

RECENT RESULTS FROM CHARACTERIZATION OF FERROCYANIDE WASTES AT THE HANFORD SITE

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ABSTRACT

Public Law 101-510, Section 3137, "Safety Measures for Waste Tanks at Hanford Nuclear Reservation," (1) requires that Westinghouse Hanford Company develop plans to resolve safety issues for tanks that could experience excessive temperature changes or pressure increases, resulting in a release of radioactive material from any high-level waste tank at the Hanford Site. Fifty-three tanks have been identified and categorized by tank contents. These include tanks that a) contain ferrocyanide compounds, b) have the potential for flammable gas generation, c) contain organics, or d) have high-heat loads.

The ferrocyanide and hydrogen gas safety issues have been declared unreviewed safety questions (USQs) because postulated accident scenarios may fall outside safety envelopes defined by existing safety analysis documentation (2). Both USQ issues were reported at Waste Management '92 (3, 4). Detailed research has been conducted to provide insight into the severity of the ferrocyanide tank safety issue. Work included waste characterization and investigation of the energetic behavior of ferrocyanide waste material. The data presented will focus on "In-Farm" simulant studies and information from tank 241-C-112, core samples 34 and 36.

BACKGROUND

Radioactive waste from defense operations has been accumulating in underground high-level waste tanks at the Hanford Site since the mid-1940's. There are 177 waste tanks: 149 single-shell tanks and 28 double-shell tanks. Over the years, waste has been systematically transferred among the various tanks. The two primary objectives of waste management operations were to segregate different types of waste and to reduce the need for additional tanks by concentrating the waste. With the increased emphasis on defense materials production in the early 1950's, tank space was at a premium. It became necessary to increase the available waste tank storage volume while minimizing the construction of new tanks. A method was developed that disposed large volumes of low activity liquids to engineered disposal sites: cribs and trenches. The treatment involved the ^{137}Cs and ^{90}Sr decontamination of uranium recovery plant waste using ferrocyanide in a carrier precipitation process. This treatment was used both on the U-Plant waste effluent and on selected wastes that had been previously discharged to the tanks. As a result of this process, occupied waste volume in the tanks was greatly reduced, while minimizing the amount of long-lived radionuclides discharged to the ground.

Tank C-112 was the last in a three-tank cascade. It was constructed of reinforced concrete with a carbon-steel liner and had a nominal capacity of 2 million liters (530,000 gallons) (refer to Fig. 1). The first waste received in tank C-112 was first-cycle decontamination waste from the bismuth phosphate process (1946-1952). These tank wastes were disposed to the ground in 1952, leaving a 57,000-liter (15,000-gallon) heel. The tank was refilled with unscavenged uranium recovery (UR) waste in 1953 and 1954. In late 1955 tank C-112 was essentially emptied. The tank was then used for settling scavenged ferrocyanide waste until 1958. During ferrocyanide-scavenging operations, waste was not cascaded through the C-110, -111, -112 tank series. Tank C-112 received the waste slurry in direct transfers from the process vessel.

Beginning in May 1955, unscavenged UR waste already stored in tanks at the chemical processing facilities at the 200 East Area of the Hanford Site was routed to the 244-

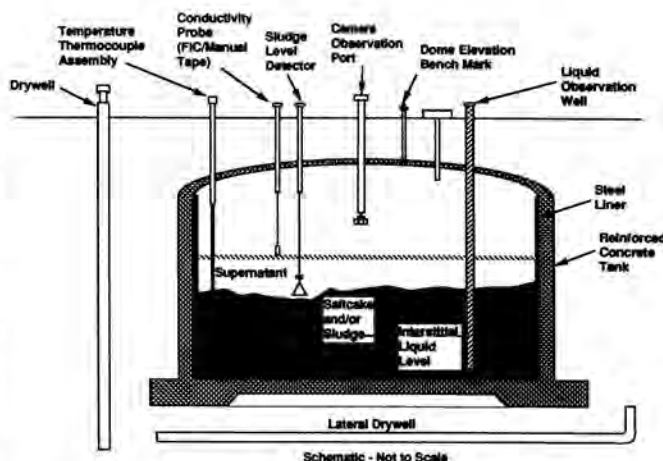


Fig. 1. Typical single-shell tank.

CR vault for scavenging (refer to Fig. 2). The 244-CR vault facility contained stainless steel tanks with chemical addition, agitation, and sampling capabilities. The pH was adjusted with HNO_3 and/or NaOH to $\text{pH } 9.3 \pm 0.7$, and $\text{Fe}(\text{CN})_6^{4-}$ and Ni^{+2} ion were added (generally to 0.005 M each) to precipitate ^{137}Cs . If laboratory analysis of the feed tank indicated additional ^{90}Sr decontamination was necessary, calcium nitrate was also added (5). Additionally, there was an effort to scavenge ^{60}Co with Na_2S . The scavenged waste was then routed to another tank for settling, sampling, and decantation to a crib. The primary settling tanks for this "In-Farm scavenged" waste were C-108, -109, -111, and -112. The first transfer of scavenged waste for settling was in the fourth quarter of 1955. In-Farm scavenging was completed in December 1957.

Available chemical process information indicates that there were three significantly different types of ferrocyanide waste. Nonradioactive waste simulants have been developed and tested using this information. The U-Plant ferrocyanide waste, accounting for ~70% of the total ferrocyanide waste, was formed from treatment of the U-Plant uranium recovery flowsheet effluent. This effluent had relatively large amounts

Ferrocyanide Production by "In-Farm" Flowsheet

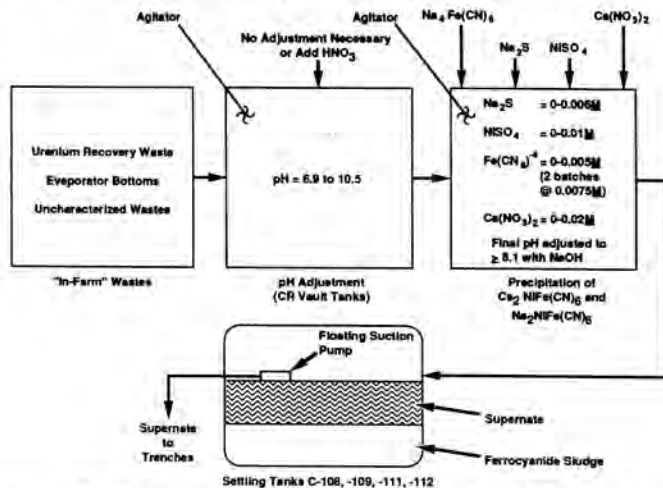


Fig. 2. Ferrocyanide production by "In-Farm" flowsheet.

of inert solids in the waste stream; thus, this waste is quite dilute in ferrocyanide. U-Plant waste simulants do not exhibit any propagating exothermic activity when examined by differential scanning calorimetry (DSC), even when dry. However, a heat of reaction can be determined by examining a large sample using adiabatic calorimetry. T-Plant ferrocyanide waste, accounting for ~10% of the total ferrocyanide waste, is a variant of U-Plant waste. The U-Plant scavenging scheme

was used on bismuth phosphate first cycle decontamination waste instead of UR waste. T-Plant waste is expected to possess energetic behavior similar to U-Plant waste; however, no simulant studies of this waste have been performed to date. In-Farm ferrocyanide waste, accounting for ~20% of the total ferrocyanide waste, was formed from treatment of waste that was already in the tanks. Most of this waste had less inert solids in the waste stream; thus, it is believed to be more concentrated in ferrocyanide than the U-Plant waste. Table I compares the values for selected analytes between the C-112 materials and the In-Farm simulants. In-Farm simulants exhibit propagating exothermic activity when examined by differential and adiabatic scanning calorimetry. The waste in tank C-112 was produced using the In-Farm flowsheet process.

After the end of scavenging in late 1957, tank C-112 remained in active service. However, the tank had limited activity from 1958 to the end of its service life in 1980 and, during that time, there were no extensive transfers of waste in or out of tank C-112. Several small transfers having relatively high concentrations of ^{90}Sr occurred after 1958. From 1960-1962, tank C-112 received several transfers from the Strontium/Hot Semiworks and transfers of highly alkaline coating waste. In 1970 and 1975, there were transfers from the C-301 catch tank and from tank C-110. During its operating history, the tank was never subject to any of the various In-Tank solidification processes; thus, there was no formation of hard salt cake in the tank. The tank was removed from active service

TABLE I
Tank 241-C-112 Comparison of Waste Materials with Simulants^a

Analyte	In-Farm Simulant Values	Core 34 Values	Core 36 Values
Ni ($\mu\text{g/g}$) ^b	27,600	Quarter segment range: 22,000-28,300 Composite value: 30,000	Quarter segment range: 900-23,000 Composite value: 12,800
Ca ($\mu\text{g/g}$)	36,400	Quarter segment range: 21,700-28,200 Composite value: 29,000	Quarter segment range: 2,100-28,600 Composite value: 20,400
Wt% H ₂ O	41-50%	Quarter segment range: 45-58% Composite value: 38%	Quarter segment range: 41-64% Composite value: 45%
Wt% total cyanide (dry basis)	9.1 - 11.3%	Quarter segment range: 0.43 to 0.83 Composite value:	Quarter segment range: 0.40 to 0.92 Composite value: 0.71
ΔH (kJ/dry g)	-1.05	Quarter segment range: -0.02 to -0.03 Composite value: -0.02	Quarter segment range: -0.02 to -0.03 Composite value: -0.04
Density	1.4	Bulk value: 1.5 to 1.6	Bulk value: 1.3 to 1.6

^a Agreement between synthetic sludge properties and observed waste characteristics are within the constraints of the synthetic recipes and assumptions regarding chemical behavior in the tank.

^b Nickel concentrations are potentially biased high; values are derived from an inductively coupled plasma - atomic emission spectroscopy assay, fusion preparation performed in a nickel crucible. However, in each case the blank value was an order of magnitude (or greater) less than the measurement. The fusion values are comparable with acid digestion values, where both are available.

in 1980. Various descriptions of the tank's transfer history can be found in several documents; "Record of Scavenged TBP Waste" (6) has the most detailed information. Borsheim and Simpson (7), Anderson (8) and Jungfleisch (9) also have tank transfer data.

FERROCYANIDE TANK 3-COMPONENT DIAGRAM

REACTION PROPAGATION VS. CONCENTRATION

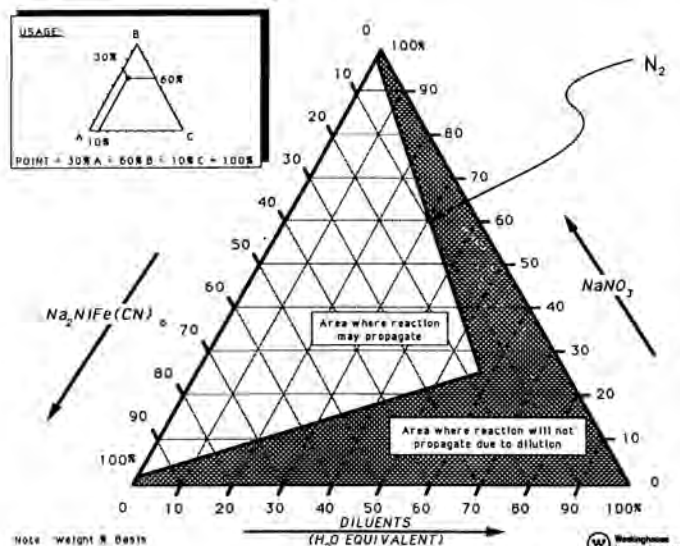


Fig. 3. Ferrocyanide tank 3-component diagram.

ANALYTICAL RESULTS

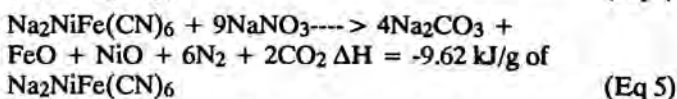
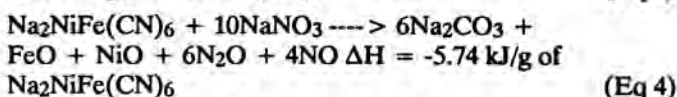
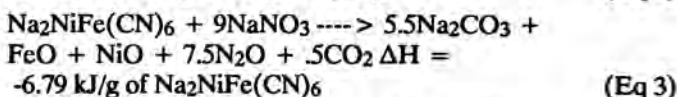
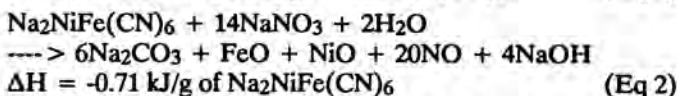
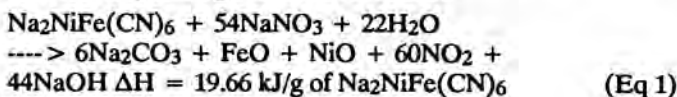
Analysis of the waste shows a very small number of analytes comprising a large portion of the waste. Water is the single largest analyte, making up between 41-65% of the total mass. Six elements (aluminum, calcium, iron, sodium, nickel, and uranium) constitute approximately 19-24% of the mass and represent over 90% of the metals detected. Two anions (NO_2^- and NO_3^-) constitute approximately 12.5% of the mass and represent over 65% of the total anions. The total cyanide in the waste was found to be less than 1.0 wt% in every case.

Gamma scans of the core samples were performed prior to extrusion. The only significant gamma emitters found in the waste was ^{137}Cs . No meaningful regional concentrations (hot spots) of radioisotopes or fuel were detected along the vertical axis in either core. Chemical analysis of the samples showed the ^{137}Cs concentration was relatively constant between core 34 and core 36, and the regions with high nickel concentrations correlated with the ^{137}Cs peaks in the gamma scans. These observations are consistent with the historical information regarding the ferrocyanide-scavenging process, the gamma activity pattern obtained from the scans, and the inductively coupled plasma-atomic emission spectroscopy cation distribution through the quarter segments. The other major source of radiological activity was ^{90}Sr , which had a very skewed distribution between core 34 and core 36, probably arising from the later waste transfers into tank C-112. The relatively high ^{90}Sr concentrations are believed to be a local phenomena because the bulk waste temperature in the tank obtained from two thermocouples is 29°C (85°F) and heat load calculations using the higher ^{90}Sr concentrations do not reflect the tank waste temperature measurements. The radiological activity of tank C-112 waste material was relatively low (ranging from 0.15 - 2 R/hr, measured through the drill string). No significant radiological activity was found in the drainable liquid in the

tank or in the water or acid digestion of the samples. This suggests that the radionuclides were relatively insoluble.

WASTE ENERGETICS

Estimates of tank waste reactivity developed after the ferrocyanide USQ was declared were based on thermodynamic estimates (10). Several chemical reaction pathways were evaluated and heats of reaction determined for each possible reaction from the published heats of formation of the reactants and the products. The theoretical heats of reaction ranged in value from $\Delta H = -9.62$ kJ/g of $\text{Na}_2\text{NiFe}(\text{CN})_6$ to $\Delta H = 19.66$ kJ/g of $\text{Na}_2\text{NiFe}(\text{CN})_6$ and are listed below with their corresponding chemical reactions.



At temperatures below 1700°C the carbonate product is thermodynamically favorable and should predominate (10). Note that considerably lower values are obtained if the reaction is incomplete, or if NO or NO_2 is formed rather than N_2 or N_2O . A three-component diagram illustrating the exothermic potential of various mixtures (in weight percent) of ferrocyanide, nitrate, and inerts is presented in Fig 3.

Next, waste simulants were prepared using the In-Farm and U-Plant process flowsheets and tested for chemical activity. Chemical and physical analyses of the In-Farm and U-Plant waste simulants shows that they contain about 50 and 65 wt% water, respectively, after centrifugation at 2,500 g. The centrifugation was done to represent 30 gravity-years of compaction that may have occurred during storage. This amount of water in the waste matrix presents a tremendous heat sink that must be overcome before any reactions can take place. During the DSC examinations, the samples exhibited very large endotherms. Results from thermogravimetric analyses being run at the same time showed a large loss of mass (i.e., evaporation of water), thus reactions were only able to take place in dry or nearly dry sample material. Total cyanide content of the waste simulants (based on all cyanide present bound in ferrocyanide) is 9.1 to 11.3 wt%. Table II presents the ΔH found for some various simulant materials.

In April 1992, three core samples of waste were obtained from tank C-112, a tank considered to contain one of the highest concentrations of ferrocyanide. All three cores were broken down into smaller subsegments and examined for reactivity using DSC; none of the samples exhibited any propagating behavior. The samples had a moisture content ranging from 41 to 64 wt% and a ΔH ranging from -0.01 kJ/g of dry material to -0.04 kJ/g dry material. The onset temperatures for

TABLE II
Heats of Reaction of Various Simulants

Material	ΔH (by Adiabatic Calorimetry)
$\text{Na}_2\text{NiFe}(\text{CN})_6$	-3.95 kJ/g of dry material
U-Plant-2 simulant	-0.35 kJ/g of dry material
In-Farm-1 simulant	-1.05 kJ/g of dry material
The onset temperatures for the reactions to take place in the simulants range from 244 to 278°C (12).	

the exotherms ranged between 275 and 290°C, close to that predicted by the simulants. Further chemical analysis indicates that the waste material has a total cyanide content of less than 1.0 dry wt%. This value is much lower than expected from the simulant formulations and, correspondingly, tank C-112 waste material is not as energetic as the analogous waste simulants. Tables III and IV present the key analytes as they relate to the energetic properties of the waste.

Thermodynamic and kinetics (propagation) studies are bounding the reactivity of the ferrocyanide/oxidizer reactions. Results indicate that U-Plant ferrocyanide wastes cannot create a propagating hazard; T-Plant waste is expected to behave similarly. Ferrocyanide waste made by the In-Farm flowsheet, representing 20% of the ferrocyanide inventory added to the tanks, is more reactive. However, moisture precludes a reaction if the In-Farm waste contains at 12 - 15 wt% water.

Indications from core 34 data show that material has physical and chemical properties corresponding to those ex-

pected for ferrocyanide waste. Water content, nickel, calcium concentrations, and density values are consistent with the simulant values. Indications from core 36 data show that the material appears to have ferrocyanide waste overlying a bismuth phosphate first cycle decontamination and/or uranium recovery waste heel. The concentration of nickel, calcium, ^{137}Cs , and uranium as a function of depth appears to confirm this observation. In addition, this behavior is consistent with historical information. However, in both cases DSC results from the suspected ferrocyanide waste in tank C-112 indicate that the material is not as energetic as the corresponding waste simulant. Figures 4 and 5 illustrate the concentrations/magnitudes of the radionuclides as a function of depth. Results of aging studies now underway on flowsheet simulants may demonstrate that radiolytic, hydrolytic, and thermal processes in the tanks, over the last 35 years, have combined to dissolve, dilute, and destroy the reactive ferrocyanide compounds. The data from tank C-112 indicate that the waste lacks the fuel to sustain any propagating exothermic behavior and a heat source intense enough to trigger a reaction.

Experimental and analytical evidence indicates that the potential risk of storing ferrocyanide compounds in Hanford Site high-level waste tanks is considerably less than postulated earlier and that the consequences of an event have been significantly overestimated.

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TABLE III
Tank 241-C-112 Core 34 Key Analytes

Quarter Segment	^{137}Cs ($\mu\text{Ci/g}$)	^{90}Sr ($\mu\text{Ci/g}$)	Wt% Total Cyanide	Wt% Water	Heat of Reaction (kJ/g waste) dry basis
1D	240	1300	0.52	45	-0.02
2B	610	4900	0.43	53	-0.03
2C	800	1100	0.83	58	-0.03
2D	510	2500	0.75	52	-0.03
Composite	750	2500	0.97	38	-0.02

TABLE IV
Tank 241-C-112 Core 36 Key Analytes

Quarter Segment	^{137}Cs ($\mu\text{Ci/g}$)	^{90}Sr ($\mu\text{Ci/g}$)	Wt% Total Cyanide	Wt% Water	Heat of Reaction (kJ/g waste) dry basis
1C	560	1900	No measurement	49	-0.02
1D	1200	15	0.72	58	-0.03
2A	880	20	0.92	57	-0.02
2B	530	70	0.75	41	-0.02
2C	100	140	0.40	64	No exotherm
2D	40	200	0.56	56	No exotherm
Composite	790	510	0.71	45	-0.04

Core 34: Radionuclides as a Function of Depth

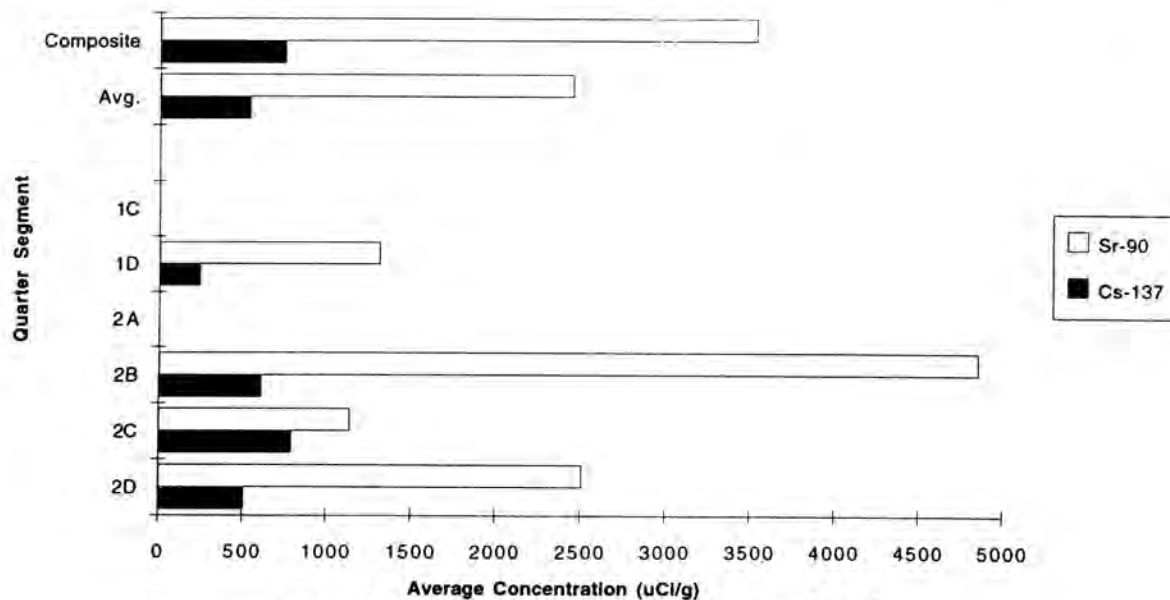


Fig. 4. Core 34: radionuclides as a function of depth.

C-112 Core 36: Radionuclides as a Function of Depth

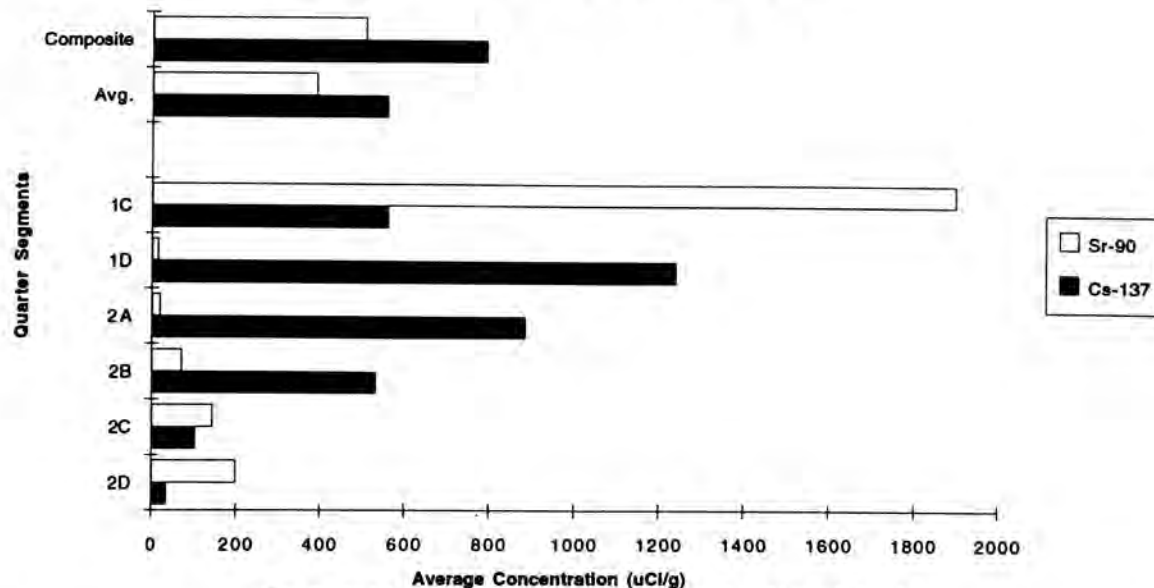


Fig. 5. C-112 Core 36: radionuclides as a function of depth.

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