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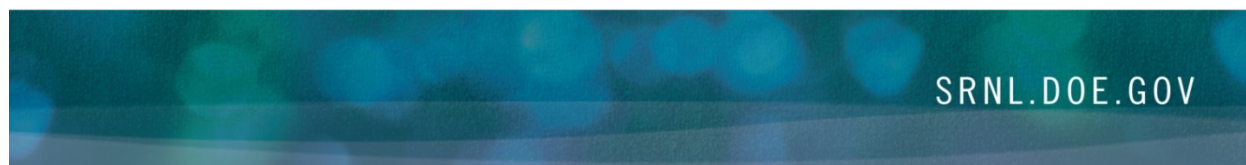


## Potential Solubility Controls for $^{129}\text{I}$ in Residual Tank Waste

**M. E. Denham**

July 2015

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## Introduction

Analyses of residual waste on the floor and cooling coils of tank 12H show the inventory of  $^{129}\text{I}$  is higher than expected. This results in a higher estimated dose from  $^{129}\text{I}$  after tank closure in performance assessment models. In the F-Tank and H-Tank Farm performance assessments (SRS, 2007 and SRR, 2012) it is assumed that there are no controls limiting the release of  $^{129}\text{I}$  from residual waste once tank liners are breached. Yet, iodine can form solubility limiting solid phases with several metals that also occur in residual tank waste. This report documents a scoping analysis of possible controls on the release of  $^{129}\text{I}$  from tank 12H residual waste.

Figure 1 shows three metal concentrations in equilibrium with 10 ug/L of iodine under oxidizing conditions. Mercury also forms low solubility solid phases with iodine (Cox and Arai, 2014). Hence, the presence of these metals in tank residual waste could potentially limit the solubility of  $^{129}\text{I}$ .  $^{129}\text{I}$  would be coprecipitated with stable  $^{127}\text{I}$ , and thus, the actual solubility of  $^{129}\text{I}$  would be the product of the ratio of  $^{129}\text{I}$  to total iodine in the solid and the solubility of the metal iodide.

Recent analyses of residual waste samples from the floor of tank 12H (Oji et al., 2015) indicate quantities of silver (0.061 wt.% average) and mercury (16 wt.% average ) that are significant compared to the quantity of iodine that is present ( $2.7\text{E-}3$  wt. % average). These analyses also indicate that the isotopic composition of iodine in tank 12H floor residual waste is dominated by  $^{129}\text{I}$ . Thus,  $^{127}\text{I}$  is not expected to contribute significantly to limiting the solubility of  $^{129}\text{I}$ . Scoping analyses were performed on one sample of residue from the tank 12H cooling coils. These data indicated that the residue was >95 wt. % mercury and  $7\text{E-}4$  wt. %  $^{129}\text{I}$  (Oji et al., 2015).

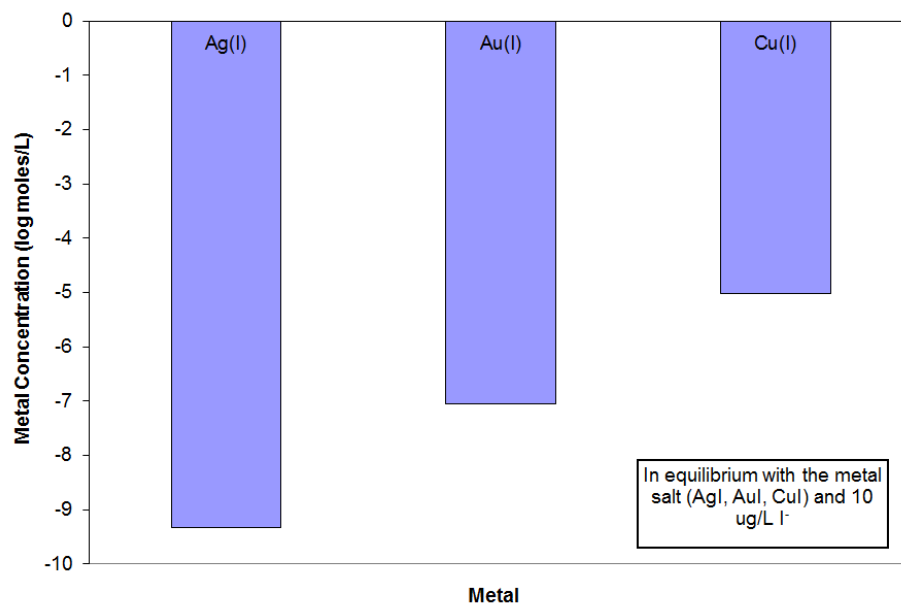


Figure 1: Solubilities of three metals in contact with a solution containing 10 ug/L iodide (modified from Denham et al., 2009).

## Scoping Calculations

Calculations of iodine solubility were done using The Geochemist's Workbench<sup>®</sup> (Bethke and Yeakel, 2012) and the Japan Atomic Energy Agency thermodynamic database (version 100331, downloaded in 2012). There is no data on gold in tank residual waste and copper does not limit the solubility as effectively as silver and mercury. Hence, scoping calculations of  $^{129}\text{I}$  solubility were done for only silver and mercury solid phases. Solubilities were calculated assuming water compositions based on those used in waste release modeling for the H-Area tank farm (Denham and Millings, 2012). For these scoping calculations  $\text{Ca}^{+2}$ ,  $\text{SO}_4^{-2}$ , oxalate, and dissolved inorganic carbon were not included to simplify the calculations. The presence or absence of these constituents does not affect the calculated solubility of iodine. The resulting initial water compositions are shown in Table 1. It was assumed that each initial water composition contained negligible concentrations of silver (or mercury) and iodine ( $1\text{E-}20$  molar) and these were reacted with solid  $\text{AgI}$  and  $\text{Hg}_2\text{I}_2$  while fixing Eh and pH and maintaining charge balance with sodium ions. At the Eh and pH values of these water compositions,  $\text{Hg(I)}$  or  $\text{Hg(0)}$  are the dominant oxidation states of mercury, and thus,  $\text{HgI}_2$  does not act as a significant solubility control. The solubilities of total iodine can be considered to be those of  $^{129}\text{I}$  because of the relative insignificance of  $^{127}\text{I}$ .

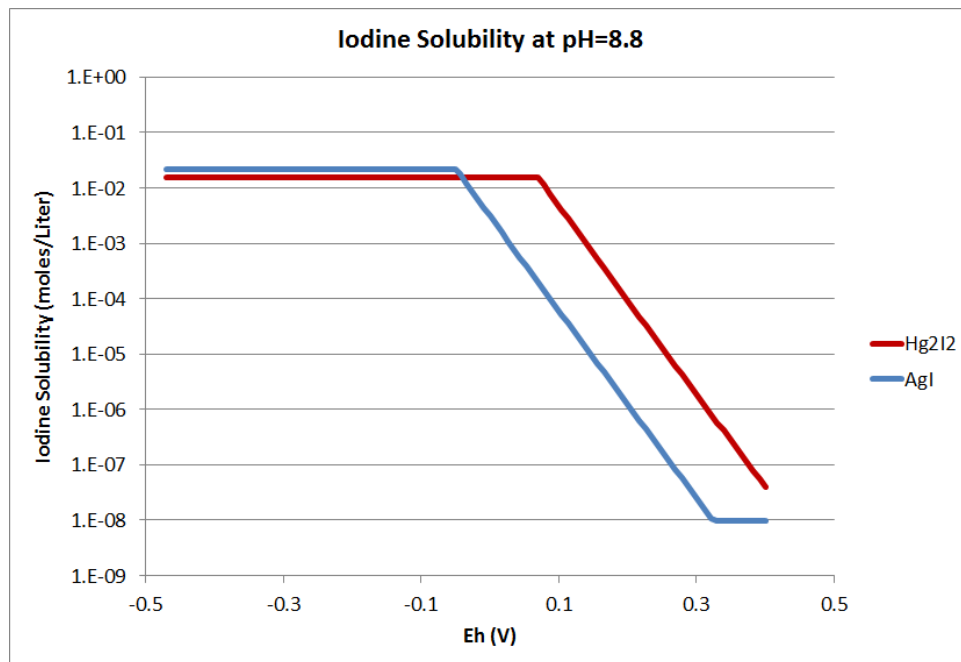
Table 1: Initial compositions of waters used in iodine solubility calculations.

Parameter	Tanks Above the Water Table			Tanks Below the Water Table			
	Red. Reg. II	Ox. Reg. II	Ox. Reg. III	A	B	C	D
pH	11.1	11.1	9.2	5.4	8.8	8.8	8.8
Eh (volts)	-0.47	0.24	0.29	0.37	0.36	-0.31	0.36
Na+ (M)	1.0E-3	1.0E-3	1.0E-3	4.4E-5	3.9E-5	4.0E-5	4.0E-5
Cl- (M)	1.0E-3	1.0E-3	1.0E-3	8.5E-5	8.1E-4	7.8E-4	8.0E-4

The calculated solubilities of iodine controlled by  $\text{AgI}$  and  $\text{Hg}_2\text{I}_2$  are shown in Table 2 for each initial water composition. The results show that under reducing conditions no solubility controls are exerted by  $\text{AgI}$  or  $\text{Hg}_2\text{I}_2$ . This is because, under reducing conditions, the stable phases of silver and mercury are the elemental metallic phases.  $\text{AgI}$  controls solubility effectively under all oxidizing conditions.  $\text{Hg}_2\text{I}_2$  controls solubility effectively for the lower pH conditions associated with tanks below the water table and less effectively for the higher pH values associated with tanks in the unsaturated zone. Figure 2 compares the solubilities of  $\text{AgI}$  and  $\text{Hg}_2\text{I}_2$  as Eh is varied and pH remains fixed at 8.8. Figure 3 shows a similar comparison at a fixed pH of 11.

Table 2: Calculated solubilities (moles/liter) of iodine for water compositions shown in Table 1.

Solid Phase	Tanks Above the Water Table			Tanks Below the Water Table			
	Red. Reg. II	Ox. Reg. II	Ox. Reg. III	A	B	C	D
AgI	No Solubility Control	2.7E-07	3.8E-08	9.8E-09	9.8E-09	No Solubility Control	9.8E-09
Hg <sub>2</sub> I <sub>2</sub>	No Solubility Control	2.0E-05	1.2E-04	1.2E-07	1.8E-07	No Solubility Control	1.8E-07

Figure 2: Calculated iodine solubility vs. Eh at a pH of 8.8 for controlling solid phases AgI and Hg<sub>2</sub>I<sub>2</sub>.



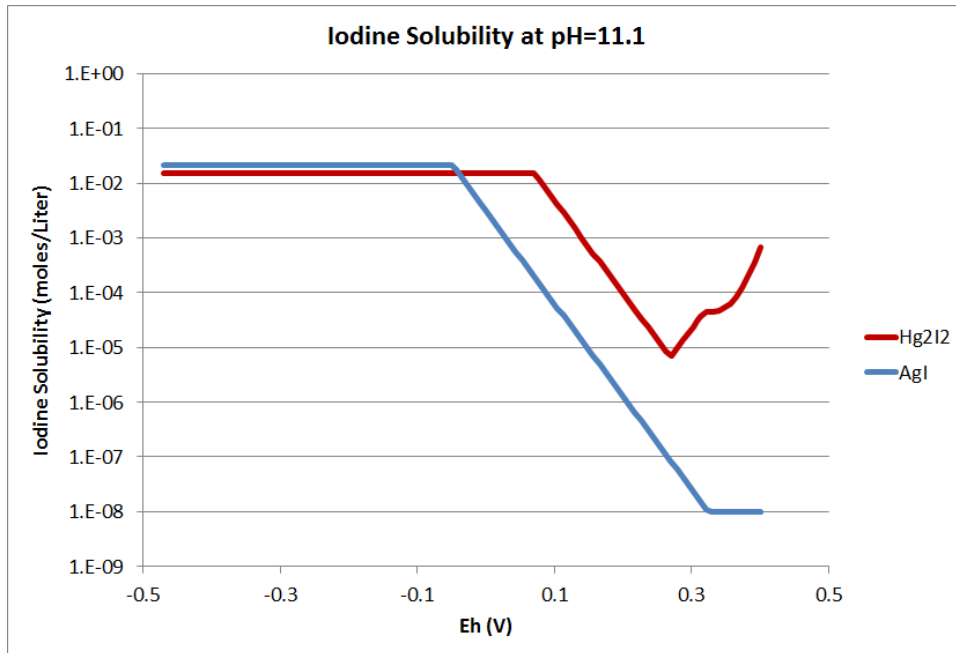


Figure 3: Calculated iodine solubility vs. Eh at a pH of 11.1 for controlling solid phases AgI and Hg<sub>2</sub>I<sub>2</sub>.

### Implications for <sup>129</sup>I Release Modeling

Estimates of solubility controls on <sup>129</sup>I suggest the possibility that silver or mercury in the residual waste can limit release of <sup>129</sup>I under certain conditions. Under the various oxidizing conditions the calculated solubility of silver iodide (AgI) ranges from 9.8E-9 to 2.7E-7 moles/liter and the calculated solubility of mercury (I) iodide (Hg<sub>2</sub>I<sub>2</sub>) ranges from 1.3E-7 to 1.2E-4 moles/liter. The lower solubilities in the ranges are associated with conditions for tanks in which the waste layer is below the water table. At reducing conditions, the elemental forms of silver and mercury are stable, and no solubility limitations from AgI or Hg<sub>2</sub>I<sub>2</sub> are applicable.

The fact that all of the iodine in floor residual waste samples from tank 12H was removed with a deionized (DI) water leach (Oji et al., 2015) is not inconsistent with active solubility controls on <sup>129</sup>I solubility. For the leaching test 0.5 grams of waste was leached with 30 ml of DI water. Essentially all of the iodine was removed and constituted an average of 2.7E-3 wt.% of the sample. Thus, the average total iodine removed was 1.4E-5 grams. This results in an average iodine concentration of 3.6E-6 moles/L in 30 ml of water. This is within the range of solubility controlled by mercury iodide compounds.

Another consideration in the transport of <sup>129</sup>I under reducing conditions in a tank is that there will be no solubility controls within the tank, but dissolved elemental mercury may migrate out of the tank with dissolved <sup>129</sup>I. As reducing waters from the tanks encounter oxidizing conditions of the vadose zone or saturated zone, a redox gradient would be established where elemental mercury would be oxidized to Hg(I) and perhaps ultimately to Hg(II). It is feasible that along this gradient precipitation of mercury iodide compounds would slow migration of the <sup>129</sup>I. Exploring this possibility further is beyond the scope of this document.

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