



# Mercury emission control: Phase II. Let's now go passive



Keith Schofield

Materials Research Laboratory, University of California, Santa Barbara, CA, 93107, United States

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## ABSTRACT

The US Environmental Protection Agency's plan for a National set of standards limiting mercury emission from coal power plants has recently hit a setback. A decision by the US Supreme Court rejected this based on the two available methods having a burdensome cost basis. Moreover, even if the activated charcoal or bromine addition methods do become standard in the US, their cost may still inhibit global implementation. As a result it is timely to develop alternate methods. This paper outlines further development of such an approach. It is based on mercury's own chemistry. Previous published work discovered that elemental mercury, although volatile, has a propensity for heterogeneous chemistry on warm non-catalytic surfaces. This paper now reports results of a second pilot plant test continuing its clarification, extension and further validation of practicality. It extends data to inexpensive base metal surfaces that can be used and indicates the extent of mercury control possible. This non-catalytic heterogeneous chemistry has been overlooked due to this disguising role of surfaces. It is this that now suggests a passive mitigation method, natural to the system. By providing inserted metal surfaces in the downstream flue gas flow, mercury can be chemically modified and controlled.

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## 1. Introduction

In spite of its well-known high neurological toxicity, we have never ranked mercury as the dangerous element it is. Children used to play with its quicksilver globules, scientists used it freely in laboratories, gold miners handled it and still do with little regard, dentists implant it in teeth and the medical profession still feels free to inject it as thimerosal into people's veins. Surprisingly, it is only in recent decades, partly as a result of global environmental assessments, that our anthropogenic additions have been realized as no longer negligible when added to what still lingers in the environment from past generations. Even more important is the realization that mercury now has left what was mainly the inorganic arena and become heavily organic. The chemistry of mercury is unusual in some ways. It is still not fully understood why it is a liquid at ambient temperatures especially when it is located between Pt, Au and Pb in the periodic table. Another oddity is that even in molecular form, when in solution or absorbed by some materials, it can revert to the element and vaporize. This is the major environmental problem in that old past mercury in the ocean or in soils can re-vaporize before finally being sequestered [1–5]. This has now been well documented to occur from certain

absorbents and also flue gas desulfurization gypsum, but its mechanism remains unknown [6–9]. One recent study endeavored to assess the current anthropogenic mercury content of the oceans. Water samples were collected from all the oceans and from depths to at least 4000 m. Although obviously a difficult task they indicated a global estimate of about 64,000 tons with two-thirds of this being at less than 1000 m deep [10]. The global mining of mercury is now ended and extensive efforts have largely removed it from all uses in both the domestic and industrial markets [11]. Already, such efforts are being reflected by observed decreases in global atmospheric levels [12]. The only remaining uncontrolled aspects of the metal are the emissions that result from coal-fired power units, cement plants, the continued artisanal small-scale gold mining, and the use in medicine and dentistry. The United Nations currently is moving to minimize any free-agent gold mining contributions and to ban tooth amalgams. Although coal contains on average only about 0.1  $\mu\text{g/g}$  this implies, if uncontrolled, a 100 ton release on burning a billion tons of coal. Global consumption currently is of the order of 7 billion tons/yr. Although the use of about 1.5 billion tons/yr in the US is argued as being a small fraction of current anthropogenic mercury in the environment, a time has been reached that total controls are necessary globally. Also, numerical modeling of the oceans and land remain uncertain and it is not known to what extent sedimentation losses are sufficient to be gradually lowering the previous excesses back towards pre-

E-mail address: [KSHome@ucsb.edu](mailto:KSHome@ucsb.edu).

industrial levels. Mercury is now contaminating the human diet noticeably, and organic methyl-mercury is not only evident in fish but also rice and other crops grown in open water sources. Fortunately, these appear not to bioaccumulate to the extent seen with fish [13]. However, the situation has reached a point that adults are being diagnosed with mercury poisoning and the risk to pregnant women is recognized but not easily resolved. Fish is regarded medically as an important nutrient. However, the contamination present in the large carnivorous fish and the growing adoption of a Japanese (sushi) diet now are of significant concern. What fish to eat can now be a risk/benefit analysis. A recent such study indicated that with blue shark this should be consumed at only one such meal per year, once a week for canned tuna and monthly for grilled tuna [14,15]. The combination of an excessive number of vaccinations coupled to a sushi diet now is potentially hazardous for pregnancies and has been suggested as the possible basis of autism in children [16]. In the US, mercury was listed as a toxic pollutant in the 1980 Clean Air Act and suggested for regulation. However, several problems then existed. Gaseous mercury could not be reliably measured at the necessary parts-per-billion in air or exhaust flue gases, its combustion chemistry was hardly known and there were no established practical methods for its capture. Mainly in the past 15 years, significant progress has been made in most of these areas. Real-time absorption-spectroscopic analyzers now are available [17]. Although there were initial problems in sampling and analyzing without modifying the sample, such difficulties are now better understood and avoided [18,19]. Recently, speciation measurements of mercury in bromine systems were also shown to be affected by heterogeneous reactions in the sampling probe [20]. As a result acceptance of earlier measurements for mercury have to be carefully reassessed. Nevertheless, as will be seen in this continuing work, monitors now are sufficiently stable, reliable and quite accurate at these low levels for the coal industry. Also, they are able to reliably measure this so-called speciation distribution of mercury's gaseous free atomic to molecular ratio with a minimal error. The chemistry remains uncertain in some areas, particularly for ash and particle absorption mechanisms where theories still exist with little clarity in spite of many studies [21–26]. However, it was realized more than a decade ago that such retained mercury is oxidized [27]. Consequently, it is apparent that that absorption by fly ash or particles involves chemisorption that does not later simply produce leachable components. It is known that Hg has no specific affinity for direct Hg–C bonding, but the presence of Cl, S and other components seem to modify the mercury under a carbon influence to retain stable and insoluble components such as HgS [28].

Two commercial methods of mercury control now have been developed with US Agency support for application by the coal industry [29,30]. However, the coal industry is dissatisfied by these solutions for various reasons. Virgin powdered-activated charcoal is an extremely poor absorber of atomic mercury. Its efficiency has to be enhanced by doping with either chlorine [31,32], bromine [33,34], or sulfur additives [35–37], but at a cost. Also at least 30% of US coal powered plants sell their ash as a filler for concrete. However, this cannot contain the charcoal additive for such use if at percentage levels, meaning the ash and charcoal have to be captured and channeled separately, otherwise if combined they become useless landfill. If ever designated as a toxic waste this would constitute a major obstacle for the industry. The second current method involves the addition of bromine to the combustor and has been shown to be effective, simple and elegant. However, it has been found to be a heavy metal corroder under these conditions even at the low levels used. In preparation for the expected 2016 regulations, various operators have begun to implement the suggested combined activated charcoal and bromine methods. However they report significant air preheater and scrubber fan

corrosion as well as damage to stainless steel parts [38]. Additionally, bromine is not an abundant element in nature and supply needs could become variable. In summary, these are methods that can be made to work but are expensive to use full-scale. An annual US cost had been estimated at \$10 billion for the US coal industry alone.

In June 2015, the US Supreme Court sided with the coal industry, various groups and 21 US States by denying imposition of the proposed standards based on indicated cost rules [39]. Even if accepted, the available control methods are costly and the other large coal burning countries of the world such as China (3.5 billion tons/yr), India (0.5), Australia (0.3), Russia (0.3) and others may be reluctant to implement them. An interesting overview of this current legal struggle between environmental regulation and centralized regulatory review and cost-benefit analyses has appeared recently [40]. Whether coal is liked or not, it remains a very large fraction of the energy needed for electricity production everywhere and will have to continue as such into the foreseeable future.

## 2. Mercury's overlooked chemistry

Quite often in the history of science a certain mindset and theory is proposed and aggressively published to the point of acceptance yet without proof. This happened with mercury and was quite understandable. Mercury has a surprisingly limited chemistry and also is an unusual metal favoring sulfur over oxygen. It has few molecules in the condensed phase and none are particularly thermally stable, HgO (<250 °C), HgSO<sub>4</sub> (350 °C), HgS (<450 °C), Hg(NO<sub>3</sub>)<sub>2</sub> (<90 °C), HgCl<sub>2</sub> (m.pt. 276, b.pt. 304 °C, stable to 450 °C when hydrolyzed by water [41]). Divalency is more stable than monovalent. Although Hg<sub>2</sub>Cl<sub>2</sub>, (m.pt. 383 °C), is known, is water insoluble and is only mildly toxic, it disproportionates above its melting point to the gaseous divalent dichloride [42]. Otherwise the mono-nitrate, sulfate, oxide are unstable and hydroxides, carbonates or hydrides are not known. The gas phase is simpler with only thermally stable dihalides. The bond strength for the dichloride is  $D_0(\text{ClHg-Cl}) = 346 \text{ kJ mol}^{-1}$  [43,44]. Although spectral systems of gaseous diatomic HgCl and HgH are well characterized, these are very weakly bound molecules, bond strengths being 100 [45] and 36 kJ mol<sup>-1</sup> [46], respectively, existing only at lower temperatures. Although considered in some older combustion studies this is now also the case for gaseous HgO ( $\approx 18 \text{ kJ mol}^{-1}$ ) [47,48], HgOH ( $\approx 40$ ) [47,49] and HgS (24 kJ mol<sup>-1</sup>) [46]. They are now only appropriate to low temperatures such as in atmospheric studies for example. As a result, initial measurements in coal combustors correctly reported that elemental mercury was being fully released from coal due to the low thermal stabilities of all its condensed phase states. However, it was found to be distributed on the fly ash particles in some molecular form, and in the gas phase as both elemental Hg and a gaseous oxidized molecular form, namely HgCl<sub>2</sub>. The latter was important being water soluble and readily removed by flue gas desulfurization systems [50,51]. The elemental Hg could not be easily absorbed or captured except by gold or silver amalgamation. One novel application invokes nano-particles of gold dispersed on activated charcoal in a regenerative mode [52]. Although functional, earlier such attempts to use valuable materials in power plants were found to be impractical. Chemical thermodynamic calculations always have indicated that all the mercury should be gaseous HgCl<sub>2</sub> [41]. Obviously this was not so and there was some constraint. As a result, because mercury is so volatile and in the gas phase of combustor flue gases, a gas phase kinetic model was proposed [53,54]. This had few mechanistic choices and had to invoke Cl-atoms in a three-body chemical reaction with Hg forming a short-lived unstable HgCl(g) that managed to react further to the

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