Mercury speciation during *in situ* thermal desorption in soil

Chang Min Park*, Lynn E. Katz, Howard M. Liljestrand

Department of Civil, Architectural and Environmental Engineering, The University of Texas at Austin, 301 E Dean Keeton Street Stop C1786, Austin, TX 78712-1173, USA

HIGHLIGHTS

- Impact of soil conditions on distribution and phase transitions of Hg was identified.
- Metallic Hg was slowly transformed to Hg^0 gas until the temperature reached 358.15 K.
- Phase change of $HgCl_{2(s)}$ completely occurred without decomposition at 335.15 K.
- HgS remained solid in dry soil sharply decreased in the narrow temperature range.
- Hg gas can be easily captured with higher vapor pressures of soil compositions.

ABSTRACT

Metallic mercury (Hg^0) and its compounds are highly mobile and toxic environmental pollutants at trace level. *In situ* thermal desorption (ISTD) is one of the soil remediation processes applying heat and vacuum simultaneously. Knowledge of thermodynamic mercury speciation is imperative to understand the fate and transport of mercury during thermal remediation and operate the treatment processes in a cost-effective manner. Hence, speciation model for inorganic mercury was developed over a range of environmental conditions to identify distribution of dissolved mercury species and potential transformations of mercury at near source environment. Simulation of phase transitions for metallic mercury, mercury(II) chloride and mercury sulfide with temperature increase showed that complete vaporization of metallic mercury and mercury(II) chloride were achieved below the boiling point of water. The effect of soil compositions on mercury removal was also evaluated to better understand thermal remediation process. Higher vapor pressures expected both from soil pore water and inorganic carbonate minerals in soil as well as creation of permeability were significant for complete vaporization and removal of mercury.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Mercury is highly mobile and among the most highly bioconcentrated metal contaminant in the environment [1,2]. It can be found in various forms including elemental (metallic), inorganic and organic mercury in the environment. Metallic mercury (Hg^0) is sparingly soluble in water (5.6×10^{-5} g L^{-1} at 25 °C), but it has high vapor pressure allows long-range transport in the air [3]. Despite its usefulness in broad range of industries, metallic mercury and its compounds are extremely detrimental to human health and to the environment at even trace levels. Once the metallic mercury is spilled on soil, it migrates downward to create a large plume in the vadose zone with infiltration due to its high density. It can also be transported in water-soluble mercury forms such as monovalent and divalent mercury via chemical redox reactions. The divalent mercury, Hg(II) is more stable than monovalent mercury, Hg(I) and common in the environment, and may undergo complexation, precipitation with inorganic ligands, and sorption onto the soil matrix.

In Oak Ridge, Tennessee (East Fork Poplar Creek), the mercury distribution is 91% of inorganic of which 85% is in the insoluble $HgS_{(s)}$ as a result of metabolism of sulfate-reducing bacteria, 0.01% of organic (as MeHg), and 6% of metallic mercury at a mercury contaminated site [4]. The soft Lewis acid, Hg^{2+} ion or MeHg (methylmercury) has a very high affinity for reduced sulfur groups (R-SH and R-SS-R) under conditions typical of soil rich in natural organic matter and inorganic sulfides in reduced environment [5–9]. HgS persists in soils even at the oxidized conditions with slow weatherization [10]. In contrast, inorganic mercury salts, $HgCl_2$,

HgO, and $HgSO_4$ are dominant form at the oxidizing conditions in soil with limited availability of organic matter, while metallic mercury remains in the reducing environments.

Recently, the impact of mercury emission from coal combustion sources or municipal solid waste (MSW) gasification systems on the atmosphere has been addressed with mercury speciation that describes the behavior of mercury [3,11,12]. The Hg pyrolysis technique is used to determine Hg-binding forms in soils contaminated by metallic mercury, mercury(II) chloride and mercury sulfide using thermally induced Hg desorption behavior [13–18]. Hg binding forms and continuous release of volatile Hg^0 on the thermal decomposition or desorption of Hg compounds from solids were determined by solid phase Hg pyrolysis at different temperature [19]. *In situ* thermal desorption (ISTD) is one of the soil remediation processes in which both heat and vacuum are simultaneously applied to the subsurface soil with high displacement efficiency [20]. In ISTD, surface heating with thermal blankets and subsurface heating with an array of vertical heater/vacuum wells placed to virtually any depth are used for contaminant removal in soil. Several contaminated sites have been treated using ISTD by TerraTherm Environmental Services, Inc. (TESI), and the operations were successful with the residuals well below the remediation goals. Previous study demonstrated two separate steps of mercury volatilization, initial vaporization of metallic mercury and subsequent volatilization of oxide or sulfate phase at higher temperatures (>230 °C) [21]. They showed that more than 95% of mercury in heavily contaminated soil (up to 2400 ppm) can be possibly removed within minutes by thermal treatment at 300 °C, and more than 99% of mercury removal can be achieved in 20 min at 470 °C. However, model development is required to identify model parameters in more detail describing several forms of mercury and volatile gas removal mechanisms, and thus determine removal strategies at mercury contaminated sites.

It is crucial to not only identify potential mercury species but also understand the fate and transport of mercury, but knowledge of mercury speciation during thermal remediation of soil is not much known. In this study, equilibrium calculations were conducted to identify dissolved mercury species and metallic or mercury solids over a range of environmental conditions at ambient temperature and its phase changes at higher temperature for thermal remediation of mercury. The impact of soil compositions on mercury removal was also examined by vaporization mechanisms with temperature increase, since other substances in soil can also be vaporized and contribute large masses to the recovered vapor stream.

2. Materials and methods

2.1. Modeling approach

Thermodynamic mercury speciation and phase change of mercury were investigated by Taube et al. [21] to evaluate the thermal treatment of mercury using FactSage 5.2, a computer software based on minimization of Gibb's free energy, for the equilibrium calculations [22]. Equilibrium calculations for thermodynamically favorable reactions were performed in various soil conditions including different availability of O, S and Cl, in general terms of high or low initial availability. In this research, all possible aqueous equilibria were formulated in MINEQL + 4.5, a chemical equilibrium model software, to calculate mercury speciation due to complex reactions participating in the soil-solution environment. Among other available software for chemical speciation modeling, WHAM 6 and MINEQL + 4.5 are the most cited in the literature. Cloutier-Hurteau et al. [23] extensively evaluated the reliability of those modeling software with Cu(II). MINEQL + 4.5 incorporates mass balance, thermodynamic reactions, and complexation reactions of inorganic ligands with an extensive thermodynamic database.

2.2. Speciation modeling in aqueous solution

In order to study mercury speciation during ISTD, aqueous speciation diagrams of mercury were calculated as a function of pH, chloride and sulfide concentrations at both ambient and elevated temperatures with equilibrium reactions and their enthalpy data collected. The model calculations were performed incorporating mono- and divalent mercury, Hg(I) and Hg(II) in the environmental conditions that can be expected at contaminated sites. The values for equilibrium constants, enthalpy and the relating thermodynamic reactions are presented in Table 1. For mercury speciation at ambient temperature, different soil compositions of inorganic soil ligands were characterized to predict dominant mercury species, especially pure solid phase of mercury in closed carbonate system in which mercury cycle undergoes in the subsurface soil. In model calculation for mercury speciation and phase transition at elevated temperature, a system of open to the atmosphere was used to consider equilibrium with the concentration of gas phase of mercury that can be collected by vacuum (typically 0.02 bar) applied to target treatment zone during ISTD [24]. Each thermodynamic reaction for gas phase transition from pure liquid or solid phase of mercury was fixed at type III species in MINEQL + 4.5 in different environmental conditions.

3. Results and discussion

3.1. Aqueous Hg speciation

In natural waters, concentration range of inorganic ligands varies for $Cl(-I)_T$ from 10^{-5} to 10^{-3}, $HS^{-1}/S(-II)_T$ (anoxic conditions) from 10^{-6} to 10^{-3}, and SO_4^{2-} from 10^{-5} to 10^{-3} [27]. Based on soil compositions in natural aqueous settings, the three model concentrations for inorganic soil ligands of Cl, HS^-, and SO_4^{2-} as well as redox potential have been determined in the simulation of mercury distribution and phase changes that can be occurred during the thermal processes. Each model condition, low $Cl(-I)_T$ and $S(-II)_T$, high $Cl(-I)_T$ and low $S(-II)_T$, and low $Cl(-I)_T$ and high $S(-II)_T$ concentrations were used to determine distribution of aqueous mercury species and solid formation of mercury for an electron activity set at pe = 0.

MINEQL + 4.5 provided predictions of the predominant and trace mercury species as a function of pH in different soil conditions. The nature of Hg(II) species present in the solution varies with pH drastically as observed in the aqueous speciation diagram in Fig. 1 where the dissolved mercury species for concentrations are greater than 10^{-24} M [33]. For low Cl and low reduced S (HS^-), or low Cl and high reduced S concentrations, the aqueous Hg^0 species was predominant over a range of pH considered. The equilibrium between dissolved $Hg^0_{(l)}$ and $Hg^0_{(aq)}$ can be described as Reaction no. 1 in Table 1. $Hg^0_{(aq)}$ are usually supersaturated in natural waters which can cause significant volatilization [30]. The dominant mercury species are $Hg^0_{(aq)}$ at low and neutral pH and $Hg^0_{(aq)}$ and $Hg(OH)_3^-$ at high pH under the conditions described above. The aqueous $HgCl(OH)_{(aq)}$ and $Hg(OH)^+$ species increased in importance with higher pH in Fig. 1a and c. For a system of high Cl and low reduced S concentrations, the most soluble mercury species, Hg^{2+} complexes with Cl^- enhancing its solubility as shown in Fig. 1b [34]. Under these conditions, the dominant mercury species are $HgCl_{2(aq)}$, $HgCl_3^-$ and $HgCl_4^{2-}$ at low and neutral pH and $HgCl(OH)_{(aq)}$, $HgCl_3^-$ and $HgCl_4^{2-}$ at high pH. Table 1 shows equilibrium constants, enthalpy and the relating thermodynamic reactions for several mercury species with Cl. However, mercury(II)