contaminant in the environment, mainly from high-temperature industrial processes such as oil and gas processing, alkali and metal processing, incineration of coal and oil in electric power stations, foundries, and waste combustion.

In the past, mining was a substantial source of mercury in some areas. For example, the hydraulic placer-gold mines of the Sierra Nevadas in the US released several thousand tons of mercury to the environment from the 1860s to the early 1900s. The US Geological Survey believes that high levels of mercury in fish, amphibians and invertebrates downstream of hydraulic mines are a result of historic mercury use.

Atmospheric mercury

Natural sources of atmospheric mercury include volcanoes, geologic deposits of mercury and volatilisation from the ocean. Although all rocks, sediments, water and soils naturally contain small amounts of mercury, some local mineral occurrences and thermal springs are naturally high in mercury.

Long-range atmospheric deposition is the dominant source of mercury over aquatic and terrestrial ecosystems. Since it is an element, mercury is not biodegradable and, although its form and availability to living organisms may change over time, mercury endures in the environment. Converted by bacterial action in lakes and waterways to a more toxic form known as methylmercury (CH_3Hg), it can bioaccumulate in fish and shellfish. Mercury is so toxic that just one kilogram of mercury is enough to render almost two million kilograms of fish unsafe to eat.

Global mercury cycle

Once it has entered the so-called "global mercury cycle", methylmercury becomes concentrated as it is transferred up the food chain to birds, animals, marine mammals and humans in a process known as biomagnification. Through this cycle, mercury can contaminate entire food webs, posing a serious threat to ecosystem health and particularly to the higher order species in the food chain, ultimately impacting on human health.

Almost all the mercury in lakes in the EU has been deposited via atmospheric transport from sources abroad, while the amount being used and released in the world is still increasing. Coal-fired power-generating plants, owing to the nature of the fossil fuel employed, are the largest man-made source of mercury emissions, while mercury is also found in many everyday household goods, such as lighting and electrical appliances, batteries, medical equipment, older dental fillings, jewellery, paint, thermometers, barometers, manometers, thermostats, pharmaceuticals and pesticides. When these products are discarded, mercury can be released to the environment in a variety of ways during the transport of the waste, its incineration, the post-incineration disposal of residuals such as ash, and in landfills.

Although mercury use has gone down in industrialised nations, emissions are growing in other regions. The burning of coal in small-scale power plants and residential heaters, particularly in Asia, are major sources of current emissions. These emissions are likely to increase significantly because of the economic and population growth in these regions.

Mercury has been found to be responsible for a spectrum of adverse human health effects, including permanent damage to the nervous system, in particular the developing nervous system, affecting learning ability and neurodevelopment in young children. It can be transferred from a mother to her unborn child, making children and women of childbearing age vulnerable populations, especially those living in close proximity to industrial plants. It also affects the kidneys and lungs.

Plant safety and structural integrity

In gas production and processing plants, trace levels of mercury could range between 0 and up to 2000 $\mu g/Nm^3$ in products, depending on the source. It poses a formidable threat to the safety of humans and capital equipment, because of this propensity to amalgamate with the materials of construction used for pipelines and equipment.

For instance, should mercury amalgamate to the pump system material or to a turbine blade, it could throw these systems out of kilter and cause immense structural damage. Liquid metal embrittlement

(LME), which weakens the original structure of steel, aluminium and other metals in process plants, is the main threat. LME is a form of cracking that occurs when certain molten metals come into contact with structural alloys. The most commonly affected materials include carbon steel, low-alloy steels, high-strength steels, 300 Series stainless steel, nickel-based alloys and the copper alloys, aluminium alloys and titanium alloys. Not all alloys are susceptible to LME, as this manifestation only occurs where specific pairings of liquid metal and structural alloy are present.

LME introduces acute risk to affected industrial plant. Mercury-induced corrosion of heat exchangers constructed of aluminium have led to catastrophic failures in the past, and common industry practice to avoid these incidents is to reduce the mercury content below the detection limit (0.01 $\mu g/Nm^3$) in an early phase of product processing. In a worst-case scenario, structural failure could cause a massive explosion in an oil refinery or LNG facility, resulting in catastrophic loss of life, excessive damage to capital equipment and long-term plant downtime.

Additional concerns with trace levels of mercury in natural gas would also include poisoning of costly catalysts used down stream, difficulties of waste handling and safety hazards for persons working with maintenance operations.

UNEP

The United Nations Environment Programme (UNEP) has been working to address mercury issues since 2003 and its current mercury programme has two main facets. An intergovernmental negotiating committee is working to develop a legally binding instrument to strengthen global action on mercury. In tandem, a UNEP Global Mercury Partnership aims to protect human health and the global environment from the release of mercury and its compounds by minimising and, wherever feasible, ultimately eliminating global, anthropogenic mercury releases to air, water and land.

Mercury is rapidly moving up the pollution control agenda in the European Union (EU), the US and Asia ahead of the legally binding UNEP global treaty on mercury to be implemented in 2013.

A UNEP report states that "mercury is a substance that can be transported in the atmosphere and in the oceans around the globe travelling hundreds and thousands of kilometres from where it is emitted. The global environmental threat to humans and wildlife has not receded despite reductions in mercury discharges, particularly in developed countries. Indeed, the problems remain and appear, in some situations, to be worsening as demand for energy, the largest source of human made mercury emissions, climbs."

The United States Environmental Protection Agency (EPA) has long supported the efforts of UNEP and other partners to address mercury, securing an agreement for UNEP to conduct a Global Mercury Assessment that has provided clear, scientific evidence of mercury's global reach. In late 2011, the, EPA finalised the Mercury and Air Toxics Standards (MATS), the first national Clean Air standards to reduce emissions of mercury and other toxic air pollutants from new and existing coal- and oil-fired power plants.

It is estimated that the US emits in the region of 50 tons of mercury per annum into the atmosphere, mostly from coal-fired power plants, cement kilns and from natural gas and oil refinery processes.

Advanced systems and methods are now required to measure lower and lower concentrations of pollutants as emission limits tighten. Increased measurement accuracy will become paramount as pollutants such as nitrous oxide, methane and possibly mercury are introduced to trading markets in the EU and US. The change will mean that once a monetary value comes into play, measurement accuracy becomes an economic target, as well as an environmental one. As legislation and action plans grow in number and stringency, the importance of monitoring and quantifying emission pollutants in an accurate and transparent manner are becoming priorities.

First on the market

In the US, The Linde Group was the first company to offer gaseous mercury calibration standards for the monitoring and detection of emissions from power generation plants. Linde has worked alongside UNEP for nearly a decade to identify technology to reduce the overall amount of mercury in the atmosphere, resulting in a 1-60 $\mu g/Nm^3$ range of globally high-precision gaseous mercury standards to calibrate analytical instruments operating at industrial processing plants.

Typical analytical instruments in this application include atomic absorption spectrometers (AAS) and inductively coupled plasma (ICP) mass spectrometers. The AAS is generally used to determine the mercury content of raw natural gas coming into a facility from the oil and gas fields. Ensuring speed of response and a direct online read, the instrument also plays a key role in the process control instrumentation loop in natural gas processing, to ensure that mercury has been successfully removed before the gas enters the compression train.

In developing its gaseous mercury standards, the Linde research programme successfully negotiated several potential roadblocks to success. These included the different forms of mercury that could be utilised, the ability to insert a known quantity of mercury into a cylinder, ensuring the stability of the calibration gas mixture over an extended period of time and determining the precise concentration of the calibration gas mixture.

The final calibration gas mixture standard is attracting a lot of attention because of its ability to deliver accurate, real-time results on site, compared with conventional sorbent sampling tubes, which take time to render a result.

The gaseous mercury standards are sold in 4.0 m^3 aluminium cylinders with a concentration range from 1 to 60 $\mu g/Nm^3$, approximately 700 parts per trillion up to 12-13 parts per billion. Through a research and development programme at Linde, and proprietary cylinder passivation procedures, gaseous mercury calibration standards are supplied with a guaranteed stability period of six months.

Linde also supplies special regulators to accompany these cylinders, which ensure that no amalgam attaches to the regulator. In terms of traceability, the standards have been certified by the National Institute of Standards and Technology (NIST) in the US, and these values are used to calibrate Linde's own instruments and to name the mixtures it produces.

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