

Interaction of Elemental Mercury with Steel Surfaces

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Abstract

Elemental mercury in fluids produced from hydrocarbon reservoirs reacts with, and thus chemically modifies, steel surfaces on equipment and piping. In this study, process piping removed from service in which mercury was a process constituent was examined using surface analytical techniques. In addition, steel coupons were exposed to mercury vapor to measure rates and amounts of mercury uptake. The steel surfaces that were examined acquired between 1 and 4 g Hg⁰/m² of steel geometric surface area (no surface roughness factor applied). The majority of the mercury present in the interfacial area is thought to be physically adsorbed on the gas/metal scale interface and some mercury incorporates into the scale itself, possibly by diffusion and substitution for iron in the scale lattice. In gas streams containing H₂S, mercury vapor reacts to form HgS on the surface of the surface oxide scale layer. The data are consistent with elemental mercury adsorption and chemisorption as the primary mechanisms of mercury accumulation on steel surfaces exposed to elemental mercury vapor in natural gas streams. Mercury penetration into steel grain boundaries could not be confirmed, or ruled out, using the analytical methods employed. The process of mercury scavenging by steel surfaces is reversible with rates of desorption depending strongly on temperature.

Keywords: mercury, steel, surface, pipeline, adsorption.

Introduction

Mercury in several chemical forms is a naturally-occurring constituent of oil and gas reservoirs [1]. When reservoirs are produced, elemental mercury (Hg⁰) and the other forms that may be present in the reservoir distribute to fluid phases (liquid hydrocarbon, gas and water) and travel throughout production and processing systems. Steel piping and pressure vessels that are used to transport and process produced fluids interact chemically with the elemental mercury in the fluids they contain. This interaction was examined to determine

the nature of surfaces contaminated by mercury and the amounts of mercury they accumulate.

This investigation examined elemental mercury (Hg^0) in natural gas streams. Other mercury species that could be present in hydrocarbon liquid streams may influence steel surface properties as well, but the arguments presented here address elemental mercury in particular because it is the vastly dominant mercury species found in produced gas and because it is the only mercury species in gas that chemically interacts with steel production equipment. [1,2].

Mercury interactions with steel surfaces have been examined in a limited number of previously reported investigations [3,4] but questions remain regarding key mechanistic aspects and practical implications. Mercury on steel surfaces is of interest because of structural integrity concerns and because mercury vapor desorption from steel equipment is a workplace hazard for oilfield and petrochemical workers. This investigation examined two primary questions:

1. How are steel surfaces modified chemically by contact with elemental mercury vapor in produced natural gas?
2. How much mercury will steel surfaces exposed to mercury vapor hold?

Mercury and Steel

Many in the oil and gas industry have observed that steel vessels and pipe that contact mercury-laden process streams retain substantial amounts. In fact, in locations where mercury is known to be present in produced reservoir fluids, rigorous safety precautions are employed to detect mercury vapor that emanates from steel vessels and pipe when opened for maintenance or inspection purposes. Likewise, welding mercury-contaminated pipe produces large amounts of mercury vapor, thus posing a vapor inhalation hazard for unprotected welders and other workers.

A mercury-contaminated steel pressure vessel in a gas processing facility will emit mercury vapor long after it has been ventilated and cleaned to remove sludge and surface hydrocarbons. Pressure vessels cleaned with detergent to a low mercury vapor level will, after being closed for some hours, continue to produce elevated mercury vapor concentrations in their interior spaces for many days, even with periodic ventilation. The observation is consistent with steel surfaces that capture and hold significant amounts of elemental mercury that desorbs slowly at ambient temperatures. When contaminated piping and equipment are repaired or modified by welding, large amounts of mercury vapor

typically evolve from the heated pipe area. A square meter of steel holding 1 g Hg⁰ can contaminate 40,000 m³ of air to a mercury concentration above human inhalation safety limits (25 µg/Sm³ of air).

One manifestation of mercury/steel interaction commonly seen in gas production is the so-called mercury lag effect, in which mercury that is in gas entering a newly constructed pipeline is not measured at the receiving end for some period of time. The following example was investigated recently.

A gas plant located approximately 200 km from offshore producing wells received dry gas and some hydrocarbon liquid. (P= 7000 kPa ,T = 10 C). The mercury concentration in gas at the wellhead was in the range 200 to 300 µg/Sm³, but the gas lost an estimated 30 percent of mercury in glycol dehydration prior to entering the pipeline. The average gas throughput over 4 years was approximately 40,000 Sm³/hr. Mercury in gas measurements did not detect any significant amounts mercury (< 1 µg/Sm³) in gas entering the receiving plant over 50 months of production. The time for mercury in gas to reach the gas processing plant was estimated as shown in Table 1. At 48 months no mercury reached the plant. The minimum capacity of the pipe surface to retain elemental mercury was therefore between 1.5 and 2 g/m².

Table 1 – Estimate of Mercury Lag Time in the Pipeline

Surface Area	Flow	Hg Flow Rate	Capacity of Pipe Surface	Time to Reach Shore
(m ²)	(1000 Sm ³ /h)	(g/h)	g Hg/m ²	(months)
200,000	40	10	1	28
200,000	40	10	2	56
200,000	40	10	5	140

The suspected mechanisms of uptake of (elemental) mercury by steels have not been studied extensively but are thought to be one or a combination of the following:

- Physical adsorption of elemental mercury to the steel surface oxide/sulfide (mill scale and/or corrosion scale).

- Reaction with surface scale constituents and incorporation into surface corrosion or mill scale.
- Amalgamation or reaction with steel at the steel/corrosion scale interface.
- Incorporation by diffusion into the steel atomic lattice.
- Incorporation into the steel surface by diffusion into the steel grain boundaries and possible reaction with steel grain boundary constituents.

Diffusion of atomic mercury into the steel atomic lattice in a manner analogous to hydrogen diffusion is highly unlikely (impossible) given the size of a mercury atom relative to steel interstitial space. Amalgamation is hard to rationalize because amalgamation requires a liquid mercury phase to contact bare metal. The solubility of iron in liquid mercury is very low [5]. Grain boundary interactions are possible to account for high levels of surface accumulation but the mechanism of retention of mercury by grain boundaries is not apparent. Physical adsorption of mercury to exposed surfaces and chemisorption to surface scales seem, at first glance, to be the most likely candidates.

Mercury Vapor Uptake by Steel Coupons

Cylindrical steel coupons (5 cm long x 0.5 cm diameter) were machined at mid-wall, parallel to the longitudinal axis of API 5LX -60 pipe (C – 0.065 wt. %; Mn –: 1.410; P – 0.016; S – 0.002; Si – 0.255; V – 0.030). The fabricated coupons were heated to 400 C for 6 hours in an air atmosphere in order to drive out any surface mercury they might contain and to develop an oxide layer on the surface. After the heat treatment, half of the specimens were polished with 600 grit sandpaper to bright metal. Eighteen coupons (9 specimens not polished after heat treatment and 9 specimens polished after heat treatment) were exposed to mercury vapor (approximately 50 mg/Sm³, balance nitrogen) at 40 – 45 C for approximately 2 months. An equal number of controls were exposed only to nitrogen at the same temperature for the same period of time. All coupons were weighed weekly (+/- 0.001 mg)

Figure 1 is a plot of coupon weight gain versus time of exposure to mercury vapor. Controls exposed to nitrogen did not show any appreciable weight gain (average less than 0.1 g/m²).

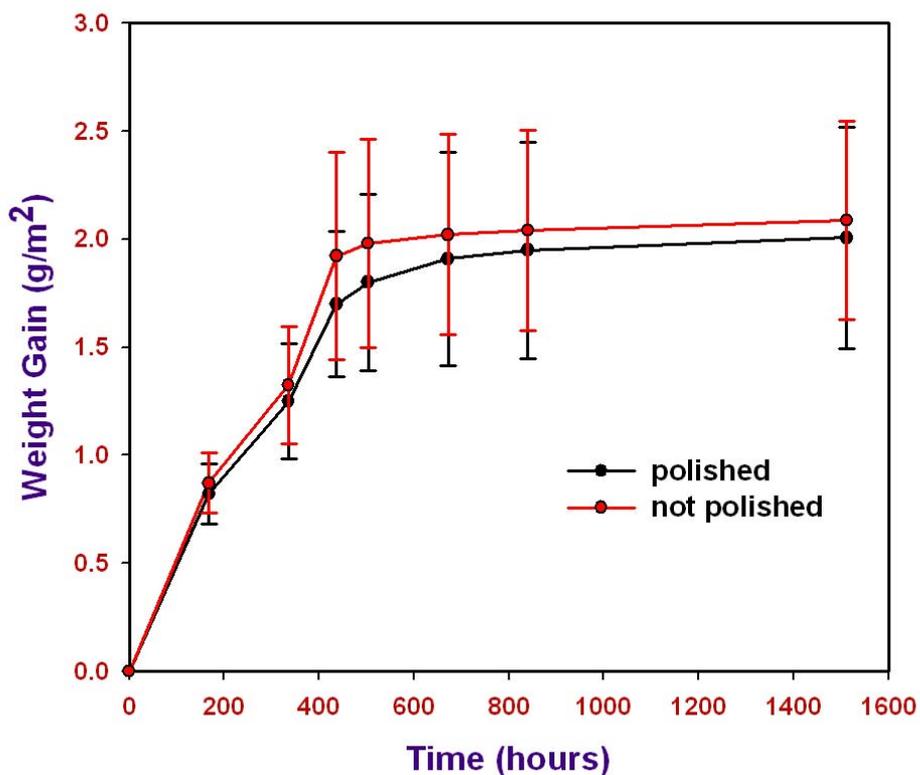


Figure 1 – Coupon Weight Gain from Mercury Vapor Exposure

Four polished and 4 un-polished coupons were immersed in liquid mercury for 700 hours and showed much lower weight gain as shown in Table 2.

Table 2 – Weight Gain for Coupons Exposed to Liquid Mercury

Surface prep after heat treatment	Coupons	Average Wt. Gain	Standard deviation
		g/m ²	
Polished	4	0.5	0.2
Un-polished	4	0.8	0.2

Mercury in Steel Pipe Removed From Service

Contaminated Pipe Specimen – A steel pipe section (8-in. OD x 14-in. length, 0.5 in. wall; ASME A106 grade B) was analyzed to determine the type and amount of mercury contamination present on its internal surface. The pipe section had been removed from the process piping downstream of the primary separator on a gas production unit. The process conditions during operation were approximately 50 C, water-saturated gas, 5 mole percent CO₂, 4–5 ppm H₂S, hydrocarbon (mostly methane) balance. The length of service was approximately 5–6 years. The concentration of mercury in gas that flowed through the pipe during the service period was estimated from occasional measurements to have been between 500 – 800 µg/Sm³.

Mercury on the Pipe Surface – A pipe section (Figure 2) was cold-cut from a larger pipe piece that had been removed from service as part of process modifications. The pipe section was stored in a sealed plastic drum for transportation. Approximately 3–4 weeks after the specimen was removed from service, it was removed from the plastic drum, rinsed with water and allowed to air dry. The paint on the outer surface of the pipe section was removed using solvent. The pipe section was then placed into a five gallon plastic bucket containing ordinary diesel fuel (the diesel initially had a total mercury content of less than 10 ppb). At the time of transfer, the process-side surface of the pipe was closely examined visually using magnification. Surface deposits of elemental mercury were not observed. The specimen was stored in the diesel environment for 6 weeks, after which it was removed and sectioned for analysis. The diesel fuel was analyzed after the six week soak and contained 2.5 ± 0.5 ppm total mercury. This constitutes a roughly saturated solution with respect to elemental mercury meaning that the diesel contained the maximum amount of hydrocarbon soluble (elemental) mercury it could hold. Table 3 calculates the **minimum** amount of hydrocarbon soluble mercury in or on the pipe interior surface. Losses of mercury to evaporation and storage materials were likely significant but not quantified.



Figure 2 – Pipe Specimen

Table 3 – Surface Mercury Soluble in hydrocarbon

Pipe ID Surface Area	(m ²)	0.2
Diesel weight	kg	15
Mercury concentration	µg/kg	2,500 ± 500 (n = 4)
Surface mercury transferred to diesel solvent	g/m ²	~0.2

Coupons (2 cm x 5 cm x pipe wall) were cut from the pipe section after the diesel soak and subjected to a series of tests to determine the amount and chemical nature of mercury in or on the pipe internal surface.

Mercury in Pipe Scale – Figure 3–2 shows SEM images of cross sections of the pipe interior (process side) surface. The compositions of phases relative to the scale cross section position were identified using energy dispersive X–ray (EDX) analysis techniques. HgS was found as a distinct phase on the surface of both specimens. The surface on which the HgS was found is that which contacts the gas flowing in the pipe. Below the HgS layer was a layer of non–stoichiometric iron oxide that extended to the solid iron bulk phase. The iron oxide scale is consistent with pipe mill scale as

modified by corrosion during service. From the thickness of the scale and EDX determination of scale concentration, the oxide/sulfide surface scale held no more than 0.2 g Hg/m² of pipe surface area, either as HgS on the surface or as Hg²⁺ chemically incorporated into the iron oxide.

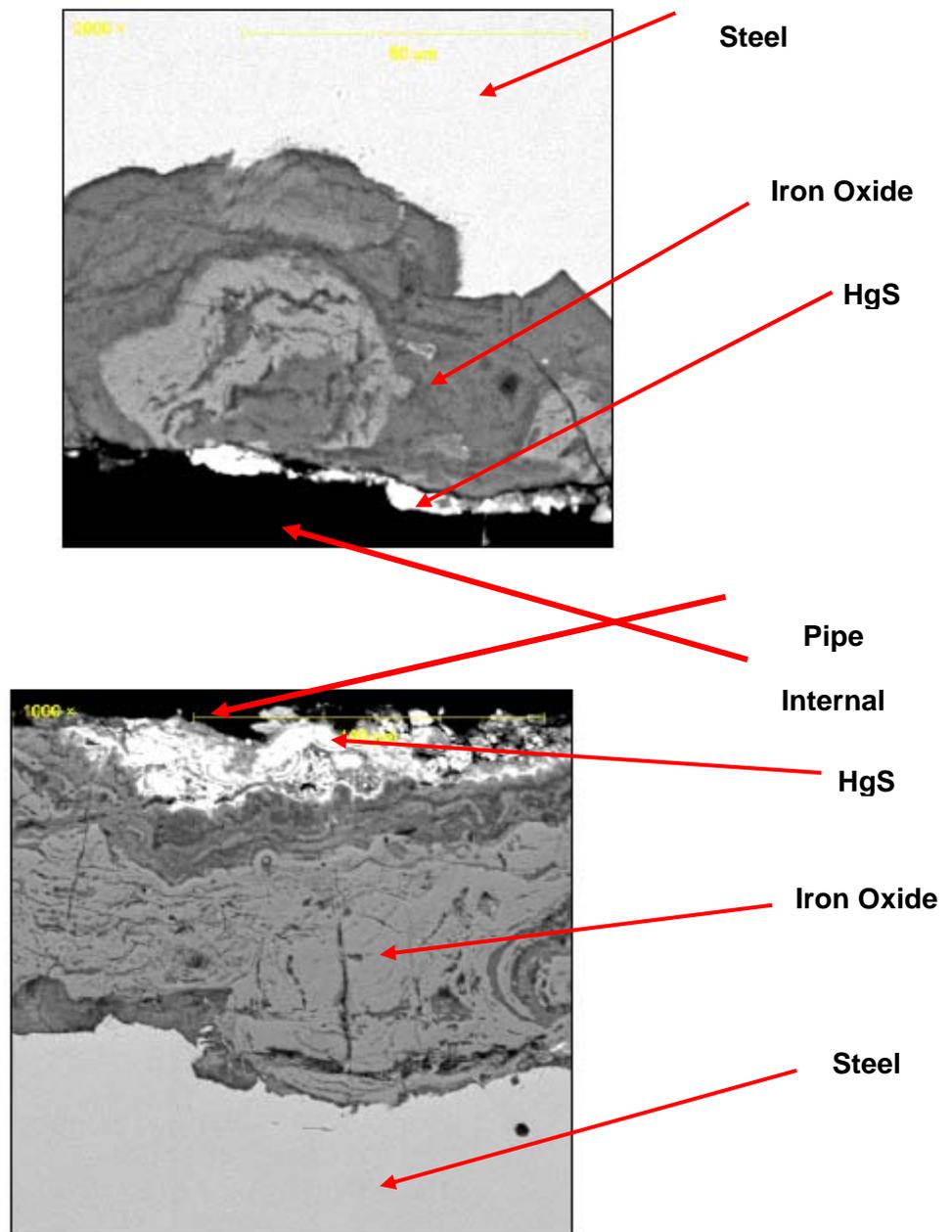


Figure 3 – Metallographic Cross-Section of Pipe Scale

Atomic Density Maps – The cross-section of the pipe/gas interface was examined using Energy Dispersive X-ray (EDX) analytical techniques. Dot maps (Figure 4) show the atomic density of Fe, Hg and S across the interfacial cross section. The density of white dots is proportional to atomic concentration. Scale areas were identified as HgS or Fe_xO_y. The HgS solid phase was found as a small layer on the interior surface and covered an iron oxide scale layer of approximately 100 μm. The HgS layer was approximately 5 – 10 μm in thickness on average. This thickness of mercury sulfide amounted to approximately 0.05 – 0.1 g Hg/m² of pipe surface. Note that mercury is detected not only in the scale but extends into the metal surface. Control specimens were not examined so it cannot be concluded from this evidence that mercury extended to the interior of the pipe. What is seen on the density maps could be only surface contamination from sectioning. Sulfur density shows the same effect.

The dot maps do not show any accumulation of mercury at the scale/metal interface as would be expected of mercury were amalgamating or reacting with the steel itself. The mercury atomic density is greater inside the metal than inside the scale layer but shows no gradient as would be characteristic of a diffusion process.

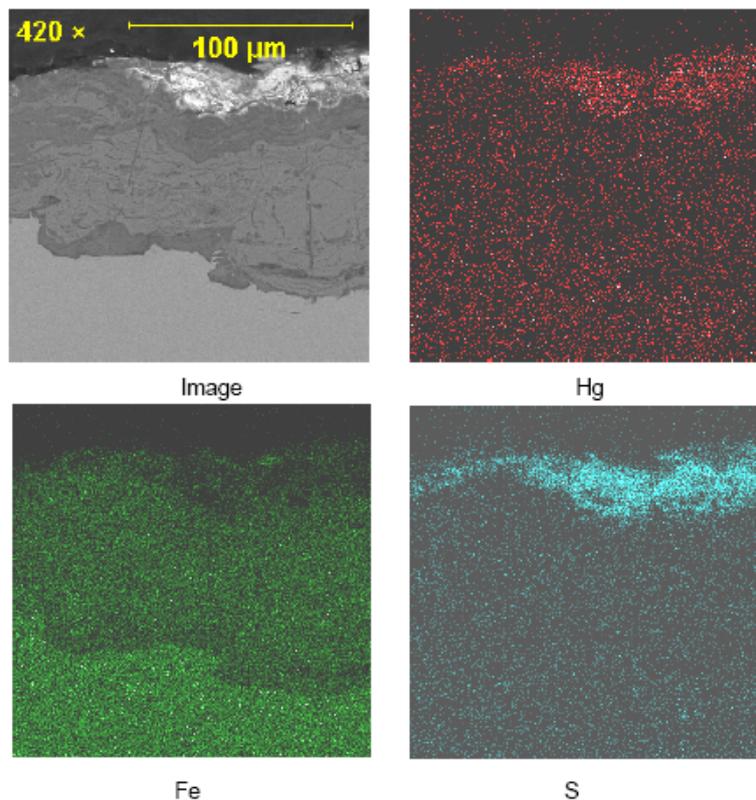


Figure 4 – Atomic Density of Fe, Hg and S

4.5 X-ray Diffraction – Surface scale was removed from two pipe coupons and subjected to (powder) X-ray diffraction analysis. The analysis of two powder samples identified the following crystalline phases (see Figure 5):

- HgS (metacinnabar): major phase (>25%)
- HgS (cinnabar): minor phase
- FeOOH (goethite): major phase (poorly crystallized)
- FeCO₃ (siderite): minor phase
- Fe₃O₄ (magnetite): minor phase

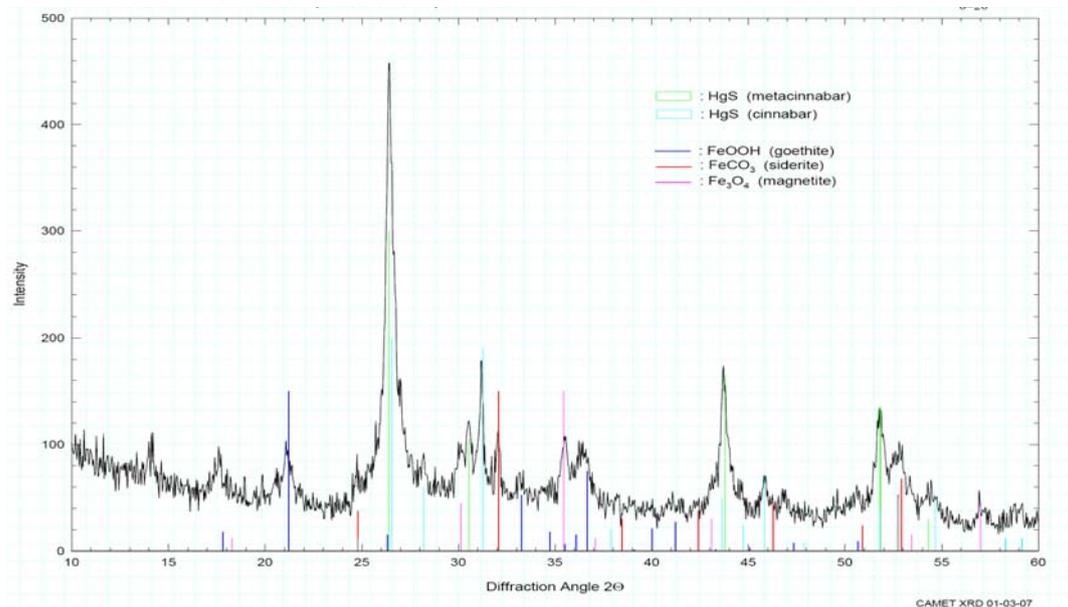


Figure 5 – X-ray Diffraction Analysis of Pipe Scale

Thermal Desorption Tests – Coupons (0.002 m² ID surface area) were cut from the contaminated pipe specimen were subjected to thermal desorption analysis. The apparatus consisted of a tube furnace and quartz tube that could be heated to temperatures in excess of 300 C while simultaneously flowing nitrogen through the tube at a controlled rate (0.001 m³/min). Volatilized mercury in the nitrogen gas stream was monitored continuously with a Lumex mercury vapor analyzer. Temperature was increased stepwise in 10 degree C increments. The total amount of mercury emitted from the pipe coupon during a temperature increase was determined by integration of the concentration vs. flow data.

Three desorption tests were conducted that differed slightly in coupon surface preparation. The shape of all three desorption curves were essentially identical. The amount of mercury desorbed varied between 1 and 3 g Hg⁰/m² of pipe ID surface area. The 1 g/m² measurement was for a coupon abraded to essentially bare metal. The 3 g/m² measurement employed a coupon with its surface scale intact. A typical desorption curve is shown in Figure 6.

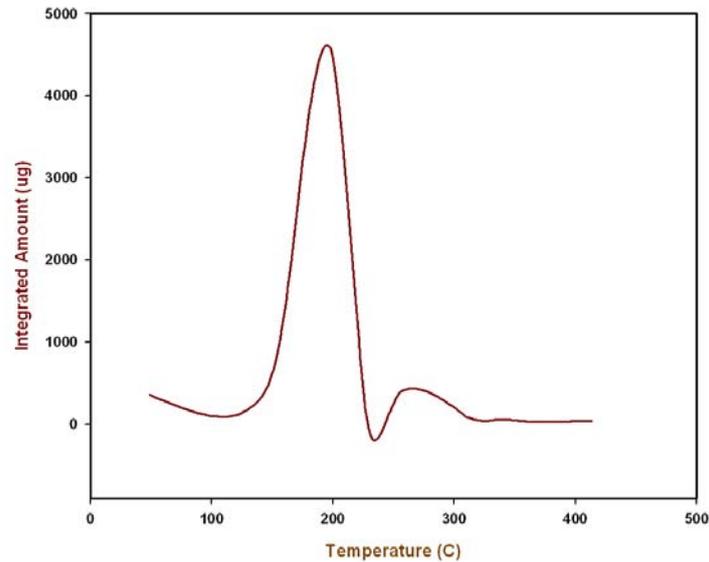


Figure 6a – Desorbed Mercury (Integrated Amount) as a Function of Temperature

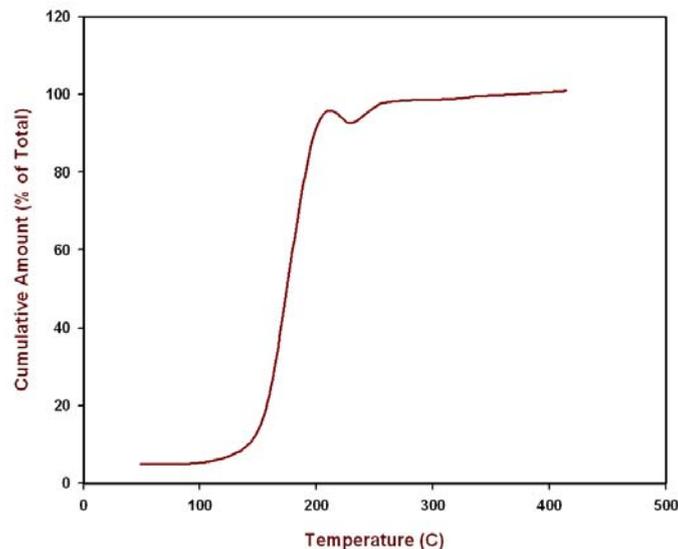


Figure 6b – Desorbed Mercury (Cumulative Amount) as a Function of Temperature

Discussion

The measurements and observations reported here support the hypothesis that mercury both adsorbs (reversible at low T) and chemisorbs (irreversible at low T) to steel surfaces. Reaction of mercury vapor to HgS is possible when gas streams contain H₂S, but the amount that forms relative to the total amount held by the surface is small in the single case examined. Some surface oxidation process must precede the reaction of Hg⁰ with H₂S. Elemental mercury and hydrogen sulfide do not react spontaneously in gas phase at moderate temperature.

The amount of mercury acquired by thermally oxidized surfaces and polished surfaces (Figure 1) differs only slightly. This observation favors a simple adsorption theory to account for mercury on fabricated steel surfaces. If mercury reacted with iron oxide easily and in large quantity, then the oxidized surface would hold more than the bare metal surface. If elemental mercury adsorbs to bare steel to produce a monolayer of mercury atoms [7], and the adsorbed mercury atom occupies a surface area having dimensions approximately equal to its atomic diameter, the monolayer would weigh approximately 0.3 mg.

Some have postulated that elemental mercury can diffuse into the metal matrix or into steel grain boundaries. In other words, steel surfaces can “soak up” mercury from exposure to mercury vapor in process gas by a mechanism other than adsorption. It is highly unlikely (impossible) that mercury atoms can actually enter the steel atomic lattice because the size of a mercury atom is simply too large to enter steel crystalline interstitial spaces, in the manner that hydrogen can, for example. Accumulation of mercury in grain boundaries that intersect the steel surface cannot be ruled out. For metals that are appreciably soluble in liquid mercury (Cu, Ag, Pt), mercury enters grain boundaries readily [6]. If it were possible for mercury to diffuse into and reside in steel grain boundaries, then one would expect some effect on steel mechanical properties, which is not observed [8].

The evolution of mercury at 200 C in thermal desorption experiments indicates that mercury strongly adsorbs or chemisorbs to the steel surface. The amount of mercury on steel as measured by thermal desorption is hard to reconcile with simple adsorption. Further investigation using more sophisticated analytical methods may be needed to answer this lingering question.

The following amounts of mercury “in” or “on” the steel surface of the pipe removed from service were determined in the experiments:

- Diesel Soak ~ 0.2 g/m²
- Scale SEM Analysis ~ 0.2 g/m²
- Thermal Desorption 1– 3 g/m²
- Evaporation not determined

The total amount of volatile mercury measured for the steel pipe removed from service does not include mercury lost to evaporation from the time of process exposure to analytical measurement. Adding the amounts of mercury lost to the solvent soak plus an equal amount estimated to be lost to evaporation plus the amount eventually measured by thermal desorption, one obtains an approximate range of mercury surface capacity of 1.5 to 3.5 g Hg⁰/m². This range compares favorably to the adsorbed mercury amounts measured in the oxidized coupon experiments. In service, pipe surfaces are sometimes covered with a hydrocarbon layer that also absorbs elemental mercury by dissolution. As the hydrocarbon layer evaporates, such as would be the case when a pipe or vessel is opened, the total amount of mercury potentially available to evaporate from the surface including hydrocarbon layer is substantial.

The capacity of steel surfaces to scavenge mercury by whatever mechanism is sufficient to account for the mercury lag effect in pipelines and the evolution of mercury vapor from contaminated vessels. Additional investigation is warranted to resolve questions on mercury's retention by steel grain boundaries. Measurements of the corrosion behavior of mercury-contaminated surfaces will be offered in a subsequent publication.

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