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VOLUME REDUCTION of radioactive waste by CARRIER PRECIPITATION

A new waste-scavenging process removes cesium-137 and strontium-90 on carrier precipitates, permitting the disposal of large volumes of wastes to ground. The demonstrated ability of metal ferrocyanides to remove Cs from aqueous wastes suggests their use in a Cs recovery process.

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After pile irradiation of uranium fuel elements has taken place, it is necessary to separate uranium and the plutonium produced and to decontaminate both products from fission products produced during irradiation as well as from unwanted components of the fuel elements. Several processes (at Hanford) accomplish this separation and decontamination, all of which generate large volumes of radioactive wastes.

These radioactive process wastes may be disposed of by various means, such disposition depending on the level of radioactivity contained. Low-level wastes such as process vessel cooling water and certain condensates may be discharged to open areas and permitted to seep into the ground. Intermedite level wastes which satisfy locally established criteria with respect to contamination of ground water may be discharged to ground directly through a "crib." Acidic intermediate level wastes are made alkaline and are passed through a "cascade" of settling tanks prior to discharge of the supernatant liquid to cribs. Much of the radioactive material is carried on alkaline insoluble materials present in the wastes. A typical settling cascade is shown in Figure 1, and a typical underground crib is shown in Figure 2.

Intermediate or high-level wastes which cannot be cribbed are stored in large underground tanks. A cross section of a typical underground tank is shown in Figure 3. These tanks are expensive to build. Although the expected normal life of such tanks is long (perhaps in the range of 100 yr.), the possibility always exists of premature rupture due to unusual chemical environment, earthquakes, or bombing in the event of war. Obviously, any process modification or addition which reduces the volume of waste to be stored reduces the cost of waste handling. Also those process changes which result in ultimate storage of high-level wastes as solids rather than as liquids reduce the hazard of ground-water contamination in the event of storage-tank rupture. As discussed in the next two sections, considerable progress has been made in accomplishing both these objectives.

Reduction of Stored-Waste Volume

Several procedures have been developed, including evaporation of intermediate and high-level radioactive wastes (*3*), reuse of slightly radioactive chemicals (*4*), use of heat generated by radioactive constituents present to evaporate stored wastes (*7*), and carrier precipitation techniques which permit discharge of supernatant liquids to ground.

An evaporator arranged for batch operation is shown in Figure 4. Continuous operation is, of course, possible. For the particular waste processed in such systems, up to 70 vol. % is removable in one pass. After the concentrated waste cools and settles, about 30 vol. % of the supernatant liquid is removed on a second pass.

Major reductions in stored waste volume per unit of uranium processed are achieved by reuse of chemicals. In two solvent extraction processes, back-cycling of aqueous raffinates from later cycles for use as salting agent in earlier cycles has reduced the volume of waste going to underground storage by a factor of about three. Even larger reductions are made in a process utilizing an acid as salting agent through recovery of most of the acid for reuse.

Further reduction in the volume of high radiation-level stored waste is made possible through evaporation in the storage tanks by the use of heat generated by radioactive decay of fission products (*7*). For a solvent extraction process utilizing a nonacid salting agent, a volume reduction of a factor of two has been attained, and a factor of three is anticipated. Where an acid salting agent is used and most of the acid is recovered, the volume of waste stored per unit processed may be sufficiently low to evaporate all the water present, in which case it will be necessary to replace the water for many years to maintain fluidity until nearly all of the radioactive heat generated has been dissipated.

Major reductions in the volume are also possible through scavenging techniques designed to remove the more hazardous radioactive materials from the waste followed by discharge of the decontaminated liquid to the ground.

Volume Reduction by Carrier Precipitation

In order to understand why certain moderately high level radioactive solutions can be safely discharged to ground at the Hanford site, it is necessary to consider briefly the climate and geology of the area.

The climate is semiarid; rainfall averages about 7 in./yr., most of which occurs in the winter months. Summers are hot and dry. Thus, surface conditions affect soil conditions to a depth of only a few feet.

The site was at one time a large inland lake which has been filled subsequently with alluvial sand and gravel to a depth of 250-300 ft. above the water table. In some places, remnants of a fine silt layer deposited while the region was covered with water remain above the present water table and act as a barrier toward movement of surface water to ground water. Data derived from numerous tests show that the motion of ground water toward the Columbia River is slow. Travel time, depending on the direction of flow, from the point where wastes are discharged to the Columbia River have been estimated to range from 50 to 1,500 yr. Other studies have shown that the clay fraction of the soil has good ion exchange properties and that cations of high charge ($>$ II) are held tightly by the soil (*6*). Cations of low charge, although adsorbed, are less tightly held (*5*). Thus, wastes discharged

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Table 1.—Typical Aqueous Waste Composition

Constituent	Concentration range, moles/liter
Na^+	2.5 to 8.0
H^+	Up to 3
NO_3^-	4 to 7
$PO_4^{\equiv}$	0.05 to 0.25
Fe^{+++}	Up to 0.02
Cs^{137}	10 to 100 μc/ml.
Sr^{90}	1 to 100 μc/ml.

near the surface of the ground must pass through a long (200-250 ft.) ion exchange column to reach ground water and then make a several-mile journey, taking many years to reach the Columbia River where they can come in contact with plants or animals. Under these conditions, radioactive constituents of short half-life (< 3 years) are of little concern.

Among the long-lived isotopes, only Cs^{137} and Sr^{90} exist in solution as low-charged cations. If radioactive wastes are discharged in such manner that neither Cs^{137} nor Sr^{90} reach ground water in hazardous amounts, the system is safe with respect to other long-lived nuclides. Soil column tests have shown that, if the concentration of Cs^{137} and Sr^{90} in a high salt content radioactive waste is low (< 0.1 mc./ml.), three to six column volumes of the waste can be passed through the soil before either of these isotopes appears in the effluent in an amount exceeding 0.1 maximum drinking water concentration (M.P.C.—maximum permissible drinking water concentration). It is a locally established objective that radioactive wastes shall be discharged in such manner that the ground water will not be contaminated in any place to greater than 0.1 M.P.C. in any long-lived (> 3 years) radionuclide.

One unit at Hanford produces large volumes of moderately high-level radioactive waste. Table 1 shows concentration ranges of significant constituents of the waste. The process adopted uses coprecipitation, followed by settling, to concentrate Cs^{137} and Sr^{90} in a sludge, leaving the waste solutions below cribbing limits. Economic and timing considerations required that the process:

(a) Be inexpensive, with cost for treatment and disposal less than 20 cents/gal.

(b) Use existing plant equipment.

(c) Be an operation in which necessary chemicals could be added to the waste as it is produced, the precipitates formed to settle in existing underground tanks.

(d) Have a final pH of 7.5 or greater to prevent corrosion, since the tanks have mild steel liners.

(e) Have Cs and Sr decontamination factors as high as 1,000.

(f) Permit precipitates to settle rapidly and cleanly, have a small settled volume, and be pumpable as a slurry.

These wastes contain ferric ion. When alkaline, the ferric hydroxide and phosphate mixture which precipitates carries most of the strontium present, particularly if the *p*H is high (>11). However, little cesium is carried. Nickel ferrocyanide is the carrier precipitate for cesium which gives the high decontamination factors required; it performs satisfactorily to a *p*H of 10, and at low cost.

Table 2 shows typical Cs removal efficiency of nickel ferrocyanide at various *p*H. High decontamination factors (>1,000), obtained at *p*H below 10 and the abrupt decrease in carrying *p*H above 10, are apparent.

Additional strontium decontamination is obtainable by addition of calcium or strontium nitrate to the waste, with calcium or strontium sulfate and/or phosphate precipitation believed responsible. Table 3 gives typical strontium decontamination data obtained with and without supplemental scavenging. Table 4 shows the dependence of strontium decontamination upon the *p*H with supplemental scavenging.

A schematic flow diagram (Figure 5) shows how the process is carried out in the plant. Sodium ferrocyanide and strontium nitrate are added to the acidic waste as produced. Sodium hydroxide and nickel sulfate are added continuously to the waste as it enters a large mixing and holdup tank. A continuous *p*H recorder-controller monitors the *p*H and controls the caustic addition rate to maintain the *p*H at about 9.5. Because the waste is not buffered in the limited operating *p*H range (7.5 to 10), close control of caustic addition is required. Continuous monitoring has proved a satisfactory means to obtain control of *p*H to ±0.5 units routinely in the plant.

The alkaline waste is then transferred to large underground tanks where the precipitates settle out. After settling, the supernatant liquid is sampled and analyzed for Cs^{137}, Sr^{90}, and other constituents of special interest in the cribbing program. Soil column tests are made to determine adsorption of Cs^{137} and Sr^{90} remaining in the supernatant liquid. Recommendations based on these data then are made on the volume of the scavenged waste which may be discharged per unit area of crib.

Supernatant liquids satisfactory for discharge to ground are decanted with a floating suction pump. Since the sludge is also pumpable, a gamma sensing device which will stop the pump if a sharp rise in gamma activity occurs is mounted on the discharge end of the pump. Extra large cribs are designed to handle the large volumes of liquid involved in this process. To insure that the entire area of a crib is covered whenever liquid is discharged to it (to prevent channeling of liquid in the soil), a flush tank similar to the flush tank on a toilet is installed in the line. This tank alternately fills at the regular pumping rate and then discharges to the crib at a rate many times the pumping rate.

Future Use of Process

So far, several million gallons of waste have been decontaminated successfully by this procedure and discharged to ground. An over-all saving

Table 2.—Effect of pH on Nickel Ferrocyanide Scavenging of Cesium

pH Before scavenging (range) (avg.)	Cs^{137} in supernatant liquid μc./ml.
	20 to 100
7	0.033
8	0.043
9	0.055
10	0.10
11	24.0
12	34.0

Table 4.—Effect of pH on Scavenging of Strontium by Addition of Nonradioactive Calcium or Strontium

pH	Sr^{90} in supernatant liquid, μc./ml. Inert strontium	Inert calcium
Before scavenging (range)	20 to 100	20 to 100
7	0.54	1.8
8	0.15	1.2
9	0.09	0.38
10	0.05	0.15
11	0.08	0.15

Table 3.—Comparison of Scavenging Methods Plant Experience

pH 8 to 10

Method	Avg. residual radioactivity in supernatant liquid, μc./ml. Cs^{137}	Sr^{90}
$Ni_2Fe(CN)_6$	0.057	0.82
$Ni_2Fe(CN)_6 + Ca_3(PO_4)_2$	0.026	0.22
$Ni_2Fe(CN)_6 + Sr_3(PO_4)_2$ or $SrSO_4$	0.016	0.046

of more than $500,000 has been realized to date on the process. It is anticipated that the process will be used, with modifications to account for local conditions, for the treatment and disposal of several more millions of gallons of waste, some yet to be produced and some already produced and stored before the process was developed.

Limitations

It should be pointed out that the process has definite limitations both as to the sites where it may be used and to the waste solutions for which it is applicable. The wastes after treatment still contain relatively large amounts of short-lived radionuclides, particularly ruthenium and zirconium isotopes. Also the amounts of Cs^{137} and Sr^{90} (0.1 μc./ml.) left after treatment are greatly in excess of the M.P.C. for these isotopes (1.5×10^{-3} and 8×10^{-7} μc./ml., respectively) (*2*). Therefore, the treated wastes would not be satisfactory for discharge to ground unless the combination exists of a long soil column capable of absorbing Cs, Sr, and other long-lived nuclides present and a long retention time in the ground water prior to any possible use of the ground water by plants or animals.

Use of mild steel tanks as settling basins (practiced at Hanford) limits the useful *p*H range for the process to from 7.5 to 10. Consequently, the process is not applicable without modifications to high salt solutions wherein the salt cation is insoluble in this *p*H range.

Other Use

The ability of metal ferrocyanides to remove cesium from radioactive wastes could easily be the starting point for an actual cesium recovery process. W. H. Burgus and H. W. Miller have reported at least one such process (*1*).

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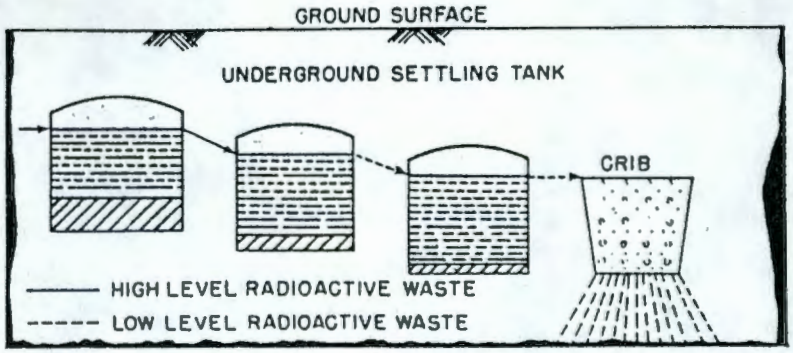

Fig. 1. Typical cascade system supernatant liquid flows to crib

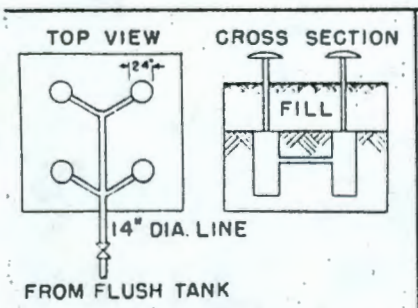

Fig. 2. Cross section and arrangement of a crib

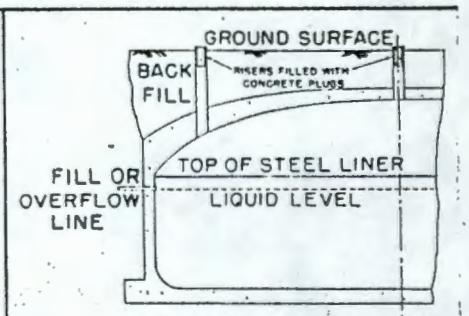

Fig. 3. Cross section of underground storage tank

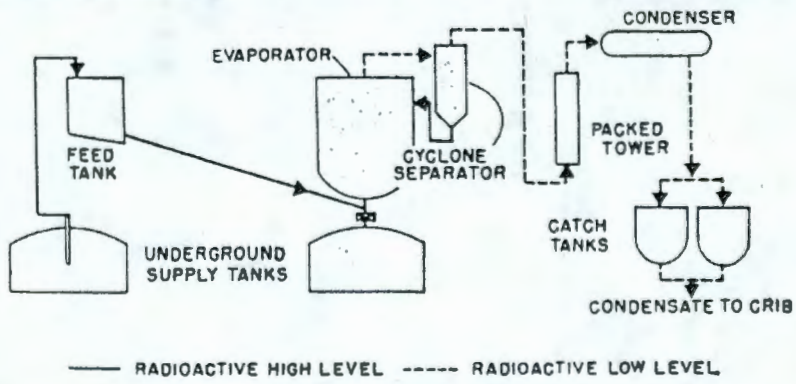

Fig. 4. Batch waste evaporator

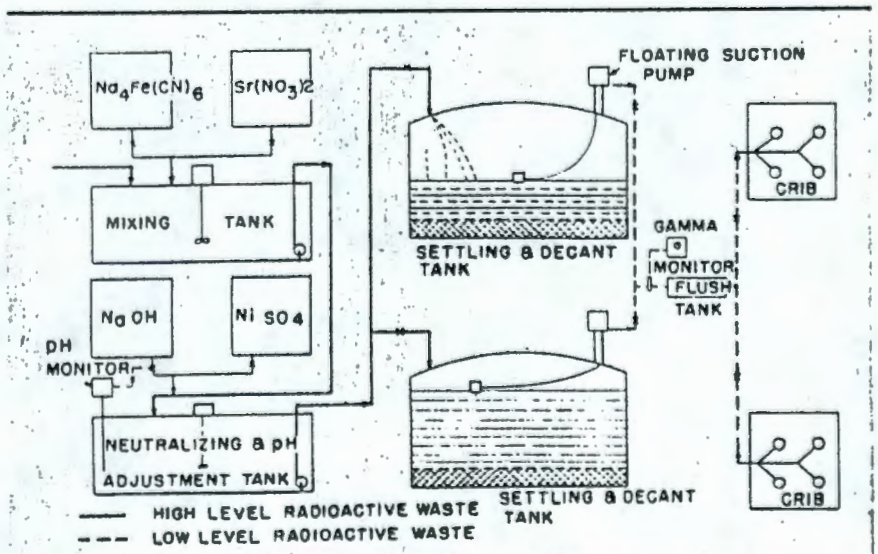

Fig. 5. Schematic flow diagram for scavenging of cesium and strontium