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SRL
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MERCURY VOLATILITY IN THE PRESENCE OF REDUCING AGENTS

The attached document describes experimental evidence for the calculations reported in DPST-85-974, "Calculations of Hg, NH₃, and Cs-137 in the F/H Effluent Treatment Facility". These experiments show that in the F/H Effluent Treatment Facility evaporator feed stream there will be chemical species capable of reducing mercuric ion to mercury metal. Once such reduction takes place the mercury will distill out of the evaporator.

It is our opinion that this event will take place some times during the actual operation of the Facility. The amount of mercury present in the evaporator overheads may be minimized by evaporator design. However, given the known behavior of mercury, once the Facility has operated for a time, process equipment will be "cured" with mercury. At that point we believe that the overheads from this step of the process will routinely show concentrations of at least 20 ppb, the solubility of Hg in water at 30°C. Our experiments indicate that the possibility for supersaturation exists giving rise to higher concentrations, as high as 600 ppb.

We recommend that you determine whether these concentrations will be acceptable. If not, we will explore alternatives to resolve the issue.

Martha G. Ebra 4/1/86
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**F/H ETF; evaporator
overheads; bisulfite
mercury; ammonia; reduction**

DPST-86-333

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MERCURY VOLATILITY IN THE PRESENCE OF REDUCING AGENTS

INTRODUCTION

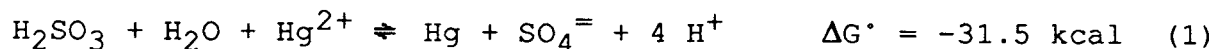
A recent publication¹ dealt with the volatility of mercury in the F/H Effluent Treatment Facility (F/H ETF) evaporator. That document predicted that, if dissolved mercuric ion should be reduced by some other substance in the evaporator feed, all of the mercury metal generated by the reduction will be volatilized into the overheads. Based on thermodynamic calculations, two chemical species that could reduce mercury, sodium bisulfite and ammonia, will be present. This document describes a laboratory study designed to determine whether mercury is, in fact, reduced by bisulfite ion and ammonia and, if so, whether the reduced mercury is volatilized at the boiling point of water.

SUMMARY

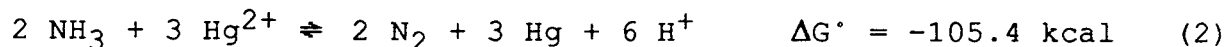
Solutions containing mercuric nitrate and various chemical reducing agents at different concentrations were distilled to reduce the volume of the solution by a factor of ten, the volume reduction factor that will be standard in the F/H ETF evaporator. The distillate and concentrate were analyzed for mercury content to determine how much mercury had been carried over into the distillate. The primary conclusions resulting from this study are that both bisulfite ion and ammonia are capable of reducing mercury in solution and that, when reduced, the mercury will all be volatilized and carried into the distillate.

THERMODYNAMIC CONSIDERATIONS

A consideration of components in feed to the F/H ETF evaporator determined two substances that could potentially reduce dissolved mercuric ion to metallic mercury. The first of these is sodium bisulfite that will be used to treat the reverse osmosis membranes to prevent growth of microorganisms or to reduce residual chlorine in solution as a result of a hypochlorite treatment to kill microorganisms.² The reaction of bisulfite (Equation 1) is thermodynamically favored.³



Similarly, reduction by ammonia, possibly according to Equation 2, is also favored.



Solutions containing flowsheet concentrations expected^{2,4} for bisulfite ion and ammonia as well as stoichiometric excesses of each substance, relative to mercuric ion present in solution, were tested. In each case, there was evidence that some reduction had occurred.

EXPERIMENTAL PROCEDURES

A simple glass distillation apparatus, representing a single stage evaporator, was assembled as shown in Figure 1. One hundred milliliters of solution were reduced to a volume of 10 mL. by

distillation of 90 mL. into the collection flask. The compositions

of the various solutions that were tested are found in Appendix 1. Both distillate and concentrate were allowed to reach room temperature and were then analyzed for mercury content. Glassware was rinsed with 0.5 M HNO_3 and deionized water between experiments. The rinses were analyzed for mercury content. Those concentrations varied widely and are not reported.

Experiments were also done with some of the solutions using a glass wool baffle in the neck of the distillation apparatus. The glass wool was expected to allow only vapor phase mercury to proceed to the collection flask and to prevent entrainment. Thus, the presence of Hg vapor was assured and the inference of reduction could thereby be made.

RESULTS AND DISCUSSION

The mercury analyses for each experiment are tabulated in Table 1. Several conclusions are in order from this data:

- o The primary indication that mercury has been reduced and volatilized in this system is the disappearance of mercury from the distillation flask. In practice mercury is deposited on the walls of the distillation apparatus, as evidenced in the presence of mercury in nitric acid rinses of the glassware. This behavior contributes to the lack of material balance for mercury between the distillate and the concentrate. The condensation of mercury vapor throughout a distillation system has been observed often in steam stripping experiments performed for the Defense Waste Processing Facility project.⁵
- o If sufficient reducing agent is present, all of the Hg^{2+} will be reduced. Once reduced, it will volatilize and, in principle, be carried into the overheads to the collection vessel. Analysis of the solution in the collection vessel should not be expected to reflect all the mercury lost from the distillation vessel. The condensate solution will be limited by the solubility of metallic mercury in water; i.e. $1 \text{ E-}7$ moles Hg/liter or 20 ppb Hg. The analyses of the condensates in these experiments all reflect supersaturated solutions.
- o Mercuric ion is reduced in solution by bisulfite ion. A stoichiometric excess of bisulfite is necessary to reduce all the mercury present.

- o Mercuric ion is reduced in solution by ammonia. This reaction is not as efficient as reduction by bisulfite ion, probably because the NH_3 is constantly being distilled from the reaction vessel in the evaporation process. Bisulfite, being nonvolatile, remains in the vessel where it can continue to react with remaining Hg^{2+} .
- o Reduction of Hg^{2+} still occurs in the presence of excess nitrate ion. Interaction of bisulfite with nitrate to produce nitrite and bisulfate could simultaneously occur, thereby interfering with the reduction of mercuric ion in the same solution. However, flowsheet concentrations of nitrate⁶ (0.15 M) and bisulfite resulted in the reduction of mercuric ion in these experiments (Solution #5). All solutions tested had at least $1.0 \times 10^{-2} \text{ M NO}_3^-$ by virtue of the fact that the mercury standard is in 1.0 M HNO_3 .

Also, some general observations can be made:

- o The presence of mercury in the distillate (and its subsequent decrease in the concentration of the distillation solution) when only deionized water and $\text{Hg}(\text{NO}_3)_2$ were used in the reaction vessel indicated the presence of some reducing agent in deionized water. It is suspected that reduction may occur because of small amounts of organic residue that are present from the ion exchange column used to prepare deionized water. When a strong oxidizing agent such as potassium permanganate, KMnO_4 , is included in the distillation vessel, reduction of mercuric ion by these organic impurities is prevented. Experimental series 1 and 2 show a slight increase in the amount of mercury volatilized from deionized water solution when KMnO_4 is not present in solution.
- o The distillations proceeded at a slow boiling rate to exclude entrainment as much as possible. When glass wool was used in the apparatus, only a slight decrease in the concentration of mercury found in the distillate was observed, indicating little, if any, entrainment. When permanganate was added to the distillation flask, there was no visual evidence that any of this highly colored, nonvolatile ion was carried over to the collection flask. Manganese analyses were not performed on the distillate because analytical instruments were not

functioning.

QUALITY ASSURANCE

Experimental data for this report are contained in DPSTN-4415. Solutions were prepared from reagent grade chemicals. Mercury and mercury compounds were handled according to DPSOL 158-2-4121. Mercury analyses were done by cold vapor atomic absorption using a Perkin Elmer Model 50A mercury analyzer. All mercury analyses were verified against standard solutions.

REFERENCES

1. WALLACE, R.M., and BIBLER, J.P., "Calculations of Volatilities of Hg, NH₃, and Cs-137 in the F/H Effluent Treatment Facility Evaporator System", DPST-85-974, December 20, 1985.
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3. *Handbook of Chemistry and Physics*, 60th Ed., Chemical Rubber Company Press, Boca Raton, Florida, 1980.
4. RYAN, J.P., and STIMSON, R.E., "Technical Data Summary, F/H Effluent Treatment Facility", DPSTD-84-114, December 1984.
5. EIBLING, R.E., private communication.
6. Current Process Flowsheet, C.T.Main, February 28, 1986.

APPENDIX 1

SOLUTION COMPOSITIONS

BLANK SOLUTIONS

1. 99 mL deionized water and 1.0 mL $\text{Hg}(\text{NO}_3)_2$ standard 1000 ppm solution. The initial Hg concentration is 1 mg/100 mL.
2. 99 mL deionized water (minus two drops), 2 drops 5% KMnO_4 , 1.0 mL $\text{Hg}(\text{NO}_3)_2$ standard 1000 ppm solution. The initial Hg concentration is 1 mg/100 mL.
3. 100 mL deionized water, 0.726 g Hg metal.

REDUCING SOLUTIONS

 NaHSO_3

4. 99 mL $1.21 \text{ E-4 M NaHSO}_3$, 1.0 mL $\text{Hg}(\text{NO}_3)_2$ standard 1000 ppm solution. The initial Hg concentration is 1 mg/100 mL.
5. 99 mL $1.21 \text{ E-4 M NaHSO}_3$, 1.0 mL $\text{Hg}(\text{NO}_3)_2$ standard 1000 ppm solution, 1.27 g NaNO_3 (0.15 M NaNO_3). The initial Hg concentration is 1 mg/100 mL.
6. 99 mL $1.21 \text{ E-4 M NaHSO}_3$, 1.0 mL $\text{Hg}(\text{NO}_3)_2$ standard 1000 ppm solution. The initial Hg concentration is 1 mg/100 mL. A glass wool baffle was used to eliminate entrainment.
7. 98 mL $1.21 \text{ E-4 M NaHSO}_3$, 2.0 mL $\text{Hg}(\text{NO}_3)_2$ standard 1000 ppm solution. The initial Hg concentration is 2 mg/100 mL.
8. 99 mL deionized water, 0.02 g NaHSO_3 , 1.0 mL $\text{Hg}(\text{NO}_3)_2$ standard 1000 ppm solution. The initial Hg concentration is 1 mg/100 mL.
9. 99 mL deionized water, 0.5 g NaHSO_3 , 2.0 mL $\text{Hg}(\text{NO}_3)_2$ standard 1000 ppm solution. The initial Hg concentration is 2 mg/100 mL.
10. 2.0 mL $\text{Hg}(\text{NO}_3)_2$ standard 1000 ppm solution, 0.5 g NaHSO_3 , 0.3 g NaNO_3 in 100 mL deionized water. The initial Hg concentration is 2mg/100 mL.

NH_3

11. 99 mL 0.0083 M NH_4OH , 1.0 mL $\text{Hg}(\text{NO}_3)_2$ standard 1000 ppm solution. The initial Hg concentration is 1 mg/100 mL.
12. 94 mL 0.0083 M NH_4OH , 1.0 mL $\text{Hg}(\text{NO}_3)_2$ standard 1000 ppm solution, 5.0 mL 15 M NH_4OH . The initial Hg concentration is 1 mg/100 mL.

SnCl_2

13. 94 mL deionized water, 5 mL 11% SnCl_2 , 1.0 mL $\text{Hg}(\text{NO}_3)_2$ standard 1000 ppm solution. The initial Hg concentration is 1 mg/100 mL.
14. 94 mL deionized water, 5 mL 11% SnCl_2 , 1.0 mL $\text{Hg}(\text{NO}_3)_2$ standard 1000 ppm solution, glass wool baffle. The initial Hg concentration is 1 mg/100 mL.

TABLE 1
Hg VOLATILITY

<u>FEED SOLUTION #</u> ^a	<u>MERCURY IN CONCENTRATE</u> ^b	<u>MERCURY IN DISTILLATE</u> ^c
1. Blank, 1 mg Hg ²⁺	.941 mg	3.15E-3 mg
2. Blank, KMnO ₄ , 1mg Hg ²⁺	.980 mg	1.98E-3 mg
3. Blank, Hg metal	1.0E-2 mg	3.87E-3 mg
4. dil NaHSO ₃ , 1 mg Hg ²⁺	.047 mg	5.70E-2 mg
5. dil NaHSO ₃ , 1 mg Hg ²⁺ , 0.15M NaNO ₃	.050 mg	3.90E-2 mg
6. dil NaHSO ₃ , 1 mg Hg ²⁺ , glass wool	.039 mg	2.52E-2 mg
7. dil NaHSO ₃ , 2 mg Hg ²⁺	.066 mg	9.90E-3 mg
8. xs NaHSO ₃ , 1 mg Hg ²⁺	none detected	8.55E-2 mg
9. xs NaHSO ₃ , 2 mg Hg ²⁺	.310 mg	3.33E-2 mg
10. xs NaHSO ₃ , 2 mg Hg ²⁺ , NaNO ₃	.960 mg	2.12E-2 mg
11. dil NH ₄ OH, 1 mg Hg ²⁺	.756 mg	7.83E-3 mg
12. con NH ₄ OH, 1 mg Hg ²⁺	.916 mg	1.21E-2 mg
13. SnCl ₂ , 1 mg Hg ²⁺	none detected	1.67E-2 mg
14. SnCl ₂ , 1 mg Hg ²⁺ , glass wool	none detected	1.58E-2 mg

- a. See Appendix 1 for complete solution compositions
- b. In a total volume of 10 mL; concentrations are an average for 3 or more runs
- c. In a total volume of 90 mL; concentrations are an average for 3 or more runs

FIGURE 1
EXPERIMENTAL APPARATUS

