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Assessment of potential mercury pollution from decommissioning/ dismantling offshore equipment

Introduction

Mercury is one of the most hazardous contaminants that may be present in the aquatic environment, but its ecological and toxicological effects are strongly dependent on the chemical species present. Depending on the environmental conditions, inorganic mercury species may be converted to many times more toxic methylated forms such as methylmercury, a potent neurotoxin that is readily accumulated by aquatic biota. In particular, monomethylmercury (MMHg), is effectively taken up and biomagnification factors in the order of 10^4 to 10^7 have been reported. Accumulation in the aquatic food chain therefore can be high even at very low environmental MMHg concentrations, *e.g.* nano gram/liter sea water may end up as mg/kg in the fish. While MMHg typically constitutes between 10 and 30% of total Hg in the water phase, more than 85% of Hg in fish is present as MMHg.

While it is fully recognized that mercury and its compounds are highly toxic substances, there is ongoing debate on how toxic these substances, especially methylmercury, are. New findings during the last decade indicate that toxic effects may be taking place at lower concentrations than previously thought. It has been documented that mercury is cytotoxic. Its biochemical damage at the cellular level includes DNA damage, and inhibition of DNA and RNA synthesis (Khera et al, 1990). Furthermore, high mercury concentrations were found in brain regions and blood of some patients with Alzheimer (AD) disease. Low levels of inorganic mercury were able to cause AD-typical nerve cell deteriorations *in vitro* and in animal experiments. Other metals like zinc, aluminum, copper, cadmium, manganese, iron, and chrome are not able to elicit all of these deteriorations (Mutter et. al, 2007). As the mechanisms of subtle toxic effects are extremely complex issues, a complete understanding has so far not been reached.

Mercury from oil/gas reservoirs

Elemental mercury in fluids produced from hydrocarbon reservoirs reacts with, and thus chemically modifies, steel surfaces on pipe lines for oil/gas transport. The scale surface inside a section of a gas pipe has been shown to be covered by an oxide/sulfide layer, either as HgS on the surface or as Hg^{2+} chemically incorporated into the iron oxide scale. The inside pipe surface area has in one case been shown to contain approximately 0.2 g Hg/m^2 . However, this amount will, of course, depend on the Hg concentration of the gas flow.

A strategy for Decommissioning/ Dismantling offshore equipment has been outlined in *The Guidance on planning...*, BP, TOTAL, ConocoPhillips, (07.18. 2006). Here it was pointed out that if the facilities were to be cleaned onshore “*waste disposal may then become an issue/concern*” and furthermore: “*Remember that a ‘duty of care’ may exist from cradle to grave for all wastes*” “*Apart from the platform inventory there are also by-products such as Low Specific Activity (LSA) material, mercury etc. Issue of removing/cleaning mercury contamination from pipelines will need to be dealt with, in solution or as a solid.*”

The oil companies realize that there are both legislative and environmental constraints which call for some degree of cleaning to be carried out. One has to ensure that all surfaces are free from hydrocarbon oils, metal scales including mercury, LSA materials etc. In order to remove contaminated materials from pipe lines and other offshore equipment different methods have been used, *e.g.* high pressure flushing and sand blasting. The latter method generates a lot of dust which may contaminate the local environment. This seems to be the case and a critical problem for the Raunes Fishfarm (RF) where a high level of mercury containing dust has been observed.

The transformation of inorganic mercury to extremely toxic organic mercury compounds.

Many of the chemical and biological processes that control Hg methylation and bioaccumulation are still insufficiently understood. Initially, it was assumed that methylation was a simple chemical reaction. However, in the early 1960s it was proposed by Jensen & Jerneløv that sulfate-reducing bacteria (SRB) are very important methylators of mercury in aquatic systems. Methylation of Hg occurs inside SRB via enzyme-mediated transfer of a methyl group, but the detailed Hg-uptake mechanism is still unknown (Benoit et al., 1999). The SRB bacteria are commonly concentrated at oxic-anoxic boundaries, where methylation rates in natural sediments are often highest. Methylation occurs predominantly in sediments and to a lesser extent in the water column, but it should be borne in mind that water column methylation is potentially more important, because the volume of water is typically much larger than the volume of surficial sediments.

The speciation of mercury has been shown to be an important determinant of its biological uptake. Neutral species are entering the cell by passive diffusive transport, as charged species hinder diffusion through the lipid bilayer (Benoit et al. 1999). Passive diffusion of neutral $\text{HgS}^0_{(\text{aq})}$ indicate this to be the dominant mercury species taken up by cells at low sulfide concentrations (Dyressen, 1989). **Early work suggested that mercury in the HgS form is not available for bacterial methylation under anaerobic conditions, but recent research suggests that dissolved HgS^0 can in fact be methylated (Benoit et al.1999).** The model is consistent with HgS^0 as an important neutral Hg compound and the form of Hg accumulated by methylating bacteria. Neutral HgCl_2 may also be a key chemical species determining cellular uptake of inorganic Hg in oxic waters while uncharged HgS^0 and bisulfide $\text{Hg}(\text{SH})_2$ complexes may be important for bacterial uptake in anoxic waters

Increased Hg solubility has important environmental implications. Dissolved organic material (DOM) from a variety of natural environments enhances the dissolution of particulate HgS with large surface area. Aerobes can also solubilize HgS by oxidizing the sulfide through sulfite to sulfate. Recently, work has focused specifically on the microbial methylation potential of nanoparticulate HgS in relation to bulk scale HgS and dissolved Hg-sulfide species (Slowey, 2010)

Sediments act both as sinks and potential sources of Hg, and once contaminated may pose a risk to aquatic life for many years depending on the physical, chemical and biological conditions (Kudo, 1992) The reaction rate of methylation varies over a wide range, 10^{-5} to 10^{-1} . It has been shown that the methylation rate is 40 times higher under anoxic/sulfide water than under oxic water. Methylation proceeds twice as fast during summer as compared to winter temperatures.

Conclusion

- i) The scale inside a section of oil/gas carrying pipes has been shown to contain a mercury/iron oxide/sulfide/chloride layer.
- ii) Onshore cleaning involves sandblasting producing mercury containing dust which has been shown to precipitate on the neighboring fish farm.
- iii) Methylation of Hg occurs inside sulfate-reducing bacteria (SRB). Neutral Hg species are proposed to enter the cell by passive diffusive transport, as charged species hinder diffusion through the cell membrane.
- iv) Early work suggested that mercury in the HgS form is not available for bacterial methylation under anaerobic conditions, but recent research suggests that dissolved HgS^0 can in fact be solubilized and methylated.
- v) The methylation rate is strongly dependent on the anoxic/oxic condition in the sediment and temperature. Most likely an area once contaminated may pose a risk to aquatic life for many years
- vi) Bioaccumulation in the food chain may concentrate trace amounts of organo mercury up to 10^4 to 10^7 times.
- vii) According to the OSPAR convention (*Convention for the Protection of the Marine Environment of the North East Atlantic*) Norway has agreed to stop all sources of toxic substances, including mercury before 2020. The strategy is to achieve concentrations in the marine environment near background values for naturally occurring substances.

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