The Proposed Ward Valley Radioactive Waste Facility: Papers Submitted to the National Academy of Sciences

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Dear Member of the NAS/NRC Panel on Ward Valley:

I believe that the enclosed material should prove useful in the deliberations of your committee. It merits your careful scrutiny.

Sincerely,

Robert Cornog, Ph.D.
[co-discoverer of tritium, 1939]

CHELATION AND K_d VALUES:
THE EFFECT ON RADIONUCLIDE MIGRATION

> [T]he presence in the waste of complexing agents such as organic chelates used in decontamination operations and natural organic acids from the soil promotes the formation of strong complexes with certain radionuclides that reduce the adsorption capacity of the . . . soil for the radionuclide.
>
> (Means and others, 1978, p. 1477)

> [L]aboratory-derived K_ds did not reflect the effects of long-term leaching of soil-adsorbed radionuclides by natural or manmade organic complexing substances to which the in situ soils were exposed. *The in situ K_ds more accurately express the sorption capacities of the mobile forms of these radionuclides, which migrate at much faster rates than predicted from laboratory-derived K_d values.*
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> (Fruchter and others, 1985, p. 8, emphasis added)

> "[T]he effect of complexants on toxic element sorption should be examined with soils from specific proposed commercial low-level waste disposal sites."
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> (Swanson, 1984, p. 2)

Introduction

It has long been recognized that the presence of naturally occurring organic complexing agents, either in soil or the waste itself, or stronger chelating compounds such as EDTA used in nuclear operations for decontamination of piping and the like, causes the formation of highly stable metal complexes that dramatically increase mobility of radionuclides in soil. These chelated radionuclides have a radically reduced distribution coefficient or soil retention factor (K_d) and will migrate very much faster in soil than in their non-chelated state. Far more rapid migration of such radionuclides than would otherwise be expected has been observed at numerous radioactive waste facilities (e.g., Maxey Flats, Kentucky; West Valley, New York; Oak Ridge, Tennessee; Chalk River, Canada) and attributed to the presence of complexing agents (Means and others, 1978, Cleveland and Rees, 1981, Akers and others, 1994). A brief introduction to the chemistry of chelates and the related matter of colloidal-enhanced radionuclide migration is attached hereto as Appendix A.

Wilshire and others (1993, p. 38 and Attachment 8) have pointed out that the potential for chelating agents to contribute to the mobility of radioactive waste at Ward Valley had not been addressed in the License Application and urged serious review of the question.

The distribution coefficient or soil retention factor, K_d, is an essential input in analyzing potential risks of transfer of radioactive materials from the Ward Valley disposal trenches to the surface above, the aquifer below, or, once in the aquifer, to discharge locations at Danby Lake or the Colorado River. The use of inappropriate K_d factors can lead to substantial underestimation of travel times and environmental risk. It must be made clear at the outset that there is no single, universal K_d value for a particular radionuclide. K_d depends upon the chemical composition and other properties of the site soils, the trench leachate, and the chemical form of the radionuclide (e.g., whether it is chelated, and if so, the nature of the chelating agent). To calculate risk, one cannot just pull a K_d value out of a book, or use one for a different site, or use one for a different chemical form (e.g., unchelated) than may be present in the situation of concern. US Ecology, however, did just that.

To estimate K_ds appropriately, one must test the specific radionuclides of importance in experiments on soils from the site in question; one needs to use radionuclides that are complexed using different chelating materials; and test the materials over different concentrations, pH, and associated conditions.

US Ecology used K_ds obtained from other sites (e.g., the U.S. Department of Energy Hanford Reservation) rather than use K_ds based on tests on Ward Valley soils. It ignored the K_ds it did measure using Ward Valley soils. Furthermore, the K_ds it used in its performance analyses were for unchelated materials. All of these actions resulted in the use of K_ds that were grossly too high, resulting in migration rate estimates and consequence conclusions dramatically too low.

In an effort to determine K_ds for use in its performance assessment, US Ecology undertook batch sorption testing on Ward Valley site soils for five radionuclides [cesium-137 (Cs-137), cobalt-60 (Co-60), radium-226 (Ra-226), natural uranium, and nickel (as a proxy for nickel-59)], which were chosen "because they are typical low-level radioactive waste (LLRW) constituents" (License Application, p. 2600-58 and Table 2600.A-10).

With the exception of uranium, however, these were *not* the radionuclides US Ecology chose to analyze in its performance assessment. The radionuclides that were in the end analyzed were plutonium-239 (Pu-239), iodine-129 (I-129), carbon-14 (C-14), and uranium-238 (U-238) (License Application, p. 6151-12 - 6151-14).[1] Numerous isotopes of importance were ignored. Of greatest importance is the fact that no tests whatsoever on Ward Valley soil were conducted on plutonium, chelated or not.

Neither the batch sorption tests conducted on Ward Valley soil, nor the literature values for other soils upon which US Ecology relied for the K_d values it ended up employing, were based on *chelated* radionuclides. Chelation causes K_d values to drop dramatically. By failing to use K_ds obtained for Ward Valley site soils, and failing to assess the full range of potential radionuclides and chemical forms of concern, the potential transfer to the general environment may have been severely underestimated.

Discussion

The profound effect that chelating agents can have on K_d values is exemplified by the measured effect founds by Means and others (1978, p. 1477):

> The following experimentally measured distribution coefficients (K_d) illustrate the pronounced effects that organic ligands have on the adsorption capacity of sediment for trace metals. We determined that the K_d values for Co^{60} in weathered Conasauga shale at *p*H 6.7 and 12.0 were approximately 7.0×10^4 and 0.12×10^4 respectively. In the presence of $10^{-5}M$ ethylenediaminetetra-acetic acid (EDTA) the K_d values were reduced to 2.9 and 0.8.

Thus, in the setting analyzed above, chelation reduced the K_d for Co-60 by approximately four orders of magnitude.

The results of such a reduction in K_d on radionuclide transport time can be quite dramatic. Means and others (1978), citing Marsily and others (1977), give the following example. Pu-239 deposited at the bottom of a 500 meter thick geologic formation, in a setting with high sorptive capacity characterized by a K_d of 2×10^3, could take more than a million years to migrate

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[1] When the controversy arose over the tritium finding at depth, an analysis for tritium was performed as well, although, as we have discussed in detail elsewhere (see Cornog and others, 1992, p. 33-47), the model was unable to match the measured data.

500 meters if the geological formation were of low permeability. Given its half-life, the plutonium would have decayed completely by the time it reached the environment. If, however, chelating compounds were present, resulting in a K_d approaching zero, the plutonium could reach the environment in as little as six years. In formations of low to moderate permeability, the plutonium would travel the 500 meters in only tens to several hundreds of years, four to five orders of magnitude faster than if the plutonium were unchelated.

Description of US Ecology's Analysis

Waste Stream Identification and Selection of Radionuclides for Transport Analysis

US Ecology's first step was to attempt to identify the Ward Valley waste stream. US Ecology's waste stream projection is reprinted in **Table 1.**[2]

Although the table is titled "Major Nuclides Considered for Analysis," it does not actually represent the nuclides that *were* analyzed in the performance assessment. Apparently, as a careful reading of the title suggests, it represents only those nuclides *"considered for analysis,"* not those that were actually analyzed. In the end, no analysis was performed on 80% of these radionuclides (which, indeed, themselves represent only a small fraction of the scores of radionuclides which will be present in the Ward Valley trenches).

US Ecology proceeded to narrow the scope of its analysis further to just one of the five trenches projected for Ward Valley, the BC30 trench. This is problematic because (1) it ignores a substantial portion of the waste, (2) the wastes for the Class A trenches are not required to be stabilized (FEIR/S, p. 2.1-14), so subsidence of the trench cap, resulting in ponding and cracking and increased infiltration is likely, and (3) the Class A trench caps are just earth fill, with a mere 100 year design life, and without the "intruder barrier and capillary break" built into the BC30 trench cap design (as questionable as may be the effectiveness of the latter cap design) (FEIR/S, Appendix - Response to Comments on Draft EIR/S, p. 96). The more primitive trench cap and lack of waste form stabilization to prevent subsidence, cracking and ponding produce substantially increased potential for downward percolation through the waste, but those wastes

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[2] US Ecology initially presented its waste stream estimates originally in License Application Table 6110-9 and several other tables. Prompted by a DHS interrogatory asking why there were discrepancies between Table 6110-9 and the other tables in the License Application, particularly Table 6151-1 for the BC30 Trench, US Ecology notified DHS that Table 6110-9 was in error and replaced it with Table 566B.1-1, which is presented here (Interrogatory Response Nos. 061B6151.1.7 and 0566B6110.B).

Table 1. US Ecology Ward Valley Waste Stream Projections.

MAJOR NUCLIDES CONSIDERED FOR ANALYSIS

** All activities in curies **

NUCLIDE	ACTIVITY	PERCENT
AM-241	1.391E+1	<0.1
C-14	7.559E+2	<0.1
CM-243	7.271E-1	<0.1
CM-244	6.714E+0	<0.1
CO-60	1.482E+5	2.8
CS-137	1.894E+4	0.4
FE-55	1.690E+4	0.3
H-3	4.868E+6	92.3
I-129	2.134E+1	<0.1
NB-94	3.054E+0	<0.1
NI-59	1.305E+2	<0.1
NI-63	1.191E+4	0.2
NP-237	4.393E-3	<0.1
PU-238	2.612E+3	<0.1
PU-239	3.448E+3	<0.1
PU-240	8.963E-1	<0.1
PU-241	6.925E+4	1.3
RA-226	3.816E+1	<0.1
RN-222	3.816E+1	<0.1
SR-90	5.746E+2	<0.1
TC-99	6.105E+0	<0.1
TH-231	1.781E+1	<0.1
TH-234	4.034E+2	<0.1
U-235	1.781E+1	<0.1
U-238	4.034E+2	<0.1
	5.272E+6	99.2

Source: US Ecology Table 566B.1-1

were excluded from the groundwater transfer analysis (License Application, Section 6151, and Appendix 6151.A). Wastes of the same longevity are permitted in the Class A trenches as the BC30 trench (License, Appendix A). The 10-fold difference in concentration limits is such that, when coupled with the increased volume of Class A wastes, significant amounts of long-lived materials can be present in the Class A trenches, , where deep infiltration may be more likely because of increased probability of subsidence, ponding, and cracking of the trench cap. Yet these wastes were excluded from analysis.

As seen in **Table 2**, a reprint of Table 6151-1 from US Ecology's License Application section detailing its Analysis of the Transfer Mechanism to Groundwater, the number of radionuclides "considered" in the groundwater transfer analysis shrank by 40% from US Ecology's Table 566B.1-1, the "major radionuclides considered for analysis." Important radionuclides such as plutonium-241 and its major decay product, americium-241, were not included, nor was consideration of the buildup of their inventory resulting from decay of parent nuclides.[3]

In the end, US Ecology conducted transport analyses on only *four* radionuclides: I-129, C-14, U-238, and Pu-239. (A fifth nuclide, tritium, was later considered when the tritium finding at depth was disclosed and the adequacy of US Ecology's transport model was challenged by USEPA and the California Regional Water Quality Control Board.) The nearly two hundred radioisotopes identified in the waste stream inventory of the License Application (Appendix 6110.D) were reduced to 25 in Table 566B.1-1, then reduced to 15 in Table 6151-1, and finally reduced to the four radioisotopes used in actual transport analysis. In the process, important radionuclides (e.g., more toxic than C-14 or U-238, or mobile than the mobility assumed by US Ecology for unchelated plutonium) were ignored.

Determination of K_d Values

US Ecology, in order to conduct the transport analyses for the groundwater performance assessment, needed to determine appropriate K_d values for radionuclides that would be present at the Ward Valley facility, if opened. After describing its decision to analyze only for C-14,

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[3] For example, the nearly 70,000 curies of plutonium-241 (Pu-241) destined for Ward Valley will decay into approximately 2,000 curies of americium-241. Unlike Pu-241, which is a beta-emitter with a relatively short half-life of 14.4 years, Am-241 is a highly toxic alpha-emitter with a half-life of 433 years. By ignoring the buildup of Am-241, US Ecology severely underestimated the amount of risk involved with the proposed Ward Valley project.

Table 2. Properties of Radionuclides in the BC30 Trench (US Ecology Table 6151-1)

Isotope	Half-Life (Years)	Activity (curies)	Specific Activity (curies/g)	Kd (ml/g)
Ac-227[a]	2.18×10^{1}	2.8922	7.23×10^{1}	40
C - 14	5.73×10^{3}	272.04	4.46	0
I - 129	1.57×10^{7}	9.9466	1.77×10^{-4}	0
Nb - 94	2.03×10^{4}	2.9577	1.87×10^{-1}	350
Ni - 59	7.50×10^{4}	106.62	8.10×10^{-2}	101
Pa - 231[a]	3.28×10^{4}	2.8922	4.72×10^{-2}	40
Pa - 234m[b]	7.65×10^{-4}	173.63	2.00×10^{6}	40
Pu - 239	2.41×10^{4}	3507.80	6.20×10^{-2}	73
Pu - 242	3.76×10^{5}	7.6722	3.93×10^{-3}	73
Ra - 226	1.60×10^{3}	15.994	9.89×10^{-1}	200
TC - 99	2.13×10^{5}	2.7589	1.70×10^{-2}	0
Th - 231[a]	2.91×10^{-3}	2.8922	5.32×10^{5}	40
Th - 234[b]	6.60×10^{-2}	173.63	2.32×10^{4}	40
U - 235	7.04×10^{9}	2.8922	1.92×10^{-6}	0
U - 238	4.47×10^{9}	173.63	3.35×10^{-7}	1

Information on table provided by US Ecology (*1989a*) with the exception of Kd values for U-235 and U-238 and specific activity data. Kd values for U-235 and U-238 obtained from Langmuir (1981). Specific activity values obtained from Wang (1969).

[a] daughter products of U-235 that reach secular equilibrium

[b] daughter products of U-238 that reach secular equilibrium

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Source: US Ecology, License Application, Table 6151-1.

U-238, I-129, and Pu-239, US Ecology stated that K_ds for these radionuclides are shown on Table 6151-1 and were "provided by US Ecology on the basis of adsorption tests conducted on these radionuclides" (License Application p. 6151-14). Despite the extensive discussion of adsorption tests performed by US Ecology using Ward Valley site soils (License Application, p. 6151-7 - 6151-8; p. 2600-56 - 2600-61; License Application Appendix, p. 2600.1A-17 - 2600.1A-28), the K_d values used in the transport analysis for carbon, uranium, and plutonium in fact were *not* obtained from adsorption tests by US Ecology using those nuclides and Ward Valley soils.

US Ecology did perform batch sorption tests on selected radionuclides using Ward Valley soils, but *none* of those tests were used in establishing the K_d values US Ecology employed in its groundwater transfer analysis. Indeed, with the exception of uranium, none of the batch sorption tests performed on Ward Valley soils were even for radionuclides considered by US Ecology in its performance assessment.

In License Application Table 2600-9, US Ecology identifies the radionuclides for which sorption tests were performed using Ward Valley soils. They are cobalt-60, cesium-137, nickel, radium-226, and uranium. Yet US Ecology did *no* analysis for transport to groundwater for any of these but uranium. The most important radionuclide for which US Ecology did do a transport analysis, Pu-239, was subjected to no testing whatsoever using Ward Valley site soils.

US Ecology took the plutonium K_ds from published values for an entirely different site, the U.S. Department of Energy (DOE) Hanford Reservation (Grant, 1994, p. 2). US Ecology used a K_d for plutonium of 73 (see **Table 2**; note that Grant, 1994, p. 2, mistakenly says the value used was 72). Grant (1994) reports that plutonium K_ds had been measured in laboratory column and batch tests using Hanford site soils over 15 years ago and that based on those tests, DOE used a K_d value of 71 in a 1987 radionuclide transport analysis for Hanford (as discussed below, this characterization is not correct). Grant (p. 2) asserts that "the values at the two sites should be comparable, since the soils and the environment are *similar*" (emphasis added). The applicability of K_d values based on measurements from soils a thousand miles apart is questionable at best, and exacerbated by the wide disparity that exists between laboratory and *in situ* measurements. For example, Coles and Ramspott (1982) reported measuring extremely rapid ruthenium migration (as fast as tritium) at the Nevada Test Site despite laboratory experiments showing high K_d values for ruthenium. In particular, they report that laboratory batch sorption tests on Hanford soil produced K_ds of 40 to 752, yet *in situ* observations found significant mobility. Coles and Ramspott (p. 1236) concluded that K_d values obtained from batch sorption tests "should be used with caution and verified with field radionuclide migration studies or more relevant laboratory studies." They pointed out that an understanding of the chemical speciation of the radionuclides in question, particularly selected actinides, "is needed in order to predict their behavior in a ground-water environment" (p. 1236). This conclusion is especially important in light of US Ecology having used a K_d from another location rather than conducting sorption tests on site soils for the isotopes in question, as well as having failed to use K_ds for plutonium in chelated form.

The significance of this is readily observable from its own table of K_d values (Grant 1994, p. 6 and 8). Asserting that the appropriate K_d value for plutonium at Ward Valley is approximately that used for Hanford soils because they are allegedly "similar," US Ecology then chose a K_d for *uncomplexed* plutonium at Hanford ($K_d = 71$) based on laboratory tests rather than the K_d of 1.4 measured at Hanford for plutonium migration in the presence of suspected organic contaminants (see **Table 3**, comparing Grant, 1994, p. 6 and p. 8). Because one does not know the characteristics of those suspected organic contaminants, the K_d for plutonium that is purposely complexed with a powerful chelating agent such as EDTA (e.g., reactor primary coolant decontamination wastes that would go to Ward Valley) is likely to be even lower than 1.4 for Hanford soils. US Ecology chose a K_d of 73 for unchelated plutonium rather than a measured value for those soils in the range of 1 for suspected chelated plutonium. As Grant (1994, p. 1-2) notes, radionuclides with K_ds orders of magnitude greater than 1 are "essentially immobile," yet US Ecology nonetheless chose a K_d yielding essentially immobility in the face of measured values for the soils and environment it claimed were similar to Ward Valley that showed very much lower K_ds (close to no retardation at all) and very much higher mobility for actual plutonium moving in those actual soils.

As to US Ecology's claim that the K_d it used for plutonium, 73, was the figure used by DOE for calculating radionuclide transport at Hanford in its safety analysis, the document they cite (DOE, 1987, p. S.17-19) directly contradicts that assertion. That study indicated that the K_d for Hanford soils would extend over a range from an upper limit of 71 for dilute uncomplexed plutonium to 0.63 for concentrated complexed plutonium. DOE created a probability density function (pdf) demonstrating that over the range of conditions examined for their assessment, the K_d would be much closer to 0 than to 71, and indeed used a median K_d of 6.0 for their analysis of the no action alternative. US Ecology thus took a figure *higher* than the *maximum* K_d value cited by DOE for dilute uncomplexed plutonium and applied it to wastes for Ward Valley that would contain substantial amounts of powerful chelating agents for which the K_d should be vastly lower. If the DOE data from Hanford were to be used at all–as opposed to measuring actual

Table 3. Comparison of Kd Values for Plutonium at the DOE Hanford Reservation.

Source	Kd Value (ml/g)	Environment	Comments	Grant's Reference
Grant (1994, p. 6)	71	Unsaturated zone at Hanford Reservation 300 Area.	Kd value said (by Grant) to be used by DOE for Hanford plutonium transport analyses.	DOE (1987).
Grant (1994, p. 8)	1.4	Hanford site wastes.	Addition of suspected organic contaminants.	Knoll (1985, 1969) and Hajek and Knoll (1966) reported in EPA (1978).

K_ds for heavily chelated plutonium using Ward Valley soils–a K_d in the range of the 0.63 cited in the DOE report for chelated plutonium would have been the most appropriate estimate.

Table 4 is a reprint of the relevant table from the DOE Environmental Impact Statement (EIS) for Hanford on which US Ecology claims it based both its decision to use a K_d of 73 for plutonium for Ward Valley soils and its defense of that figure for *chelated* plutonium.

Table 4. K_d Values Used in Hanford Plutonium Transport Analyses.

Environmental Impact Assessment	**Median**	**Low** (Concentrated Complexed)	**High** (Dilute Noncomplexed)
Plutonium K_d for No Action Alternative	6.0	0.63	71

Source: DOE, 1987, p. S.17 - S.19.

One readily sees that even were it appropriate to use K_ds determined for Hanford soils and apply them to the Ward Valley situation, there is no basis for a K_d of 73 for plutonium if it is combined with a complexing agent. Since the transuranic wastes to go to Ward Valley would be complexed with the strongest and most persistent chelates possible (e.g., EDTA), in order to strip the "crud" from the inside of reactor piping during reactor primary coolant decontamination operations, an appropriate K_d for these heavily chelated wastes headed for Ward Valley would be in the range of the 0.63 cited in the Hanford study, not the 73 US Ecology claims the study recommends.

US Ecology has claimed that the K_ds it used are appropriate for chelated radionuclides such as plutonium because the values are assertedly at the lower end of reported values (for unchelated nuclides). Let us examine for a moment the data that do exist regarding sorptive capacity of Ward Valley soil, and whether it is at the low or high end of measured values reported in the literature for other locations and soil types. As indicated above, US Ecology did batch sorption testing using Ward Valley soils for five *unchelated* radionuclides or their surrogates: Co-60, Cs-137, nickel (as a surrogate for Ni-59), radium-226, and uranium. The mean, minimum, and maximum K_ds measured are listed in **Table 5** (License Application, Table 2600-9). Also see **Table 6** (License Application, Table 2600-10), which includes a compilation of literature values for K_ds for various soils for the same radionuclides, prepared by US Ecology.

When compared to literature values from a range of soils, Ward Valley soils have relatively little sorptive capacity–even for uncomplexed radionuclides. The measured mean value for Co-60 at Ward Valley was 64.88; US Ecology's literature search showed a range of 24 to 800. The mean at Ward Valley for Cs-137 was 166.85, the literature range is from 30 to 3165. Uranium was 6.92 at Ward Valley, and ranges from 0 to 270 in US Ecology's literature compilation.

The most interesting results were for radium-226 and nickel. The mean K_d measured value for nickel at Ward Valley was a surprising 0.20–essentially as mobile as water. This is *below* the range of 5 to 102 US Ecology reports from its literature search. For radium-226, the mean measured value at Ward Valley is 1.98, while the low end of the range US Ecology reports from the literature *begins* two orders of magnitude higher, 200 to 500.

Thus, actual K_ds for Ward Valley soils are not only at the very low end of reported literature values, but in two very important cases, nickel and radium, they are far below any literature value reported. When Grant (1994) asserts that K_ds for plutonium go far higher than the 73 used in the US Ecology assessment, that is no argument for use of a high K_d for Ward Valley. Ward Valley soils, by US Ecology's measurements, are at the very low end of sorptive capacity–even without considering chelating compounds.

Table 5. Mean, Minimum, and Maximum Distribution Coefficients for Ward Valley Soils (License Application, Table 2600-9).

Radionuclide	Mean	Minimum	Maximum
Cobalt-60	64.88	46.57	96.11
Cesium-137	166.85	66.05	266.27
Nickel	0.20	0.06	0.28
Radium-226	1.98	0.14	3.36
Uranium	6.92	3.86	17.56

Table 6. Literature Compilation of Distribution Coefficients (Kd) for Soils (License Application, Table 2600-10).

Radionuclide	Kd Range	Reference
Cobalt-60	24 - 800	7
Cesium-137	30 - 3165	1, 2, 3, 4
Nickel	5 - 102	6
Radium-226	200 - 500	6
Uranium	0 - 270	5

References:

1 - Nork et al. (1971)
2 - Parsons (1962)
3 - Isherwood (1981)
4 - Dosch and Lynch (1978)
5 - Rancon (1973)
6 - US Ecology (1989)
7 - Ames and Rai (1978)

License Application, Tables 2600-9 and 2600-10. In Table 2600-9 (shown here as **Table 5**), US Ecology reported the results of its batch sorption tests, listing the mean and range of Kd values measured for five radionuclides in Ward Valley soils. In Table 2600-10 (shown here as **Table 6**), US Ecology reported the range of Kd values found for these radionuclides in its literature search. Measured mean Kd values from Ward Valley soils for cobalt-60, cesium-137, and uranium correspond to low-end Kd values in the ranges reported in the literature. The measured mean Ward Valley soil Kd values for nickel (0.20) and radium-226 (1.98) fall below the range values reported in the literature (nickel = 5, radium-226 = 200). Thus, when compared to measurements at other locations, Ward Valley soils appear to have very little sorptive capacity. In its assessment of radionuclide transport to groundwater, US Ecology analyzed the impact of plutonium-239, iodine-129, carbon-14, uranium-238, and tritium relying upon Kd values from the literature. (Source: License Application, p. 2600-60.)

US Ecology chose not to use its own actual measurements of K_ds in Ward Valley soil when assembling the table of K_d values to be used in its performance analyses (License Application Table 6151-1). Despite the clear evidence that nickel would be essentially non-sorbed in Ward Valley soils, and a measured K_d value below the minimum it says was reported in the literature, US Ecology used a K_d of 101 (License Application, Table 6151-1), at the very top of the literature range for other soils and 500 times higher than it had measured on Ward Valley soils. The measured very low K_d for nickel at Ward Valley–and failure to use that K_d or even perform a transport analysis at all for nickel–is significant given the very long life of Ni-59 (75,000 years half-life) and the relatively large amount estimated to be present in the Ward Valley waste (130 curies, according to US Ecology's Table 566B.1-1, 293 curies in our estimate (CBG, 1994, Ward Valley waste stream hazards index Table 1), enough to contaminate on the order of half a million acre-feet of water to levels in excess of EPA drinking water standards (CBG, 1994, hazards index Table 2). With that level of toxicity and environmental persistence, a measured K_d in Ward Valley soil of very nearly zero (0.2), even when unchelated, is cause for serious concern. The failure to perform any transport analysis whatsoever on Ni-59 and the reliance, in deciding not to perform such an analysis, on a K_d one hundred times higher than that measured at Ward Valley, are difficult to explain.

For radium-226, US Ecology measured a mean K_d in Ward Valley soils of 1.98, with a minimum measured value of 0.14 and a maximum of 3.36 (License Application, Table 2600-9). Yet it used a K_d of 200 (License Application, Table 6151-1), one hundred times higher than its own measured value. Since US Ecology cites the same source[4] for all the K_d values it did employ in Table 6151-1, with the exception of uranium, it is reasonable to assume that the same over-estimation of K_d values occurred for the radionuclides for which sorption tests were not performed at Ward Valley (e.g., plutonium). It is clear that Ward Valley soils were measured and found to have very low sorptive capacity for the nuclides tested, and yet far higher K_ds, taken from other soils, were apparently used.

[US Ecology obtained K_d values for uranium-235 and -238 from a source different from the one it used for all others isotopes. For those two isotopes, US Ecology presents a K_d of 0 and 1 respectively. K_ds should be the same for isotopes of the same element, so the use of two different K_ds is clearly in error. The DHS reviewer pointed this out in Interrogatory No.

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[4] US Ecology's cited source of Kd's is, in fact, not a published study but rather an April 20, 1989, letter from one of its own employees, J. Glenn, to D. Hochmuth, an employee of US Ecology's contractor, Harding Lawson Associates (see License Application, p. 6151-13 and 6151-28). It is unfortunate that the document US Ecology cites as its sole source for all the Kds it employed except for uranium is neither available in the published literature nor even part of the public Administrative Record, frustrating efforts to confirm US Ecology's Kd assumptions.

0601B6151.1.7, but US Ecology declined to use a consistent K_d for uranium. The groundwater transport assessment was done only for U-238, using a K_d of 1. Since US Ecology reports a K_d of 0 for U-235, and K_ds should be identical for both isotopes, had that K_d been used in the U-238 transport calculation, 5 to 11 times less soil retention (Grant, 1994, p. 1), and equivalently faster travel times, would have resulted. Note that measurements for uranium K_d in Ward Valley soil based on unchelated uranium produced a low value, so a K_d of 0 for chelated uranium is not unreasonable.]

Additional Concerns About Chelation

Despite assertions to the contrary by Grant (1994), many of the chelating agents expected to be present in Ward Valley wastes–for example, EDTA, widely used in reactor coolant loop decontamination operations–are extremely stable and will not appreciably biodegrade, even over very long periods of time (see Appendix A).

In addition to dramatically increasing mobility of radionuclides in soil, chelating agents also enhance migration out of waste packages. For example, the migration of radioactive materials out of cement is increased by one to two orders of magnitude when chelating agents are present (McIsaac and others, 1991, p. 108). Furthermore, chelating agents also markedly increase uptake and retention of radionuclides ingested. For example, DTPA has been found to increase the amount of plutonium absorbed approximately 700-fold (Baxter and Sullivan, 1972). Although chelates also increase excretion, the net effect is an overall increase in plutonium retained in the body, a 2.7-fold increase in retention for DTPA and a 80-fold increase for citrate. The dose to a person from the same amount of plutonium, for example, would be 3 to 80 times higher if the radionuclide were chelated with either of these complexing agents.

Conclusions

1. US Ecology performed batch sorption tests using Ward Valley soils for only five radionuclides, but then discarded the values it had measured. The measured values were among the lowest reported anywhere in the literature, indicating very low sorptive capacity for Ward Valley soils.

2. US Ecology then used K_ds from the literature, values much higher than it had measured for Ward Valley soils, indeed, as much as two orders of magnitude higher.

3. In the end, US Ecology's performance assessment was, in all but one case, based on different isotopes, for which no Ward Valley measurements of K_d had been made. Only five radionuclides were analyzed; many extremely important ones were not.

4 The K_ds US Ecology ended up using, particularly for plutonium, were based not on Ward Valley but Hanford soils, a thousand miles away.

5. Reliance on literature values for Hanford soils, rather than measured values for Ward Valley, is improper. Even so, US Ecology chose the wrong K_ds from the Hanford data–very much higher than DOE recommended be used.

6. None of the K_d values reported in the License Application were for chelated radionuclides, and thus were all too high, greatly overestimating (by orders of magnitude) travel times and retardation factors.

7. Environmental risks were therefore severely under-assessed.

Recommendations

1. K_d measurements should be made on actual Ward Valley soils using a range of such soils from different depths, given the heterogeneity present; using a significant sampling of radionuclides, not just five, but certainly including plutonium; using a range of complexing agents, including strong chelates used in reactor decontamination operations; and measured over a range of concentrations and pH.

2. In the absence of such measurements, transport calculations should be redone done with $K_d = 0$ for uranium-238, and between 0 and 1 for plutonium.

3. Conclusions based on the US Ecology calculations in the License Application, premised as they are on erroneous K_ds and the absence of chelation, should be discarded.

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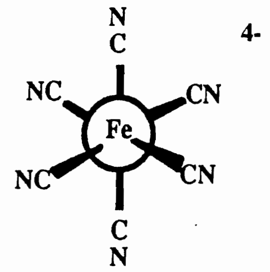
APPENDIX A

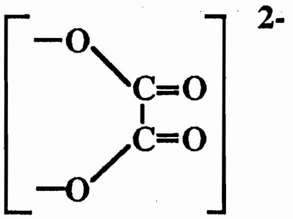
A BRIEF DESCRIPTION OF CHELATE COMPLEXES AND COLLOIDS

Historical. – Nearly 250 years ago in Europe a primitive technology was developed to produce pigments for artists' paint and for inks. It consisted of (1) leaching ashes, filtering the solution, and evaporating to dryness (the residue was mostly potassium carbonate); (2) mixing this material with scrap iron and animal byproducts, such as leather, dried blood, and hooves, and then heating strongly; (3) after cooling, extracting the mass with water, filtering, and evaporating to dryness. This yielded crystals known as "yellow prussate of potash," from which pigments such as Prussian blue and Berlin green were made. About a century later, chemists identified "yellow prussate of potash" as a double cyanide of potassium and iron, formulated as $4KCN{\cdot}Fe(CN)_2$. Brilliant research in the 1890s by the Swiss chemist Werner demonstrated that in these "complex compounds" all of the cyanide ions are bonded to the iron, and that the structure of the "complex" ion is octahedral, as sketched. Thus the formula was written as $K_4Fe(CN)_6$. Hundreds of thousands of complex compounds are known today. The atoms or molecules bonded to the central atom are known as ligands. Aside from octahedral structures, others are linear, triangular, tetrahedral, square, or other geometrical forms. Many biologically active substances, such as hemoglobin and chlorophyll, are complex compounds.

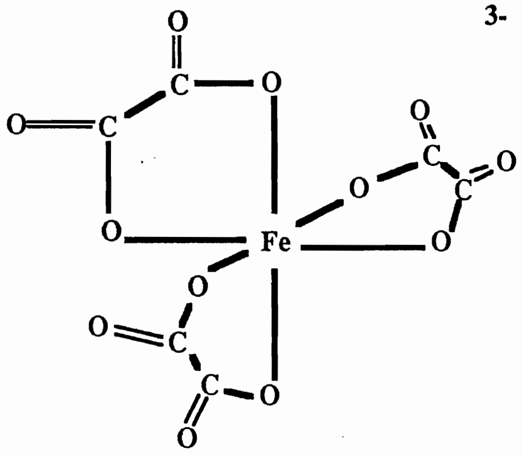


Structure of iron-cyanide complex.

Chelates. – Many ligands are bonded to the central atom by two or more atoms. An example is the oxalate complex of iron, sketched. The oxalate ion is:



Since the iron atom, in the center of an octahedron, has its bonds directed to the six corners, it can accommodate six oxygen atoms, and thus three oxalate ions. When this type of structure was first realized, the oxalate ion, seizing the iron atom in pincers, was likened to the claw of a crab. The name **chelate** was adopted for such complexes, from the Greek word for claw, *chele*.



Iron-oxalate complex.

Chelates in general tend to be more stable than simple complexes with the same type of atoms. Stability is quantified by the equilibrium constant representing its formation. Thus for the copper ion (Cu^{2+}) and ammonia (NH_3), the complex is $Cu(NH_3)_4^{2+}$. Its formation constant is 10^{12}. But if four ammonia molecules are bound together into a linear molecule (by replacing some of the hydrogen atoms with organic groups), the ligand becomes:

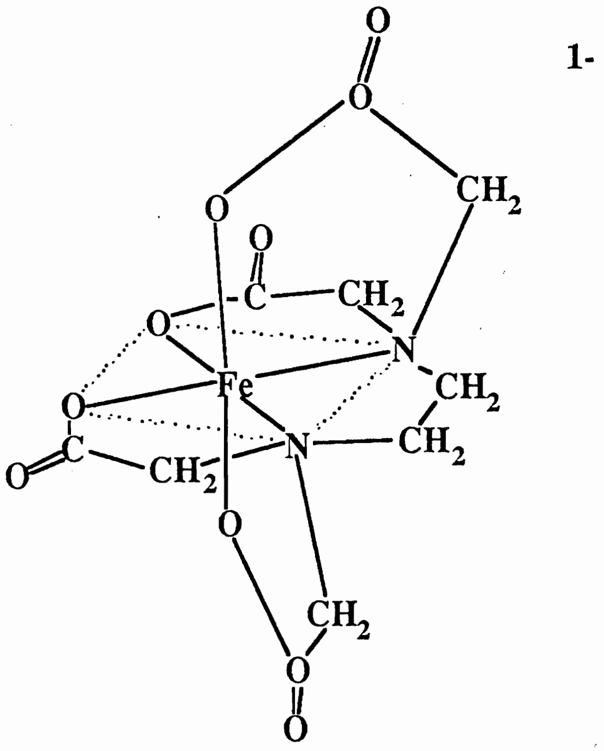
$$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$$

On reacting with copper ion, the long molecule wraps around the metal atom and all four nitrogen atoms link to the metal, forming a strongly-bonded chelate. Its formation constant is 10^{20}, a value one hundred million times that of the simple ammonia complex.

Chelates in Reactor Waste. – It is this enhanced stability, among other factors, which enable certain chelating agents to remove the scale of oxides and related materials from the cooling piping of nuclear reactors. The most important chelating agents used are:

EDTA, ethylenediaminetetraacetic acid, $[HOOC\text{-}CH_2]_2NCH_2CH_2N[CH_2\text{-}COOH]_2$
NTA, nitrilotriacetic acid, $N(CH_2COOH)_3$
Picolinic acid, alpha-pyridinecarboxylic acid, C_5H_4NCOOH
Oxalic acid, HOOC-COOH
Citric acid, $HOOC\text{-}CH_2COH(COOH)\text{-}CH_2COOH$

In the case of EDTA, loss of the four hydrogen atoms from the -COOH groups permits all four oxygen atoms, as well as the two nitrogen atoms, to bond to a metal. Thus this single molecule is able to form exceedingly stable chelates. The structure of the iron chelate is shown here:



Iron-EDTA chelate.

EDTA is resistant to degradation by radiation and to microbial decomposition. It is frequently employed in reactor cleaning cycles. Both oxalic and citric acids degrade by microbial action.

Sorption of Ions by Soil. – Many components of soil are capable of sorbing ions of metals. These include clays such as kaolinite and montmorillonite, zeolites, hydrated iron oxides, hydrated silica and titanium dioxide, and organic matter. The process is quantified by an approximate equilibrium constant (the distribution constant, K_d), which has dimensions of volume per mass unit of metal ion. When this constant is zero, it means no adsorption takes place. The higher the value, the more strongly the metal is adsorbed. The values are affected by the acidity level (pH) and other factors, all of which must be specified.

There is frequently a considerable difference in the degree of adsorption of a metal ion (positively charged) and the same metal in chelated form (generally negatively charged). For example, on kaolinite at pH 6, unchelated cadmium ion (Cd^{2+}) has a K_d value of 15, meaning it is sorbed significantly. In chelated form ($CdEDTA^{2-}$) the value is 4, meaning it is not sorbed nearly as much. In general terms, this behavior can be attributed to the charge at sorption sites on the kaolinite. If these sites bear a negative charge, as is often the case with clays, they attract the positively-charged cadmium ion in unchelated form, but repel the negatively-charged chelate ion. In addition, there is a size effect: The smaller cadmium ion can closely approach a small site, while the larger chelate cannot. These arguments are not always the case, however, and laboratory tests using samples of the soil in question should be conducted. No simple rule applies to all cases. Owing to the porous nature of soil components, equilibrium is generally reached slowly.

Any radioactive waste which contains EDTA or similar chelating agent is more likely to leak dangerous radionuclides than waste without the complexants. This mobilization of radioactive elements is a serious consideration to be taken into account in repositories.

Colloids. – Colloids are aggregates of molecule or ion assemblies which have radii of 50 to 100 nanometers. Ions range up to 1 nanometer in radius. Colloidal suspensions look turbid owing to their property of scattering light. Suspended in water, colloids pass through ordinary filter paper, and require an ultra centrifuge to throw out of suspension. Most often, colloids bear either a positive or negative charge because of adsorbed cations (positive) or anions (negative). Positively charged colloidal particles, on close approach to each other, mutually repel; negative colloids behave the same way. This property leads to stabilization of colloidal suspension. If the charge on a colloid is neutralized by sorption of a suitable ion of opposite charge, the charge on the particles disappears and coagulation takes place; in fact that is how deltas are formed when colloidal silt runs into the ocean, and suspended material precipitates.

Clearly colloidal particles have large surfaces. If they sorb radionuclides, they are capable of transporting the material great distances. This possibility is another which one must cope with in designing radioactive waste repositories. Test should be made for the presence of colloidal matter in groundwater, and a study of its carrying capacity made.