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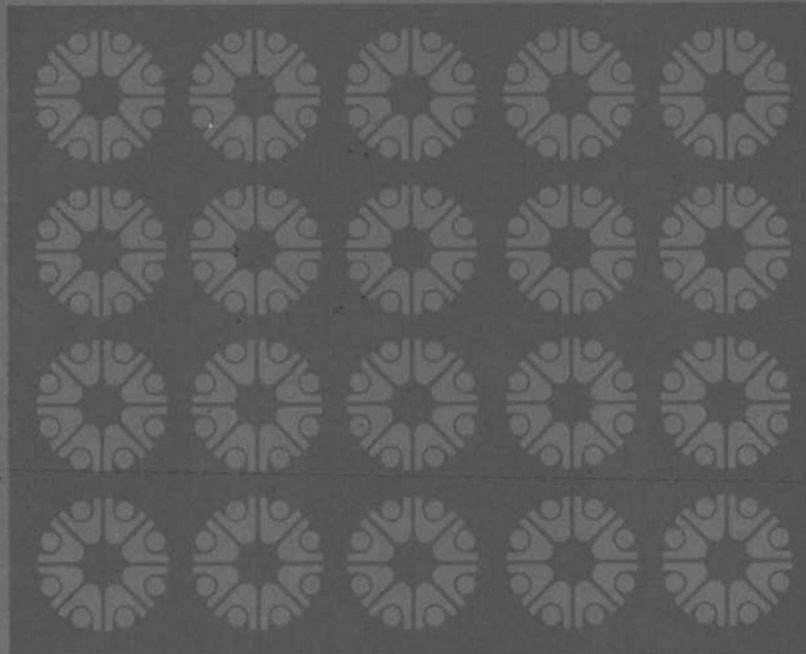
Pacific Northwest Laboratories
Richland, Washington 99352

AEC Research and
Development Report

**FIXATION OF RADIOACTIVE WASTES
IN SOIL AND SALT CAKES
WITH ORGANIC POLYMERS**

**B.W. Mercer
A.J. Shuckrow
L.L. Ames**

April 1971



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FIXATION OF RADIOACTIVE WASTES
IN SOIL AND SALT CAKES
WITH ORGANIC POLYMERS

B. W. Mercer, A. J. Shuckrow, and L. L. Ames

Water and Land Resources Department

April 1971

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A B S T R A C T

Organic polymers of the type used in fiberglass laminates were evaluated for use in the fixation of radioactivity in soil and preformed salt cakes. In situ fixation of the radioactivity is to be accomplished by injection of the polymers into soil or preformed salt cakes. This approach circumvents the costs and hazards associated with the alternate method of excavating the highly radioactive soil or salt for processing or burial. The results of laboratory studies show that water leach rates of radioisotopes or ions from the soil and salt cakes were reduced by 99.9% or more by incorporation of the soil or salt in a suitable resin matrix. Injection of catalyzed liquid resin into soil with subsequent polymerization to form a hard mixture was successfully demonstrated in both laboratory and field experiments.

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FIXATION OF RADIOACTIVE WASTES IN SOIL AND
SALT CAKES WITH ORGANIC POLYMERS

B. W. Mercer, A. J. Shuckrow, L. L. Ames

INTRODUCTION

Highly radioactive liquid wastes produced at Hanford are stored as alkaline slurries in large underground storage tanks. In order to minimize long-term demand for operational control, the long-lived heat producers, ^{90}Sr and ^{137}Cs , are to be removed from the stored salt waste where necessary and the salt wastes reduced by evaporation to salt cakes in the existing underground storage tanks. The problems of tank leakage and the transfer of liquid wastes to new storage tanks is thereby minimized.

Advantage has also been taken of the favorable geochemical and meteorological conditions existing on the Hanford reservation to safely store some of the low-level wastes in soil. The soils beneath the 200 Areas effectively act as both a filter and a chemically reactive media to retain the long-lived radionuclides, ^{90}Sr and ^{137}Cs .

Barring unforeseen catastrophic occurrences or changes in climate and with continued surveillance and control of both the underground storage tanks and soil disposal areas, isolation of the hazardous radionuclides from important life forms is assured with a high degree of probability.

The very long period (several centuries) required for decay of the ^{90}Sr and ^{137}Cs does, however, make prudent the continuation of studies of alternative methods which may provide additional assurance that the

wastes remain isolated from the environment. Excavation and transfer of the salt waste and radioactive soil to a national disposal site is possible as is excavation of the salt and soil and subsequent blending into asphalt or plastic mixtures. Both of these approaches suffer from the hazards and costs associated with excavating the radioactive salt and soil. Fixation of the radioactive salt and soil in situ provides an attractive alternative to the approaches above.

This report describes a feasibility study on the use of organic monomers which can be injected into soil or salt cakes and subsequently polymerized by suitable catalysts to reduce the leachability or mobility of the radioactivity contained therein.

SUMMARY

Organic polymers of the type used in fiberglass-resin laminates were evaluated for use in the fixation of radioactivity in soil and **preformed** salt cakes. Results of laboratory studies show that water leach rates of radioisotopes or ions from soil and **salt** cakes are reduced by 99.9% or more by incorporation of the soil or salt in a suitable resin matrix. The resin-salt leach rate is much less than that reported for waste calcined by a fluid bed calciner but is greater than the leach rate reported for asphalt salt mixtures. Resin-soil and **resin-salt** mixtures have a physical stability comparable to that of concrete, thus greatly reducing the possibility of mechanical dispersal of radioactivity from waste disposal sites. Injection of the catalyzed liquid resin into soil with subsequent polymerization to form a hard mixture was successfully demonstrated in both laboratory and field experiments.

The presence of water in the soil or salt inhibits the polymerization of most of the resins studied. Results with simulated ITS salt waste show that successful polymerization occurred when all interstitial water was removed from the crystals. This could be accomplished by drying in an oven, but not by vacuum filtration. Normal drainage of water from the soil below crib disposal sites is expected to reduce soil moisture to tolerable levels for **successful** application.


Tests made to demonstrate the feasibility of including active ion exchange sites in the polymer were inconclusive. The particular resin tested was unsatisfactory due to the nonreproducibility of the setting characteristics. Subsequent tests indicated leach rates, while lower than soil or salt cake alone, were higher than the other non-ion exchange polymers tested.

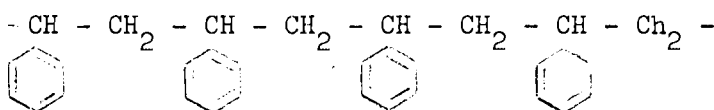
Flammability studies have demonstrated that the soil-resin combinations will not support combustion. Mixtures of resin and sodium nitrate will support combustion although the burning is not vigorous; the degree of flammability is reduced as the percentage of inert salts is increased. Mixtures of resin with a simulated waste salt will only marginally support combustion.

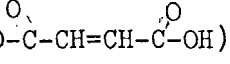
DISCUSSION AND RESULTS

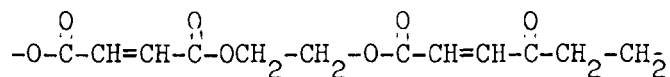
Polymerization Reactions

A comprehensive discussion of polymer formation is beyond the scope of this report; however, a brief review will serve to elucidate the fundamental reactions involved and define the terms used. The term "polymer", as used in this report, refers to a high molecular weight molecule formed

by the continuous reaction of simple molecules. These simple molecules are usually referred to as "monomers." Some monomers polymerize by addition through their unsaturated bonds. For example, a molecule of styrene (C=CH₂) contains a vinyl double bond. Polystyrene is formed by styrene molecules adding together at their double bonds and therefore contains no unsaturation:



Polymers may be formed by a condensation reaction in which water is produced. An example of this type of reaction is the polycondensation of maleic acid () with ethylene glycol (HO-CH₂-CH₂OH) to form a long-chained ester:



The type of polymer shown above is commonly referred to as a polyester.

Polyesters or more specifically unsaturated polyesters, may be cross-linked or copolymerized with monomers such as styrene to produce strong, highly stable materials for construction or fabrication (i.e., fiberglass laminates). The polyester is dissolved in the monomer and the polymerization reaction is initiated at the time of use. The polymers thus produced are called thermosetting resins, which cannot be subsequently reformed by heat. The polymerization reaction is exothermic and proceeds through two distinct stages. After suitable initiation (or catalyzation) the first stage is the formation of a soft gel. This stage may require but a few minutes or take several hours or even days. Little or no heat is evolved in this step. Immediately following the gelation stage the cure stage is rapidly propagated with considerable evolution of heat. In a large insulated resin mass the temperature may go as high as several hundred degrees F with extreme rapidity. The total quantity of heat liberated depends on the degree of unsaturation of the resin.

Addition polymerization, as in the case of polystyrene formation, proceeds by the free radical mechanism. Free radicals can be produced by the decomposition of labile molecules by heat, light, fast nuclear particles, or in the course of a chemical reaction. Benzoyl peroxide is an example of a compound that decomposes to give free radicals for initiating an addition polymerization reaction. Benzoyl peroxide and other organic peroxides used to initiate or catalyze polymerization reactions are commonly called "initiators" or "catalysts." Substances such as cobalt naphthenate or dimethyl aniline which activate the initiators are called "promoters" or "activators."

Liquid monomers and thermosetting resins used in this work are listed in Table I.

Table I
Liquid Monomers and Thermosetting Resins

Product	Type	Viscosity, Poise	Specific Gravity	Manufacturer
Derakane 114	Vinyl Ester	0.52		Dow Chemical Company, Midland, Mich.
Derakane 118	Vinyl Ester	0.12		Dow Chemical Company, Midland, Mich.
Epon 815	Epoxy	13		Shell Chemical Company, Union, New Jersey
Laminac EPX 154-4	Polyester	5-7	1.10	American Cyanamid Company Wallingford, Connecticut
Polylite 31-007	Polyester	2.75-4.0	1.10-1.12	Reichhold Chemicals Incorporated White Plains New York
Polylite 33-052	Polyester	2.5-6.5	1.10-1.12	Reichhold Chemicals Incorporated White Plains New York
Ethyl Acrylate	Monomer		0.92	Rohm and Haas Company, Philadelphia, Pennsylvania
X-980	Monomer		--	Rohm and Haas Company Philadelphia, Pennsylvania
Hydroxyethylmethyl Acrylate	Monomer		1.05	Rohm and Haas Company Philadelphia, Pennsylvania
Glacial Acrylic Acid	Monomer		1.06	Rohm and Haas Company Philadelphia, Pennsylvania
Styrene	Monomer	.0076	0.91	Dow Chemical Company, Midland, Mich.
Devinyl Benzene	Monomer	.009	0.90	Dow Chemical Company, Midland, Mich.

Resin-Soil Mixtures

Preparation

Standard formulations for catalyzed resins used in the laboratory experiments with both soil and salt waste are listed in Table 2 along with the respective gel times. The soil-resin mixtures were prepared by blending two parts of soil with one part of catalyzed resin. The mixtures were allowed to settle and cure in polyethylene containers after which the excess resin was removed prior to testing. The soil used was Burbank fine sand sub-soil, characteristic of that in the 200 Areas. Figure 1 shows a photomicrograph of a cut surface of a casting of Derakane 118 and soil which illustrates the sandy nature of the Burbank fine sand sub-soil. The connotation "dry," and "wet" refers to soil moisture contents of 2, and 10 weight percent, respectively. Because of their high viscosity, Derakane 114, Laminac EPX 154-4 and PolyLite 33-052 were not used in soil-resin experiments. The high viscosity is largely due to a relatively low styrene content. A low viscosity is needed to facilitate injection of the catalyzed resin into the soil.

The standard Derakane 118 formulation gelled in six hours and set well overnight. Addition of dry soil to the above formulation did not appreciably change the time required to gel. Wet soil added to the above formulation, however, resulted in a failure to gel or set for several days. Therefore, the use of the standard Derakane 118 recipe in wet soils is not feasible.

The standard Derakane 118 formulation was varied with respect to the quantity of initiator and promoter added while maintaining the same 10

Table 2

Standard Formulations of Thermosetting Resins with Gel Times

Resin	Benzoyl Peroxide %	Dimethyl Aniline %	Methyl Ethyl Ketone Peroxide %	Cobalt Napthenate %	Xylene %	Triethylenetetramine %	Gel Time minutes
Derakane 114	0	0	1.0	0.1	0	0	30
Derakane 118	0	0	1.0	0.1	0	0	270
Epon 815	0	0	0	0	23	12	165
Laminac EPX 154-4	2.5	0.2	0	0	0	0	5
Polylite 31-007	2.5	0.2	0	0	0	0	11
Polylite 33-052	2.5	0.2	0	0	0	0	6

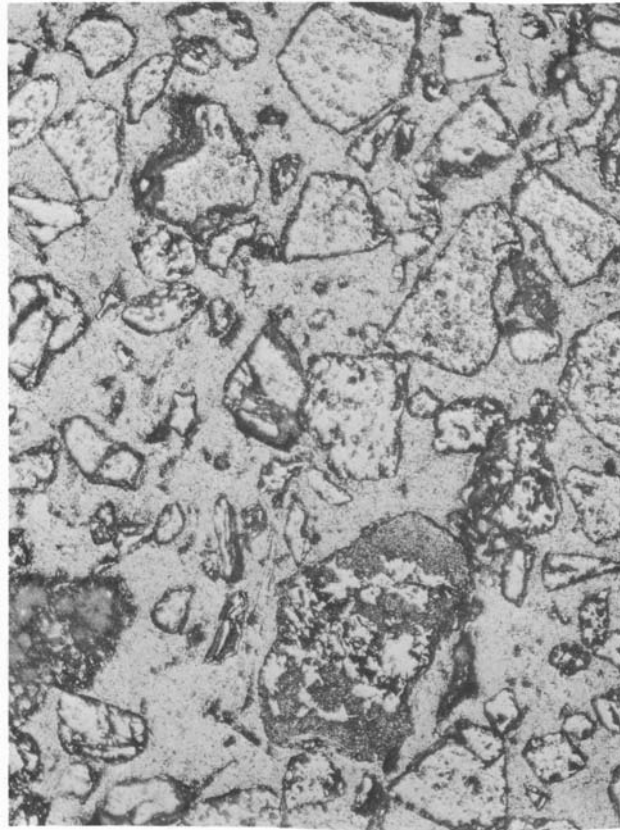
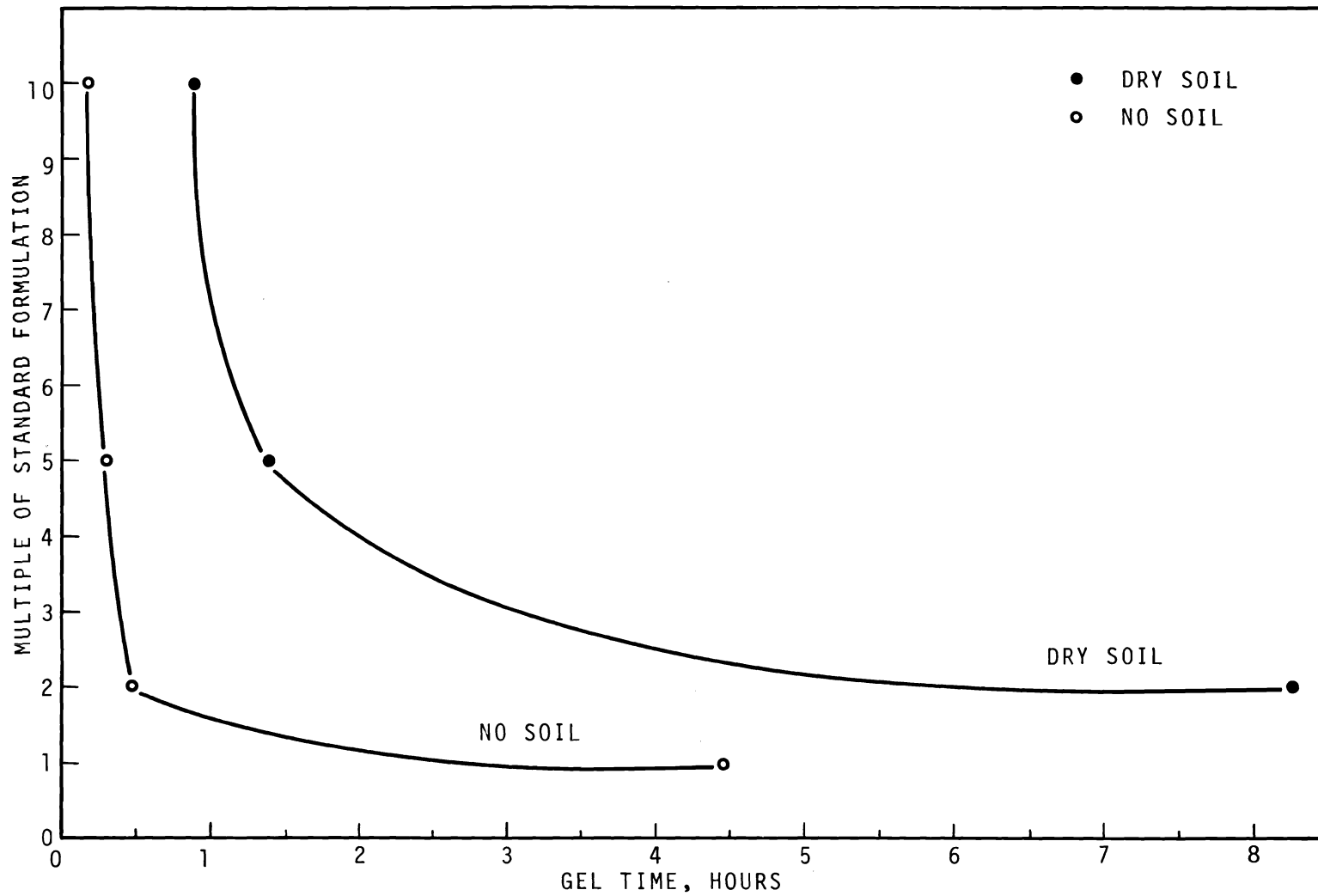


Figure 1

Photomicrograph of Darakane 118 -
Soil Mixture at 100 Magnification

to 1 initiator to promoter ratio. The results with and without dry soil are given in Figure 2. Because the gelling and setting of the resin is a thermally-dependent process, it is not surprising that added soil, acting as a heat sink, slows the resin polymerization. Overheating and cracking resulted for the Derakane 118 formulations containing more than the standard amounts of initiator and promoter and no soil.



Neg. PN 711860-3

Figure 2 Effects of Soil and Initiator Promoter Concentrations on Derakane 118 Gel Time

Various amounts of dimethyl aniline were added to the standard Derakane 118 formulation with fair results. Gel and set times were shortened both with and without soil added. For example, gel and set times for the standard formulation without soil were shortened to 30 minutes and 45 minutes, respectively. However, wet soil still did not set properly in the standard formulation.

Epon 815 was the only resin that showed a decrease in gel time when soil was added to the standard Epon 815 formulation. Xylene was added to reduce both viscosity and gel time of Epon 815. Approximately two hours were required to gel the standard formulation with either dry or wet soil, but 2.75 hours were required to gel the standard formulation without soil added. The standard Epon 815 formulation with dry soil and no soil set well in 2.25 and 2.9 hours, respectively, but the sample containing the wet soil did not progress past the gel stage in several days.

The standard PolyLite 31-007 formulation gelled very rapidly with or without soil added. About eleven minutes were required to gel either alone or with wet or dry soil. Only eighteen minutes passed before final set began. Viscosity is high and gel time too rapid for practical use of PolyLite 31-007 with soils, however. Acetone was added to the PolyLite 31-007 to lengthen time to gel and reduce viscosity. Addition of 5 g of acetone to the standard formulation nearly doubled the time required for gel initiation. However, the product is rubbery, much like Epon 815 with xylene added. Styrene seemed to reduce PolyLite 31-007 viscosity without softening the final plastic and still lengthened time to gel initiation. For example, 0.5 part of styrene added to 1 part of

the standard Polylite 31-007 formulation without soil gelled in ten minutes, 1 part of added styrene gelled in 18 minutes and 1.5 parts of styrene in 25 minutes. The above formulations containing an additional 33%, 50% and 60% styrene, respectively, set in 30 minutes, 55 minutes and 1.5 hours. A formulation containing 2 parts styrene to 1 part of Polylite 31-007 did not set properly. The addition of normal soil to the above formulations resulted in gel times of 1 hour and 22 minutes for the 33% additional styrene sample, two hours for the 50% additional styrene sample and 3.5 hours for the 60% additional styrene sample. All set properly overnight. Two hundred, 300 and 400 g of soil were added, respectively, to compensate for the added volume of the styrene.

All of the above experiments were initiated at room temperature. The effect of a lower temperature on resin gel and set times also was determined.

At 7 °C, the formulation 50 g Derakane 118 + 0.5% Cobalt naphthenate + 5% M.E.K. peroxide gels in one hour and 45 minutes, compared to 17.5 minutes for the same formulation at 23 °C. The standard Polylite 31-007 formulation took 55 minutes to gel at 7 °C and 11 minutes to gel at 23 °C. The standard Epon 815 mixture did not gel in 18 hours at 7 °C while at 23 °C, the mixture gelled in 2 hours and 45 minutes. At 60 °C, the Epon 815 formulation sets in less than 20 minutes.

Several formulations using styrene were tried, because styrene is considerably less expensive than the resins investigated. It is also considerably less viscous as well. Benzoyl peroxide paste and dimethylaniline were used as promoter and initiator without success due to the limited solubility of benzoyl peroxide in styrene. Cobalt naphthenate

and methylethylketone peroxide were then used as promoter and initiator. Gelling was very slow and progressed until setting was complete in about 48 hours. When ten wt % of divinylbenzene was added to the above standard styrene formulation of 50 g styrene + 6 g methylethylketone peroxide + 2 ml cobalt naphthenate, the mixture set well in about 40 hours. When 200 g of 234-5 soil were added to the above styrene-DVB formulation, the mixture set well in about 48 hours. When the divinylbenzene was omitted from the mixture, only the surface of the sample set.

Mechanical Properties

Castings of resin-soil mixtures were prepared for mechanical testing by filling 20 ml polypropylene centrifuge tubes with unpolymerized resin-soil mixtures. The mixtures were centrifuged at 2500 RPM for one minute to remove air bubbles and compact the soil prior to setting. Test specimens were cut from the castings which measured 9/16 inch in diameter. The mechanical test data for the resin-soil mixtures is given in Table 3. Basically these materials are in the "brittle" class, such as concrete, except that they exhibit substantially more plasticity. The strength of the standard Epon 815 mixture was significantly less than that of the others which is believed to be the result of the xylene addition for viscosity reduction. Standard Polylite 31-007 with and without 10% added styrene exhibited the greatest mechanical strength. As previously noted, moisture decreases the mechanical strength of the mixtures.

Mechanical strength is desirable with respect to possible water or wind erosion of the soil disposal sites. The relatively high mechanical strength of the resin-soil mixture would substantially reduce the dispersal of radioactivity compared to that of untreated soil if some unforeseen change occurred to significantly increase present erosion rates.

Table 3

Mechanical Test Data of Resin-Soil Mixtures

Resin	Soil Moisture	Tensile Strength psi	Compression Strength psi	Shear Strength psi
Standard PolyLite 31-007	Dry	1760	10,300	2200
Standard PolyLite 31-007	Wet	1200	8100	1650
Standard Epon 815	Dry	180	790	126
Standard PolyLite 31-007 plus 10% added styrene	Dry	1820	10,600	2100
Standard PolyLite 31-007 plus 10% added styrene	Wet	880	6300	1000
Derakane 118 with 10 times the standard initiator and promoter concentrations	Dry	1420	6480	2440
Styrene with 9% divinyl benzene, 4% cobalt naphthenate and 11% methyl ethyl ketone peroxide	Dry	550	4170	987
Concrete		150-350	3000-7000	1500-3500

Soil Leaching Studies

Cesium chloride solution labeled with ^{134}Cs was passed through a column of soil until the soil was essentially cesium based. This soil was then used in all of the leach tests conducted with the various resins. Leach rates were determined from the quantity of ^{134}Cs detected in the solution phase.

In order to obtain some frame of reference by which to evaluate the effectiveness of the thermoplastics in reducing leaching from the soil, a modified static leach test was conducted on the soil itself. Two 100 g portions of the cesium based soil were placed in 8 oz polyethylene bottles and loosely packed so as to give a fairly uniform surface. A 100 ml aliquot of tap water was then placed on top of each soil sample. After various time intervals the supernatant liquid was decanted and replaced with a fresh aliquot of tap water. It was determined that equilibrium was established at a solution activity of approximately 8000 cpm/ml. Meaningful leach rates for the soil alone cannot be reported since initial rates were high ($\sim 5000 \frac{\text{c}}{\text{cm}^2\text{-day}} \frac{\text{m/ml}}{\text{pm}}$) and rapidly fell off as equilibrium was approached. This made the apparent leach rate highly dependent upon the time interval between determinations.

Resin soil castings were prepared by thoroughly blending together 100 g of the cesium based soil and 50 g of the appropriate thermoplastic in 8 oz polyethylene bottles. This mixture was then centrifuged so as to produce compaction of the soil and obtain a thin layer of excess resin on top. The standard resin formulations were used in the preparation of all castings.

Each casting was allowed to cure for 24 hours or more and was then cut with a hacksaw to remove the top portion of the casting including the resin layer and a portion of the soil-resin mixture. The top surface of the bottom portion of the casting was abraded with emery cloth to produce a smooth surface. This section of casting was then placed in a 8 oz polyethylene bottle from which the neck portion had been removed. A hose clamp was tightened around the bottle at the top of the casting to form a seal and prevent any leakage of water around the sides and bottom of the casting. Only the top face of the casting (surface area 26 cm^2) was in contact with the 100 ml aliquot of tap water which was then placed in the container (Figure 3). The ^{134}Cs content of the solution was determined at appropriate time intervals and the water was replaced with a fresh 100 ml aliquot at the time of each such determination. Replacement of the leaching solution was timed so that an equilibrium condition was never approached and therefore, meaningful leach rates could be determined.

Figure 4 presents the results of static leach tests conducted with four resins compared with the leach rate of an asphalt-salt mixture⁽¹⁾. Duplicate samples of Polylite 31-007 and Laminac showed good agreement over a 50-day period. All of the resins tested significantly reduced the leaching of cesium from the soil. However, Derakane 118 exhibited the most rapid reduction in the leach rate and compared favorably with the asphalt-salt mixture.

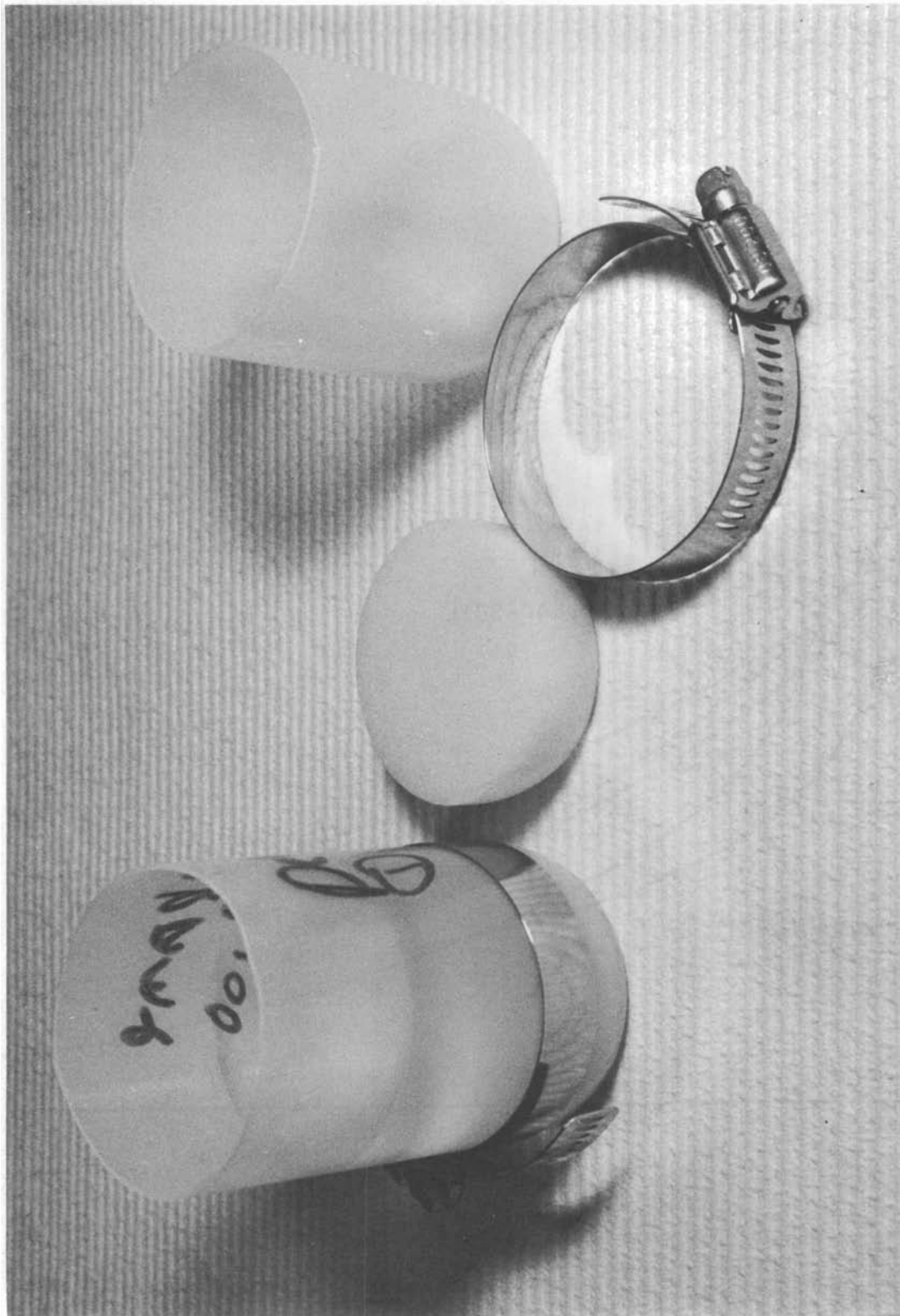
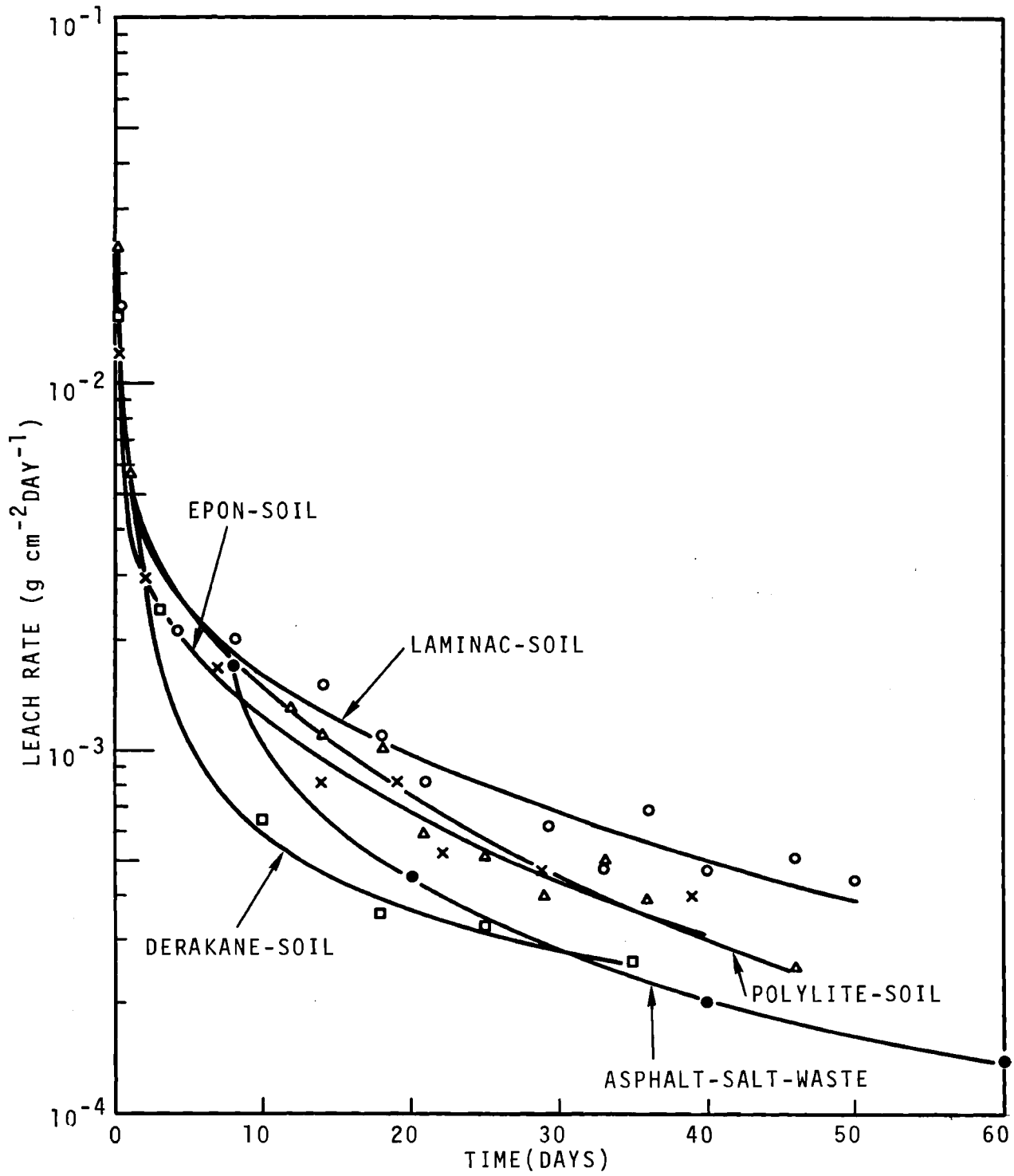


Figure 3 Materials Used in Static Leach Determinations



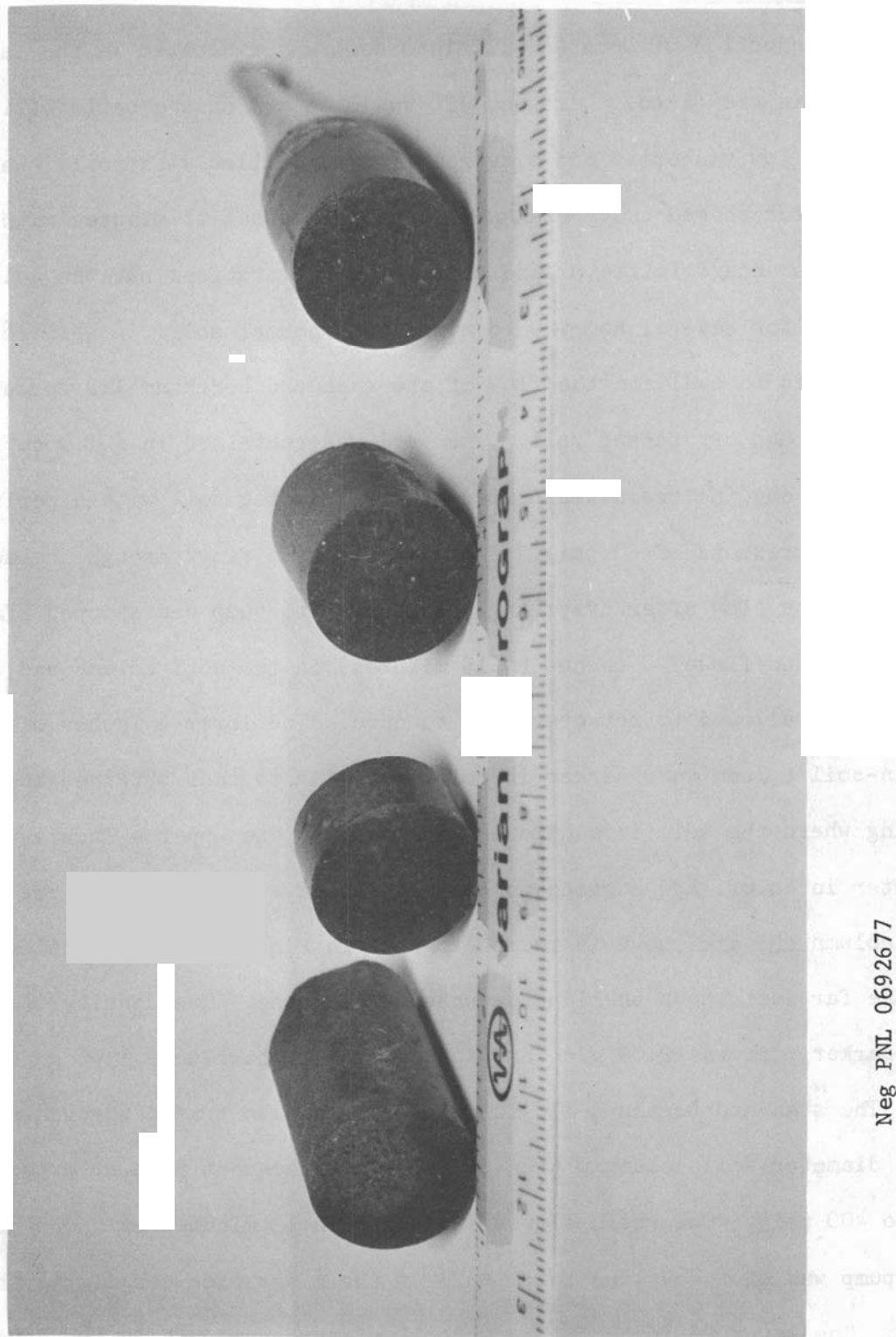
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Figure 4 Cesium Leach Rates Resin-Soil Mixtures Compared with that of an Asphalt-Salt-Waste Mixture

Resin Injection into Soil

The injection of Derakane-118 into soil was evaluated in the laboratory and in the field. Derakane-118 was selected on the basis of its relatively low viscosity and slow gel time when mixed with soil. Laboratory studies showed that Derakane-118 gels in about 15 minutes with 3 times the standard initiator and promoter concentrations but the gel time is delayed for several hours when mixed with normal soil. A soil column was prepared to evaluate the flow of the standard Derakane 118 formulation through dry packed soil. The soil was contained in a 1.9 cm ID glass tube and the resin was pumped upflow into the soil with a peristaltic pump at a pressure of 60 psig. The rate of resin flow through the soil became quite slow after traveling 3 inches. The pump was stopped after the resin had flowed 8 inches (\sim 15 minutes) in the soil column and the column was allowed to set overnight to cure. The lower 4 inches of the resin-soil column were darker in color, similar to that obtained in batch mixing where the soil is saturated with resin. The upper 4 inches were lighter in color, and assumed to be unsaturated. Sections were cut from the column and are shown in the photograph in Figure 5. The section at the far left shows the lighter unsaturated zone. The density of the darker zone was 2.09 g/cc and that of the lighter zone 1.96 g/cc.

The standard Derakane-118 formulation was also pumped through a 2-inch diameter soil column with a positive displacement pump at pressures up to 400 psig. The resin flowed 42 inches in 13 minutes at which point the pump was shut down due to rupture of the glass pipe containing the soil. The lower 26 inches of resin soil mixture hardened in two days but the upper 16 inches failed to set which represents some loss of resin due to unsaturation.



Neg PNL 0692677

Figure 5 Resin-Soil Column Sections

An injection experiment was conducted in the laboratory with the standard Derakane-118 formulation and normal soil contained in a 15 gallon can. The resin was injected into the soil through a 3/8 inch steel tube which was perforated at one end. The perforated end was inserted 15 inches below the surface of the soil and ninety pounds of lead bricks were placed on the soil surface to prevent expansion of the soil. Resin was pumped into the soil at a flow rate of 500 ml/min until 3400 ml were injected. The resin-soil mass was allowed to set for 2 days. A hard resin-soil mixture was obtained (see Figure 6) which weighed 7.81 Kg and had an average density of 1.87 g/cc. Less than half of the resin was recovered in the hard resin-soil mass. The remainder was lost largely as a result of unsaturation.

A field test was carried out about one-half mile south of the 234-5 building using Derakane 118 containing 3 times the standard initiator and promoter concentration. A steel pipe with a well point was prepared and perforated at the 5-foot level. The pipe was hammered into the soil and connected to a positive displacement pump as shown in Figure 7. On the first attempted injection the resin surfaced around the pipe after about one gallon of resin was pumped into the soil. After flushing the pipe with uncatalyzed resin, it was driven down to the 7-foot level for a second attempt. Resin was poured around the pipe at the surface in order to form a seal. This resin layer was allowed to harden and then 11.5 gallons of resin was injected through the pipe at a flow rate of 0.13 gal/min.

Four days after injection, the resin-soil mixture was excavated and was found to be solidified into a hard mass. The resin did not spread

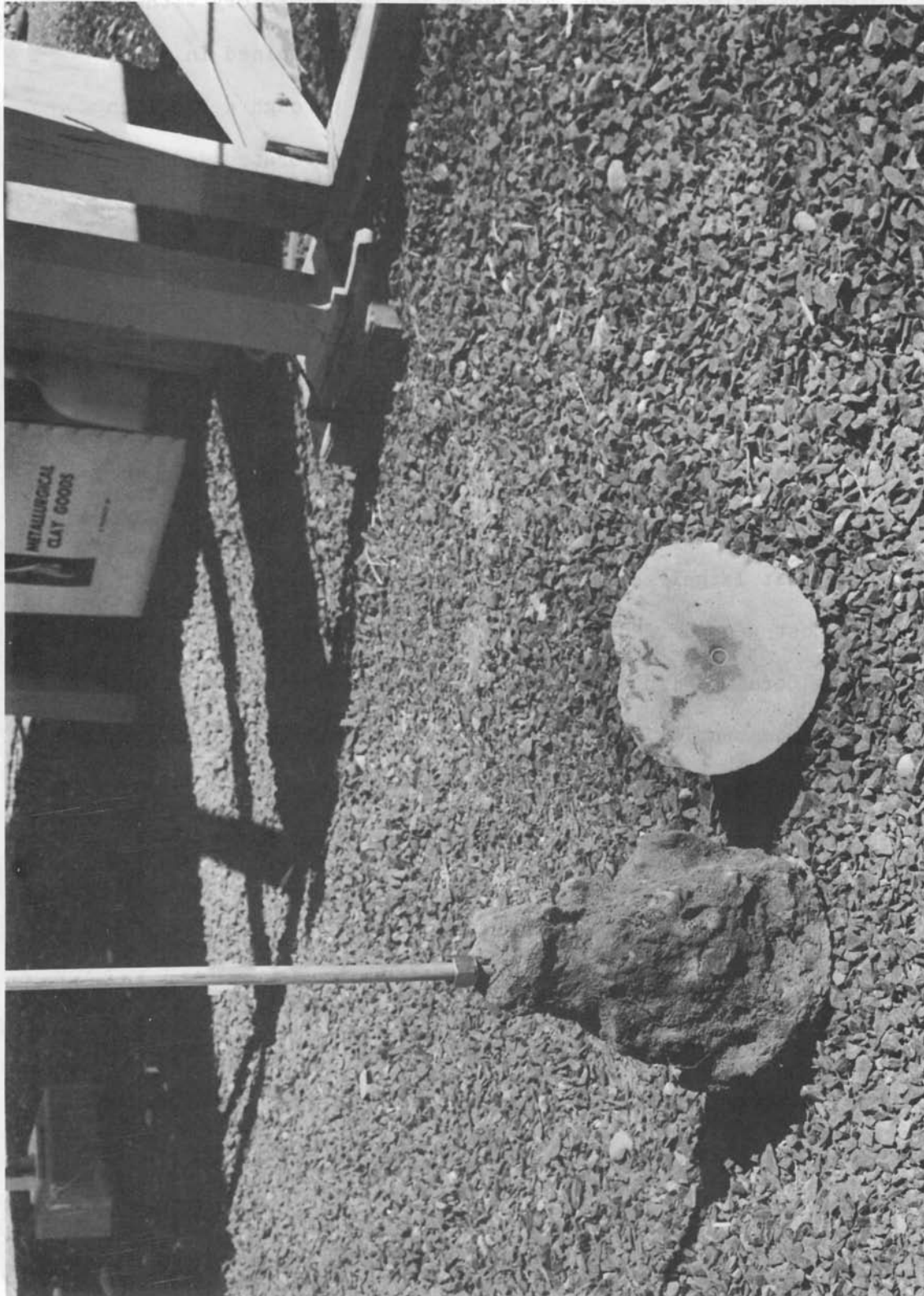


Figure 6 Resin-Soil Mass Formed by Injection of Derakane 118 into Soil



Figure 7 Photograph of Resin Injection Equipment at Field Test Site

evenly from the injection point as shown in the photograph in Figure 8 prior to excavation. The resin appeared to follow an old root system. Figure 9 shows the excavated resin-soil mass after it was cut up in sections. The total volume of the resin-soil mass was 3.2 cu ft and the weight was 395 lbs. It is estimated that 70% of the resin injected was recovered in the mass. The average compressive strength was 5300 psi.

Resin-salt waste mixtures

Pure Salts

This phase of the investigation was initiated with an examination of the characteristics of resin-NaCl mixtures. Standard resin compositions as listed in Table 1 were employed. Mixtures containing 100 g of NaCl and 50 g of Derakane-118, PolyLite 31-007, PolyLite 33-052, or Epon 815 were prepared, aged for 24 hours and subjected to static leach tests. All of the resins tested mixed well with NaCl and little or no effect on the setting characteristics of the resins was observed. Addition of 10 g of water to 90 g of NaCl before mixing with the resin produced a product which would not harden in the case of Derakane-118 and Epon 815. PolyLite 31-007 did harden and form a satisfactory product.

Samples of several of the resin-salt mixtures were polished with diamond dust to produce a glossy surface suitable for microscopic examination. Photomicrographs (100X magnification) of the surfaces of two of these samples are presented in Figures 10 and 11. The distribution of the salt crystals in the resin is clearly shown in these figures. It is believed that, following the high initial rate of dissolution of the surface crystals, leaching proceeds slowly through points of contact

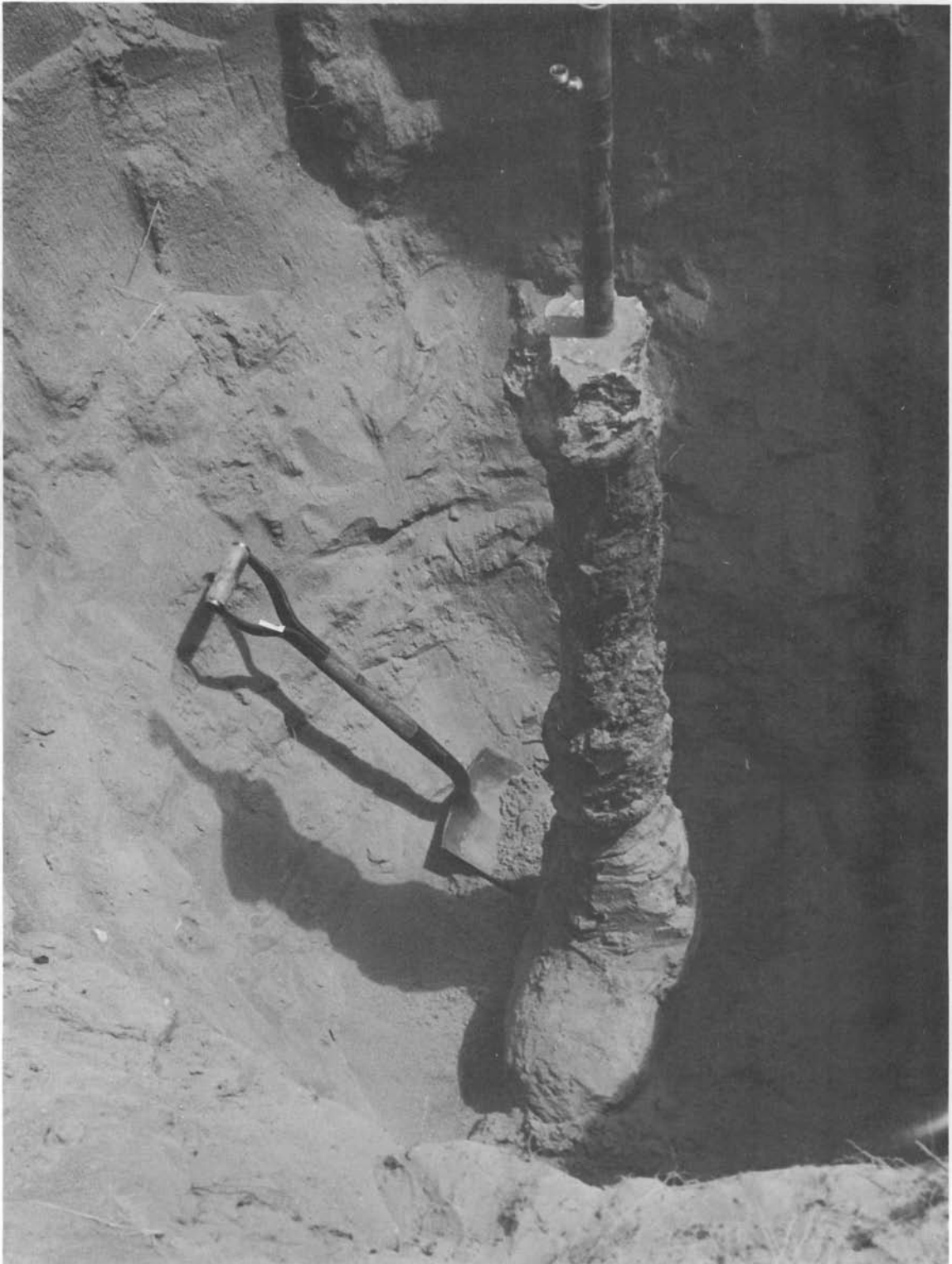


Figure 8 Photograph of Resin-Soil Mass at Field Test Site



Figure 9 Resin-Soil Formed in Field Test with Derakane 118 after Excavation and Sectioning



FIGURE 10

Photomicrograph of Derakane 118 -
NaCl Mixture at 100X Magnification

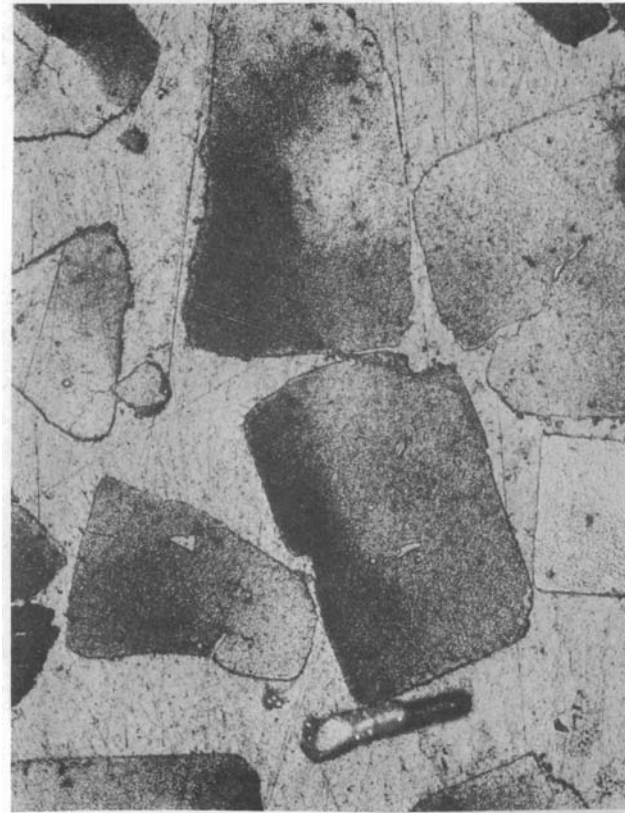


Figure 11

Photomicrograph of Polylite 33-052 -
NaCl Mixture at 100X Magnification

between crystals.

The procedure employed in the leach tests was identical to that described for the resin-soil mixtures except that distilled water rather than tap water was used in this case and Na^+ ion concentration was regarded as an index of leaching from the mixture. An approximate initial leach rate of pure NaCl was determined to be $7.5 \text{ g Na/cm}^2/\text{day}$. Figures 12 and 13 contain the results of the leach tests for the various resin-salt mixtures. All of the resins were effective in producing significant reductions in leaching. Polylite 33-052 produced the mixture with the lowest leach rate.

A comparison of the leaching characteristics of wet and dry NaCl -Polylite 31-007 mixtures is possible upon inspection of Figure 13. It is evident that although the wet salt-resin mixture did harden in this case, the product leaches at a much higher rate than the dry salt-resin mixture.

Mixtures of resins (Derakane 118, Polylite 31-007, and Epon 815) and NaAlO_2 , Na_2CO_3 , NaNO_2 , NaNO_3 and NaOH were also prepared. Epon 815 hardened when mixed with any of the salts other than NaOH and Polylite 31-007 with all of the salts except NaNO_2 . Derakane 118 did not harden when mixed with NaOH or NaNO_2 and required approximately 7 days to harden in the presence of NaAlO_2 .

Simulated Salt Waste

A synthetic salt waste was prepared by evaporation to 50% of its original volume of a solution whose composition is given in Table 4. The end product of this operation which had a pasty consistency was then

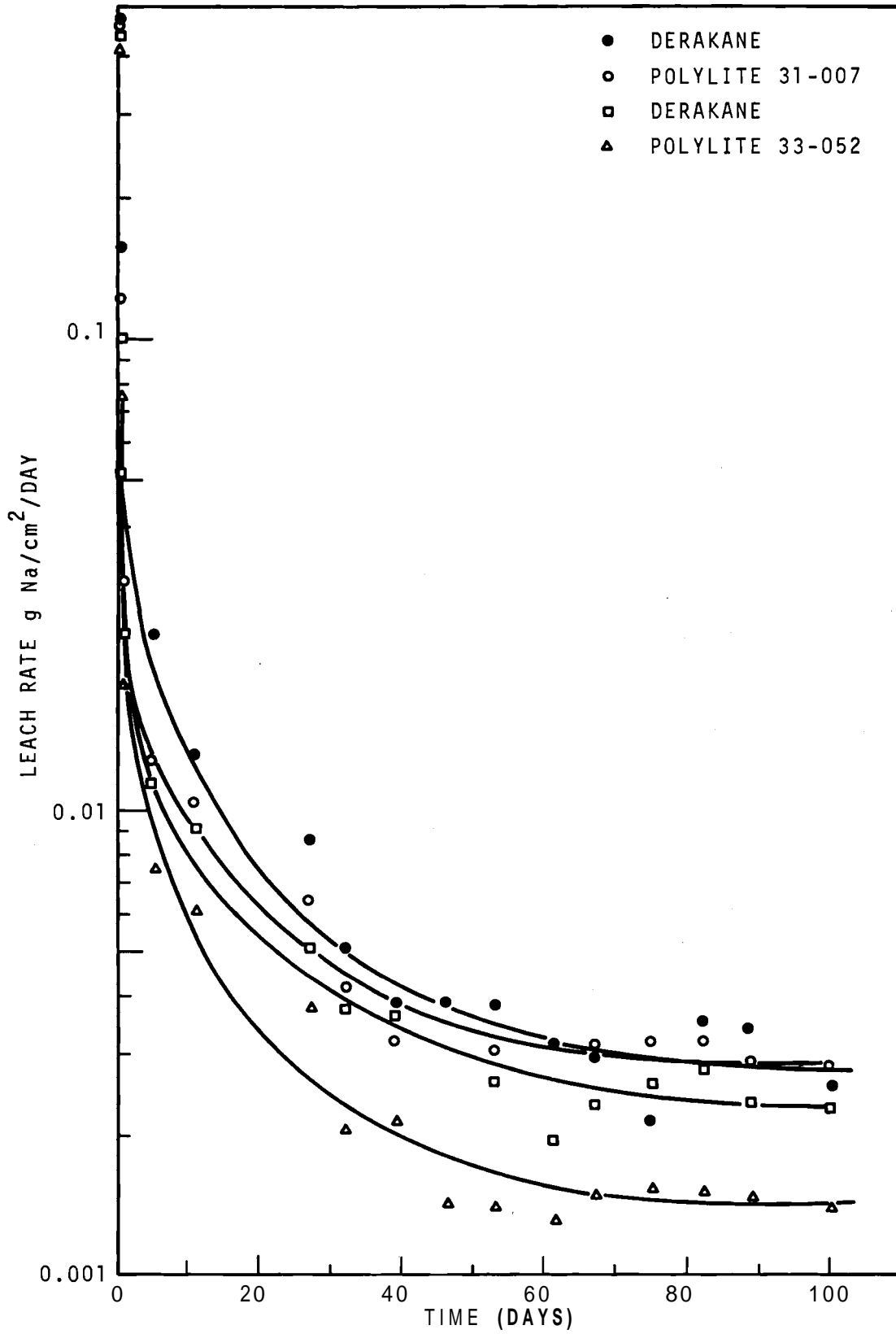


Figure 12 Na⁺ Leaching of Resins with NaCl Salt

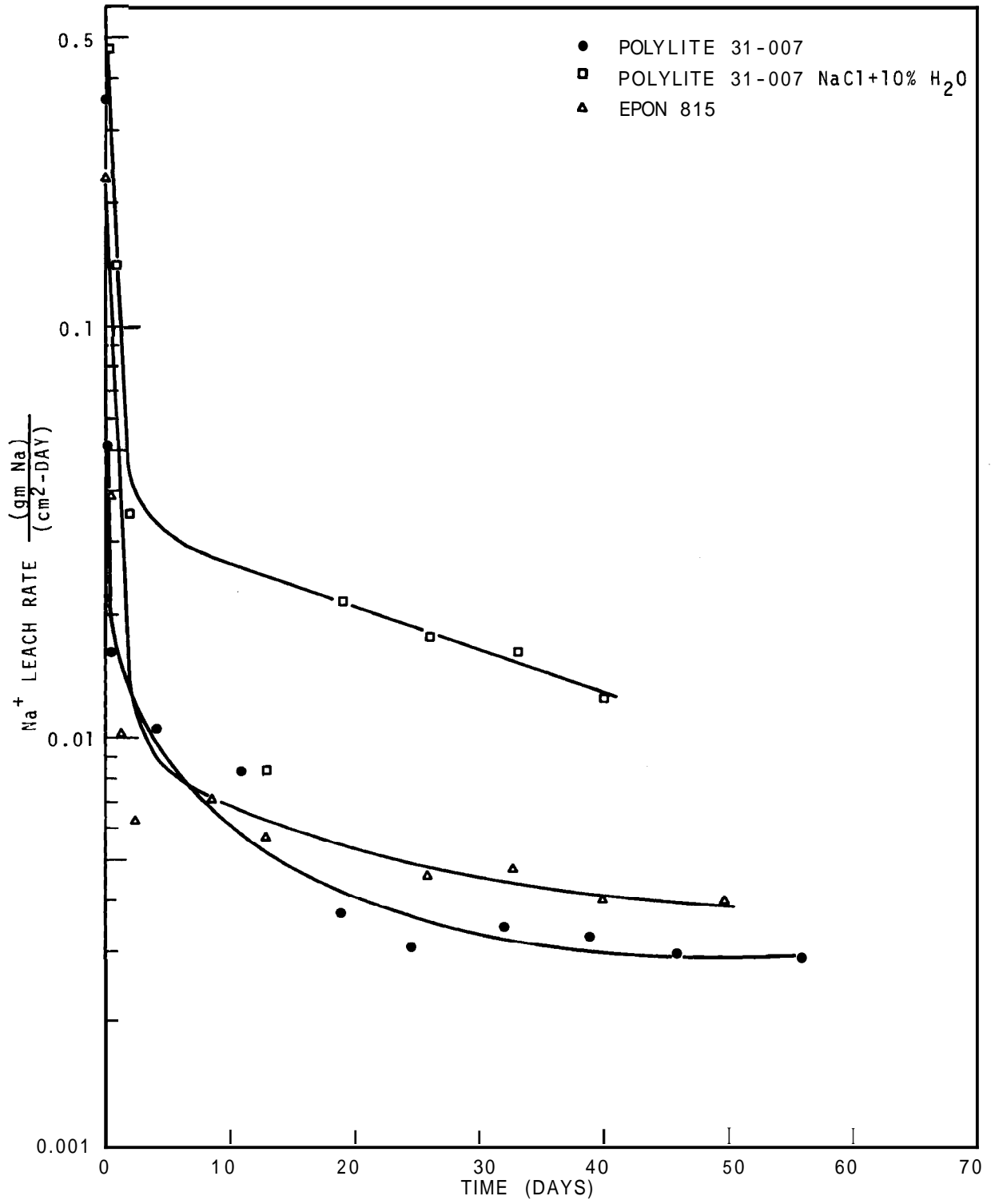


Figure 13 Na⁺ Leach Rate of Resin with NaCl salt

Table 4
Synthetic Salt Waste Solution

Compound	Concentration	
	(M)	(g/l)
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.597	223
NaOH	4.14	166
NaNO_3	0.48	40.8
NaNO_2	0.46	31.7
Na_2CO_3	1.14	120.8
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	0.008	3.04
NaCl	0.052	3.04
NaF	0.021	0.88
Na_2SO_4	0.01	1.42
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.036	1.45
$\text{NaSiO}_3 \cdot 9\text{H}_2\text{O}$	0.0065	1.85

dried at 100 °C for 12–24 hours. This produced a dry salt cake which was then ground to a coarse powder with a mortar and pestle. Early in this phase of the investigation an attempt was made to omit the drying step. However, none of the resins tested would harden when mixed with the wet salt. Moreover, a sufficiently dry product could not be produced by vacuum filtration. This observation leads to the conclusion that salt wastes would have to be nearly completely dewatered prior to mixing with any of the resins tested.

Derakane 118 would not harden when mixed with the dry salt waste and was therefore rejected for further study. Leaching experiments were conducted with Polylite 31-007 and Epon 815 and the results are summarized in Figure 14 along with leach rates reported for an asphalt-waste mixtures"). The latter contains 40% asphalt whereas the resin-waste mixtures contain 33% resin. Only the initial portion of the asphalt-waste leach curve is shown in Figure 14. The data reported⁽¹⁾ shows an increase in the leach rate of asphalt-waste mixtures after 80 days after which it stabilizes at about 2×10^{-4} g/cm²/day at 100 days. Three leaching curves are presented for Epon 815 and represent castings made from the products of three separate preparations of the salt waste from the standard composition solution described in Table 4. The initial leach rate for the synthetic salt waste itself was determined to be $\sim 19 \frac{\text{g Na}}{\text{m}^2\text{-day}}$

Incorporation of salt waste in a resin matrix will render the waste less leachable for two reasons: (1) the salt crystals will be encapsulated in insoluble material, and (2) the resin-salt mass is essentially impermeable to the passage of water. Radioactive cesium is readily leached from calcined

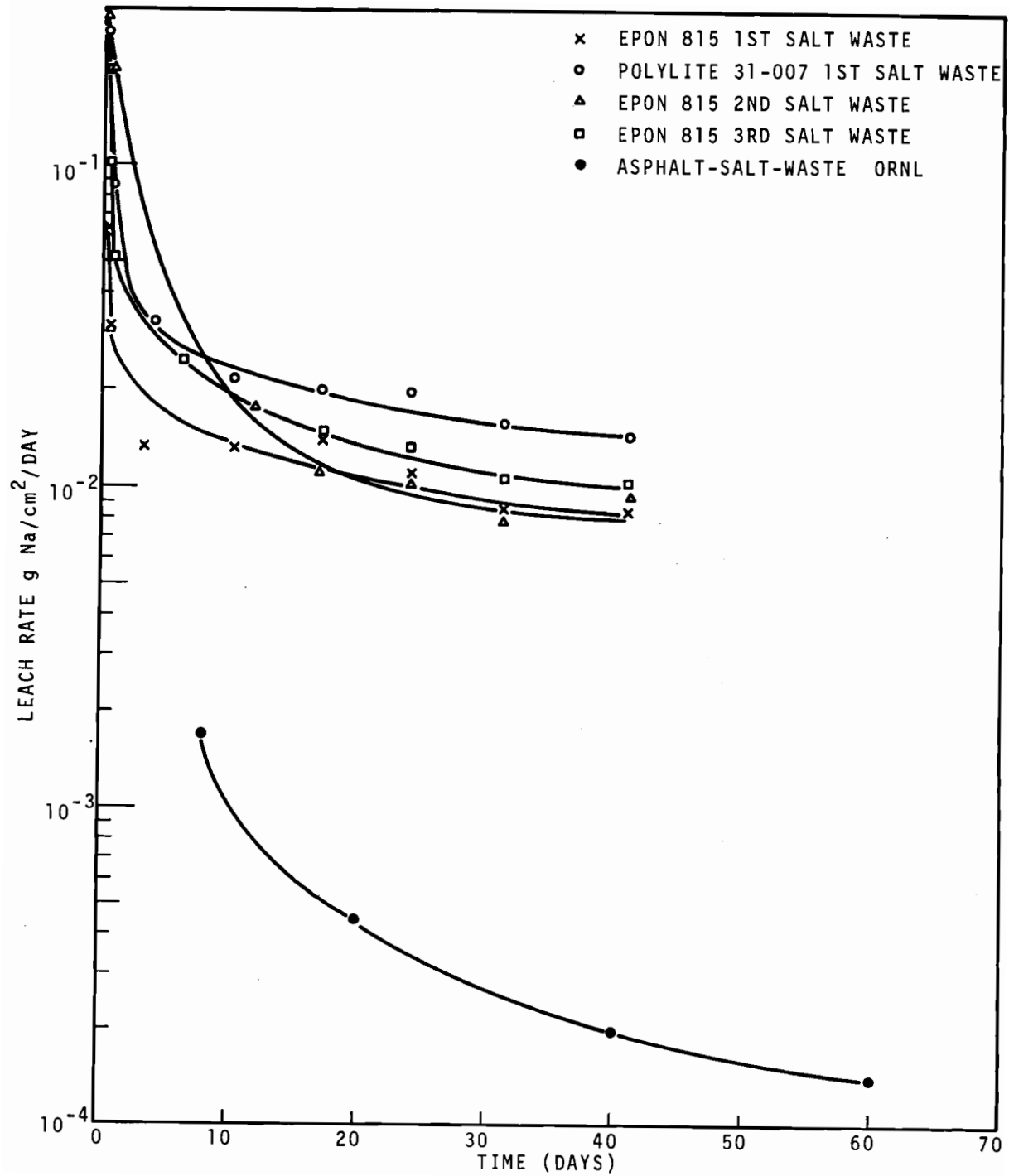


Figure 14 Sodium Leach Rates of Resin-Salt-Waste Mixtures

alumina and zirconia wastes by the passage of water through the granules^(2,3). The amount of cesium leached over a period of thirty days from alumina waste and zirconia waste is 93% and 53%, respectively. The estimated sodium leached from the Epon 815 - 1st salt waste mixture (Figure 14) over a 30 day period was 13%. Although the data are not strictly comparable, it is nevertheless evident that a considerable reduction in leach rates can be accomplished by incorporating the salt granules in a resin matrix.

Mechanical Properties

Samples of resin-salt mixtures were prepared for mechanical testing as previously described for resin-soil mixtures. Table 5 summarizes the results of the mechanical tests.

Polylite 31-007 proved to be superior to the other resins tested with the synthetic salt wastes. The one major problem associated with this resin was the very rapid setting time of ~ 15 minutes. Attempts to prolong the period of time prior to setting by adding styrene to the resin before mixing with the salt waste resulted in a product which would not harden. Unless some effective method of delaying the setting of this resin is developed, PolyLite 31-007 could not be used in a practical field situation.

Table 5
Mechanical Properties of Resin-Salt Waste Mixtures

	Polylite 31-007	Epon 815
Tensile Strength (psi)	1380	250
Compressive Strength (psi)	8100	1000
Shear Strength (psi)	2100	380

Both Epon 815 and PolyLite 31-007 were effective in reducing leaching from the synthetic salt waste. However, unless some practical means of drying actual salt waste is developed or a resin capable of hardening with the wet salt is found, the feasibility of application of resins to contain salt wastes is doubtful.

Samples of resin-salt waste mixtures were tested for **flamability** by ignition with an oxygen-propane torch. The samples would burn under the torch but would not sustain combustion by themselves whereas the resin or a mixture of resin and sodium nitrate would support combustion. Samples of resin-soil mixtures would not support combustion.

Ion Exchange Resins

It was postulated that it might be possible to formulate resins with ion exchange properties in order to contain the radioactivity in soil mixtures by means of ion exchange as well as physical entrapment. The criteria for preparation of the ion exchange resin (polymerization at ambient temperatures with ion exchange sites in place) rules out a number of common ion exchange resins. For example, it is necessary to introduce the active sites (SO_3H) on styrene-divinylbenzene polymer after the polymerization process. This may be accomplished by sulfonating or by hydrolyzing amide groups placed on the resin structure during the polymerization process. In either case it is not practical to do this with large masses of resin since penetration of reagents would be extremely slow. Phenolic condensation resins are prepared at elevated temperatures. Weak base (COOH) acrylic resins appeared to have the best chance for **in situ** polymerization. A formulation for an acrylic ion exchange resin was obtained from the Rohm and Haas Company.

Difficulty was encountered in developing a procedure for the formulation of an acrylic resin which would harden. The procedure finally adopted for production of the acrylic is as follows:

1. Mix together 40% ethyl acrylate, 20% X980 (Rohm and Haas monomer solution) and 15% HEMA (hydroxyethyl methyl acrylate).
2. Dissolve 1/2% benzoyl peroxide paste in the mixture.
3. Inject 1/4% dimethyl aniline and mix until the solution has shown a 4 °C rise in temperature (24°-28 °C in the laboratory).
4. Mix in 25% acrylic acid.

If the acrylic acid is added too early it apparently reacts with the dimethyl aniline and the mixture will not set.

The acrylic polymer was observed to set up and harden with soil in 25 minutes to 2 hours depending upon the temperature. A resin to soil ratio of 50 g/50 g was employed. Acrylic mixed with soil from the field test site was observed to harden in the soil within 50 minutes if placed in the sunlight at 32 °C. However, the excess liquid on top of the soil-resin mixture required more than a day to harden. On the other hand, cesium based dry soil-resin mixtures set in 25 minutes at 24 °C and in this case the excess top resin layer hardened in the same time period. Samples in small test tubes required longer set times unless heated (4-6 hours at 24 °C, 25-50 minutes at 32 °C).

Finely ground acrylic resin was suspended in water and titrated with 0.1 N NaOH in order to obtain an estimate of its ion exchange capacity. The exchange capacity thus determined was 5 meq Na⁺/gm resin.

Static leach tests for soil-acrylic mixtures were conducted over a twenty-day period. Procedures used in these leach tests were identical

with those outlined for the thermosetting resins. Leaching data are presented in Figure 15. Although the acrylic soil mixtures leach at a considerably lower rate than the soil alone, leach rates of these mixtures are consistently higher than observed for comparable mixtures of thermosetting resins. No advantage in the use of the acrylic resin was determined. It may be possible to devise a superior acrylic formulation than that employed in the current studies. The acrylic formulation used in this investigation was highly unsatisfactory since it was impossible to consistently reproduce the setting characteristics of the resin. From a practical standpoint, it is unlikely that the procedure outlined above could be feasibly followed in a field or process situation. However, this procedure was necessary to produce an acrylic which would harden. Based on the above observations, the acrylic resin shows little promise.

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