

Appendix C

Chemical Fractionation of Tank Waste

The chemical inventory estimates for single shell tanks (Agnew 1996) provide an indication of tank contents or total inventory based on process history. An understanding of the relative distribution of constituents of interest in the liquid phase versus the total (or solids plus liquids) provides some indication of the constituent solubility (or initial mobility) prior to release into the soil column. The reactivity of tank waste supernate with the soil or sediment matrix can also influence the relative mobility of constituents of concern. Serne et al. 1997 evaluated both sorption and chemical reactions between tank waste supernate and Hanford soils with emphasis on cesium (and strontium) mobility. The following discussion is limited to the major RCRA-related constituents and key radionuclides and is based on information from Serne et al. 1997 and Agnew (1996; 1997) and other literature as cited.

C.1 Major RCRA Constituents

The principal RCRA-related chemical components are nitrate, aluminum, hexavalent chromium, and hydroxide (due to its corrosiveness). We will assume that nitrate was unfractionated (it remained completely in solution and thus other chemical constituents, when normalized by dividing by the molar concentration of nitrate, provide an indication of deviation from the initial makeup chemical composition or inventory. The molar ratios observed in groundwater samples with the highest recent technetium-99, chromium, and nitrate concentrations (well 2-W22-46), are used for comparison with the tank waste ratios. Table C.1 summarizes this approach with some available analytical results for Tanks S-102 and S-110. Other recent analytical data on tank sample fractions (drainable liquid, salt cake, sludge) may also be useful for this type of comparison. Recent single shell tank analytical data is accessible on the Hanford Web page as it becomes available.

The molar ratios shown in Table C.1 suggest that the total inventory composition for Tanks S-102/110 are not markedly different than the supernate measurements. The aluminum and chromium appear to have about the same proportions in supernate as in the estimated total that went into the tanks based on process knowledge. This is consistent with the amphoteric nature of aluminum (formation of anionic aluminate at high pH) and the chemical thermodynamics of hexavalent chromium suggesting it should remain as a soluble species at high pH.

Table C.1. Molar Ratios of Major RCRA Dangerous Waste Constituents (normalized to nitrate)

Phase	Molar Ratio		
	Nitrate ^(a)	Aluminum	Chromium
Estimated Total Tank Inventories^(b) (solid & liquid):			
S Tanks (mean of 12 tanks)	1	0.44	0.03
SX Tanks (mean of 15 tanks)	1	0.79	0.26
S-SX Tanks (overall mean)	1	0.6	0.14
Measured Supernatant:^(c)			
Tanks S-102/S-110 (mean)	1	0.4	0.03
Groundwater:^(d)			
Well 2-W22-46	1	<0.002	0.001
(a) Nitrite and nitrate listed in Agnew (1996) were combined. (b) Agnew (1996); based on process knowledge and campaign history. (c) From Schulz (1978); based on analysis of drainable liquid from sludge samples. (d) Appendix B data; based on results from sample with the highest nitrate.			

The higher mean chromium-to-nitrate ratio (total) for the SX tanks than for the S tanks is of potential significance. For example, the ten-fold difference between the two tank farms may be useful in differentiating S and SX farm sources of groundwater contamination (provided this difference is borne out by analytical results for all the tanks).

The aluminum concentrations in groundwater were above detection limits but below the quantitation limit (Appendix B). Thus the result is of only qualitative value. Nevertheless, aluminum was detected and it suggests significant fractionation occurred in the vadose zone. Chromium in groundwater also indicates fractionation as compared to the original tank waste, especially as compared to SX tank waste. These marked departures from the tank waste composition may be attributable to soil chemical reactions, discussed as follows.

C.1.1 Soil Chemical Reactions

The marked depletion of aluminum relative to nitrate in the groundwater sample with elevated nitrate and technetium-99 can be explained as follows. As long as the pH remains high, the aluminum remains soluble as the aluminate anion. As Serne et al. 1997 point out, however, as the tank waste supernate reacts with the soil aluminosilicate mineral phases, the hydroxide is consumed and the pH drops. Upon reaching the water table and mixing with groundwater, the pH would approach the ambient level of around 8. At this much lower pH (relative to tank liquor at up to a pH of 14), aluminum hydroxide

[Al(OH)₃], a gelatinous precipitate should form. The waste liquor-soil matrix reaction both consumes hydroxide and results in formation of a non-mobile phase of aluminum. The preliminary or scoping laboratory studies conducted by Serne et al. 1997 using simulated SX tank waste tend to support this explanation.

A different mechanism is required to explain the apparent fractionation of hexavalent chromium outside the tanks as suggested by the ratios shown in Table C.1. The anionic hexavalent chromium (as CrO₄²⁻ in natural environments) should not form precipitates and should remain anionic over the natural pH of groundwater and soil moisture under Hanford subsurface conditions (pH of around 8.0). The ability of soils to adsorb anions is quite low, especially soils with natural pH values of 8 or above. The presence of Cr in the shallow groundwaters along the Columbia River at several 100 Area inactive reactor sites is an indication that adsorption is not strong.

One possibility is that reducing conditions may occur at the surface of basaltic sand grains prevalent in Hanford soils. Reducing conditions attributable to Fe(II) in some minerals such as basaltic sand grains could lead to reduction of Cr(VI) to immobile Cr(III). James and Bartlett (1983), Leckie et al. (1980), Masscheleyn et al. (1992), Powell et al. (1995), and Rai et al. (1988) showed that iron oxides and organic matter in soil can reduce Cr(VI) to Cr(III) and precipitate Cr(III) as a (Fe, Cr)(OH)₃ mineral and/or increase adsorption of the Cr(III) cation. Also, studies conducted by Rai et al. (1988) show that DCB extractable Fe content is a good indicator as to whether a soil can reduce significant quantities of Cr(VI) which results in higher K_d values. It is important to note the total iron oxide content is a poor indicator of a soil's Cr(VI) reducing capacity and that DCB extractable Fe better represents the fraction of Fe content that would reduce Cr(VI) to Cr(III).

If this type of reduction occurs, it could explain why the chromium observed in groundwater is less than expected based on the tank inventory or supernate concentrations relative to nitrate. Another explanation could be that the source of the chromium observed in groundwater from well 2-W22-46 (located at the southeast corner of SX tank farm) is from a source with a different composition than that used for Table C.1. Confirmatory analytical data for all the tanks and neighboring liquid disposal facilities (cribs, trenches, and ponds) would be needed to determine if there are certain tanks or liquid disposal facilities with unusually low chromium to nitrate ratios.

The above considerations and the work of Serne et al. 1997 suggest the soil column may attenuate the impact of the RCRA/dangerous waste components of tank waste by chemical reactions that consume the hydroxide, precipitate the aluminum and possibly reduce some of the hexavalent chromium.

C.1.2 Radionuclides

Radionuclides in tank waste are also subject to chemical fractionation effects. Comparison of supernate and sludge predicted composition and sample analytical measurements indicate that most of the technetium-99 and cesium-137 remain in solution or are present in tank solids in a readily soluble form while strontium-90 is associated with solids and not readily resolubilized.

Based on total inventory estimates (Agnew 1997) for tanks S-102 and 110 (tanks used for the fractionation example given Table C.1), the cesium-137/strontium-90 ratio should be about 1.3. The observed ratio in supernate or drainable liquids (mean of results for both tanks) is 33 (from Schulz 1978). Thus significant depletion of strontium-90 apparently occurred from the liquid phase. Americium-241, an important transuranic constituent of concern, has an apparent fractionation factor similar to strontium-90.

The phase separation noted above probably occurred soon after sodium hydroxide was added to neutralize the highly acidic waste stream generated from the REDOX process in S plant. Thus strontium-90 and americium-241 in liquids lost to the soil from either transfer lines and distribution boxes or from tank leaks should be predominantly associated with a particulate or solid phase. Deviations could occur, however, depending on specific tank conditions (for example the presence of complexing agents). Thus analytical results for each tank, as they become available, are needed to check the generalization noted above.

After release from tanks or the waste distribution system, attenuation due to sorption and chemical reactions in the soil column are expected to further alter the proportions reaching groundwater (Serne et al. 1997). Studies are underway at Pacific Northwest National Laboratory to elucidate sorption mechanisms and waste liquor-soil chemical reactions that influence contaminant mobility in the vadose zone beneath the S and SX tank farms.

C.2 References

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