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# Historical Review of Oak Ridge National Laboratory Grout Injection Program

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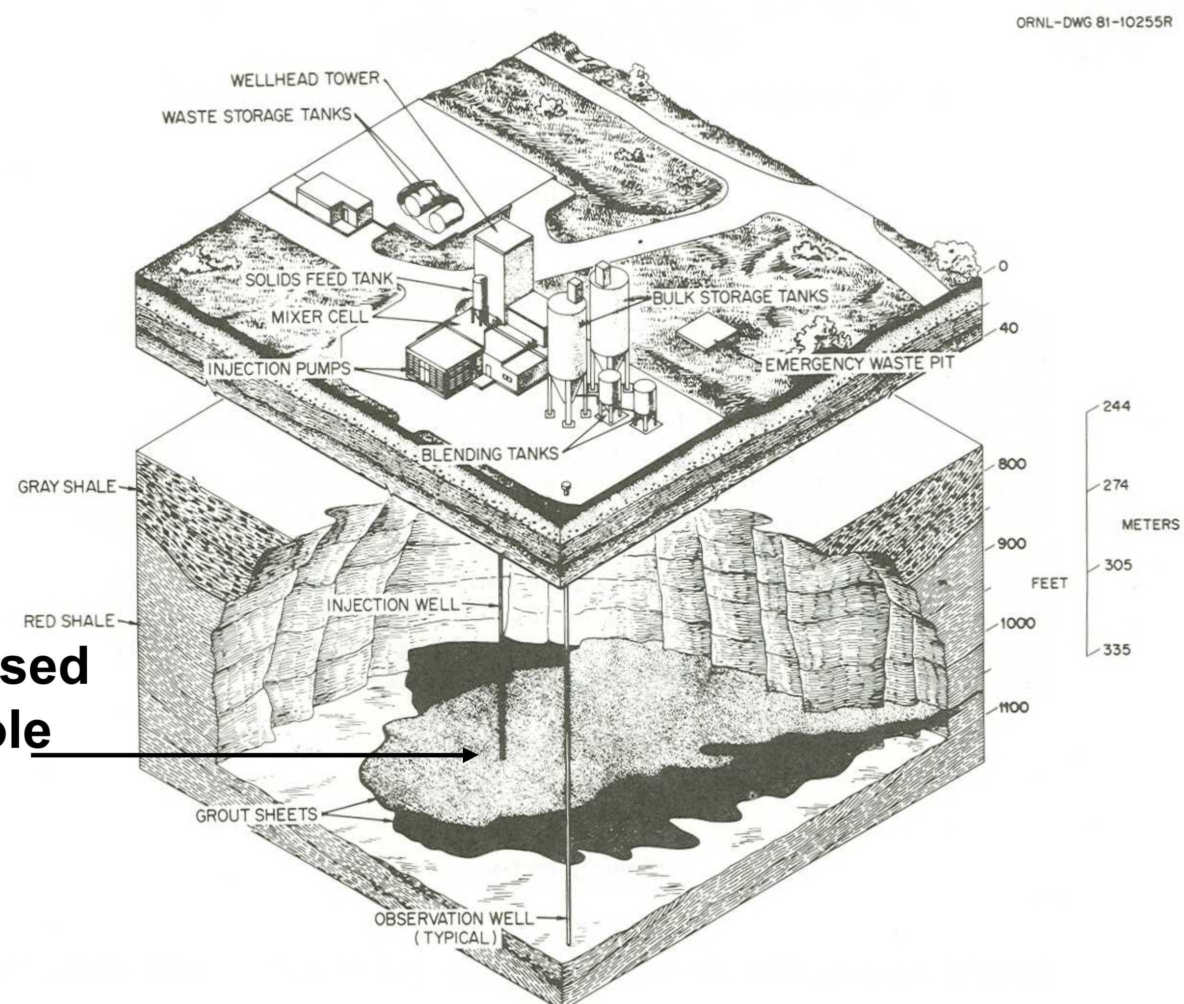
# Schematic Drawing of the ORNL Grout Injection Facility




**Fluid Portland cement based grout is injected down hole at sufficient pressure to hydrofrac the formation.**

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# ORNL Hydrofract Program

## X-10 Site: site development started in the early 1949's

**Initially:** as a "pilot plant" to demonstrate Pu production and separation

**Later:** non-weapons chemical separations of nuclear products and radioisotope production for medical, industrial and research purposes

Wastes from some of these activities were disposed of in nearby Melton Valley

Some wastes were buried in shallow unlined trenches and auger holes:

Contaminated both surface soils and groundwaters, $^{90}Sr$, $^{137}Cs$ and $^{3}H$

Grout-waste mixes from X-10 were also injected into the Pumpkin Valley Shale of the Conasauga Group – started in the late 1950's, ended 1982:

111 wells ranging in depth from from 200-300 meters

As of 1997 no known groundwater contamination from this practice

# Regional Geologic Map of Oak Ridge Reservation

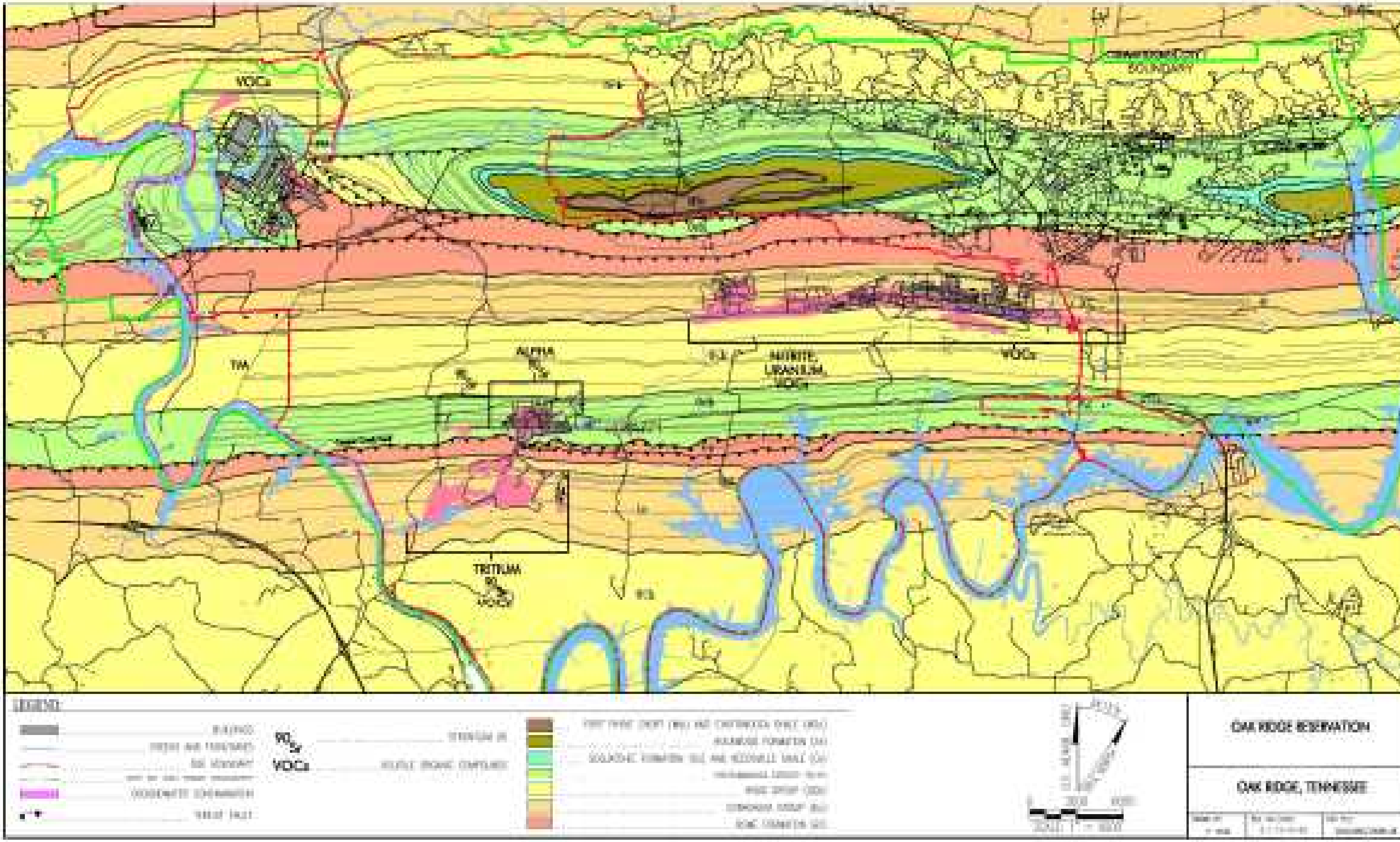
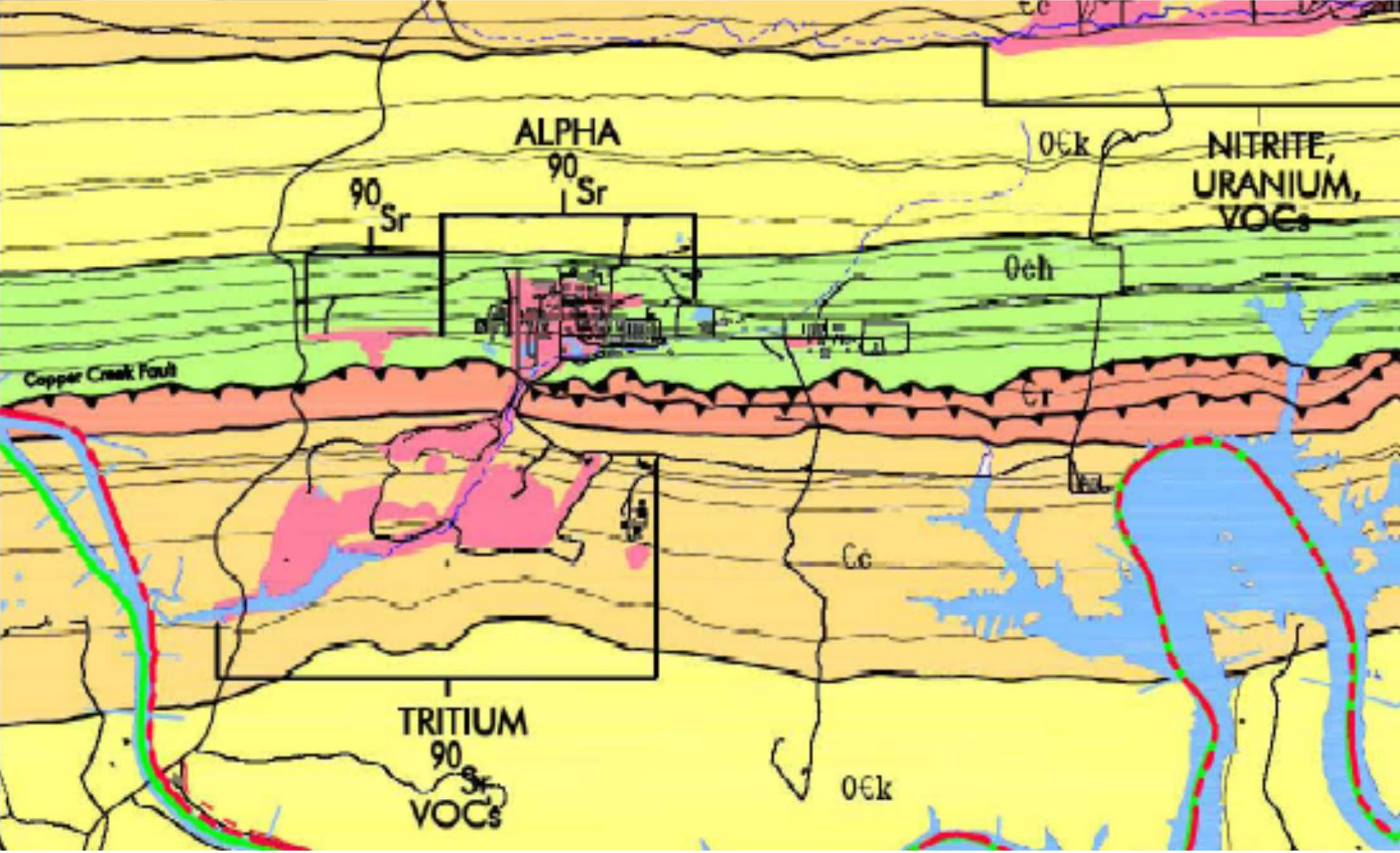



Figure B-1: Geologic Map of the ORR and Groundwater Contaminant Plumes




# Detailed Geology of Grout Injection Site

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# Grout consisted of Portland cement, "additives"

**Type I Portland Cement – 42%**
**Class F flyash – 34% ,** Aids in Sr retention, lowers cost
**Attagel – 150 clay (attapulgite) – 16%,** Absorbs water
**Indian Red Pottery Clay (illite) – 8%,** Aids in Cs retention

# and liquid wastes (from X-10) :

**Tank W-7 Liquid Waste Simulant:**

| | | |
|---|---|---|
| **$Al(NO_3)_3.9H_2O$** | **2.8** | **g/l** |
| **NaCl** | **5.4** | **g/l** |
| **$Na_2CO_3$** | **20.1** | **g/l** |
| **$NaNO_3$** | **68.9** | **g/l** |
| **NaOH** | **7.2** | **g/l** |
| **$Na_2SO_4$** | **13.3** | **g/l** |
| **$NH_4NO_3$** | **0.24** | **g/l** |
| ***Sugar (retarder)*** | ***0.17*** | ***g/l*** |
| ***TBP (defoamer)*** | ***0.4*** | ***ml/l*** |

**Spiked with: $^{85}Sr$ (514 kev γ ), $^{137}Cs$ (511 and 1,176 kev γ) and ppm to pp-thousand levels of Hg, Cd, Cr, Ni, Sb, Pb, Co, Ba, I, Cu, As.**

**500 ml of liquid waste blended with 419 g of dry solids: see ORNL/TM- 9879, 1986, for details**

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# Leaching tests done in distilled water, shallow (dilute) groundwater and a deep brine simulant:

## Groundwater simulant compositions:

| | Shallow Groundwater | Deep Well Water |
|---|---|---|
| Ca | 5.1 mg/l | 10 g/l |
| Ba | 0.13 mg/l | ---- |
| K | 1.5 mg/l | 0.14 g/l |
| Mg | 1.1 mg/l | *2.0* g/l |
| Na | 83 mg/l | 39 g/l |
| Cl | 13 mg/l | 99.8 g/l |
| $SO_4$ | 7.4 mg/l | ---- |
| $CO_3$ | 200 mg/l | ---- |

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# MCC-1 Leach Procedure: Static leaching with solutions analyzed after 4, 7, 14, 28, 56, 94, 112 and 140 days

# ANS 16.1 Leach Procedures Were Also Used:

**Solutions replaced seven times after 2, 7, 24, 48,72, 96, and 120 hours;**

**Provides effective solid diffusion coefficients ($D_e$) for each time interval and, in turn, a "leachability index for each species**

$$L_i = (1/7)\sum_{i=1}^{7}\log(1/D_e)_l$$

**Radionuclide releases presumed to be diffusion controlled.**

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# Leachability Index, $L_i$, for ORNL Grout (24 day cure time)

| | Distilled Water | Shallow Water | Deep Brine |
|---|---|---|---|
| $^{137}Cs$ | 10.6 | 10.5 | 8.8 |
| $^{85}Sr$ | 10.6 | 11.7 | 8.6 |
| As | 13.6 | 12.7 | 11.3 |
| Ba | 13.1 | 12.1 | 8.9 |
| Cd | 17.3 | 17.1 | 10.9 |
| Co | 13.9 | 13.9 | 10.5 |
| Cr | 13.8 | 13.4 | 11.4 |
| Cu | 15.1 | 14.3 | 10.7 |
| Hg | 13.4 | 13.3 | 8.1 |
| Ni | 15 | 15.1 | 11.1 |
| Pb | 15.3 | 15.3 | 10.3 |
| Sb | 13.1 | 12.1 | 9.7 |

## Findings:

$^{137}Cs$ and $^{85}Sr$ were more readily released than a variety of conventional pollutants

Brine aggressively attacks the grout: Ca and Cl are rapidly taken up by the grout while Mg uptake is slower but a higher percentage of the initial inventory was consumed.

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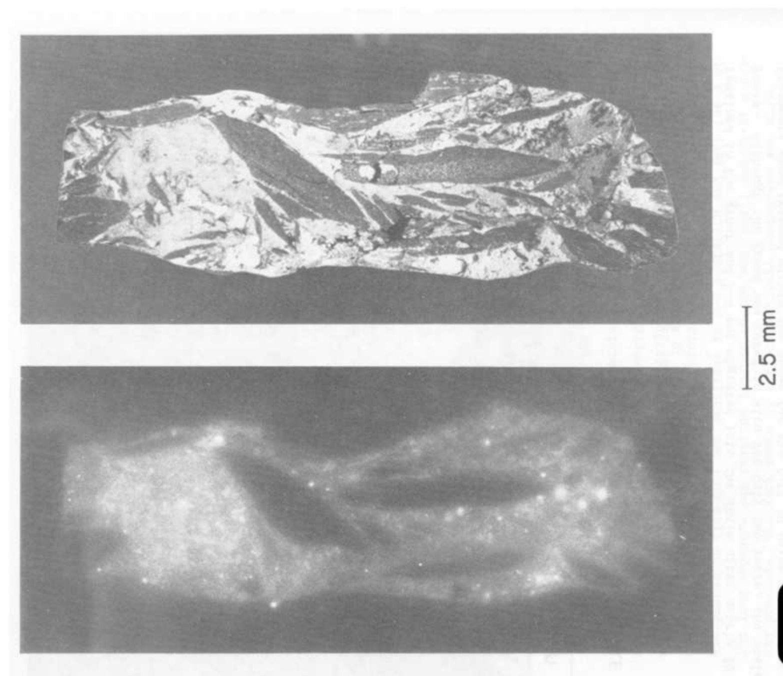
# One early experimental grout injection site was back-drilled after curing for 2 years underground – then stored in the lab for an additional 20 years before being characterized:

**X-ray diffraction showed extensive calcite formation in addition to normal cement phases; probably formed quickly due to the high carbonate content of the waste fluid.**

**Apparently the injection  process is rough enough to break off shale fragments which then become suspended in the solidified grout.**

**Autoradiography showed that the radionuclides had not migrated into the shale.**

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# Conclusions:

A combination of low leach rates from the grout and a very impermeable shale host rock made this disposal technology an attractive alternative at the time.

However, releases of $^{137}Cs$ and $^{90}Sr$ were still not low enough to be satisfactory in the more demanding regulatory climate that developed later so the practice was stopped in 1982.

These early studies have a legacy that lasts today in the proposed use of grouts to close of high level waste tanks at Hanford and Savannah River.

Some grouts have been proposed that include radionuclide "getters" together with the Portland cement.

A better practice would be to first apply the getters, then be sure the radionuclides were "fixed" in an insoluble form, and finally use the grout to cement the getter particles together.

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