BNL-21571

CONF-760622--5

Some Techniques for the Solidification of Radioactive Wastes in Concrete

P. Colombo and R. Neilson, Jr.
Department of Applied Science
Brookhaven National Laboratory
Upton, N.Y. 11973

June 1976

To be presented at 1976 Annual Meeting of American Nuclear Society, June 14-18, 1976, Toronto, Canada.

MASTER

This research was performed under the auspices of the United States Energy Research and Development Administration under Contract No. E(30-1)-16.

OT E(30-1)-16

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

BNL-21571

SOME TECHNIQUES FOR THE SOLIDIFICATION OF RADIOACTIVE WASTES IN CONCRETE

P. Colombo and R. Neilson, Jr.

June 1976

ABSTRACT

This paper discusses some techniques for the solidification of radioactive wastes in concrete. The sources, storage, volume reduction and solidification of liquid wastes at Brookhaven National Laboratory (BNL) using the cement-vermiculite process is described. Solid waste treatment, shipping containers and off-site shipments of solid wastes at BNL are also considered.

The properties of low heat generating high level wastes, simulating those in storage at the Savannah River Plant (SRP), solidified in concrete were determined. Polymer impregnation was found to further decrease the leachability and improve the durability of these concrete waste forms.

SOLIDIFICATION OF BROOKHAVEN NATIONAL LABORATORY (BNL) LIQUID AND SOLID WASTES

Sources

Brookhaven has no high level waste from chemical fuel reprocessing operations. The semi-solid radioactive material that was generated during the days when the Brookhaven Graphite Research Reactor (BGRR) was fueled by natural uranium is still in storage at the Waste Treatment Facility. At present, there is about 100 cubic meters of wet sludge which when recently assayed was found to contain approximately 10.5 Ci ^{239}Pu, 1.4 Ci ^{238}U and 100 Ci of mixed fission products (MFP). Plans for the packaging and off-site shipment and storage of this material will be initiated during FY 1976 and extend through FY 1980. Preliminary and tentative plans which have been developed to date indicate that the material will be processed and packaged according to existing technologies and then committed to retrievable storage at Oak Ridge.

The largest producer of radioactive waste at BNL was the air-cooled BGRR. Since its shut down in 1968, the major volume of active wastes originate at the Hot Laboratory complex and the High Flux Beam Reactor (HFBR). Other facilities which contribute contaminated waste include those operated by the Biology, Chemistry, Medical and Applied Science departments. It has been BNL policy to reduce waste volume to a minimum since much of it must be disposed off-site.

Liquid Waste Storage and Treatment Facilities

BNL has three 3.8×10^5 liter tanks at the Waste Treatment facility which serve as temporary storage. Liquid radioactive wastes in tank storage eventually are pumped into a 38,000 liter blending tank where the pH is adjusted to ~ 7 prior to being fed into an evaporator for volume reduction. Figure 1 shows the flow sheet of the Vapor Compression Evaporation unit at BNL, which has been in operation since 1952(1). A concentration factor of about 100 is achieved with an overall decontamination factor of 10^6-10^7 which results in a product containing $\sim 30\%$ solids. Before evaporization, typical waste contains 5×10^{-9} Ci/cc consisting mainly of beta and gamma emitters.

The slurry produced by the evaporator contains essentially all the activity of the initial waste, except ^3H, which is carried over in the distillate. The slurry is transported in portable tanks to a 19,000 liter below ground interim storage tank at the Waste Management Area for eventual solidification. Storage in this tank generally does not exceed one year.

Solid Waste Treatment Facilities

A power baler was installed at the Waste Management Area in 1957 for reducing the volume of solid combustibles. Burning them in an enclosed system has proved uneconomical and difficult, so incineration of solids has not been pursued. Ion exchange columns used in the treatment of liquid wastes are disposed of as solid wastes rather than being regenerated as was formerly done.

Packaging and Solidification for Disposal

Prior to 1959, BNL used 55 gallon drums (nominally 208 liter capacity) as the standard package for sea disposal. Slurry from the evaporator was mixed with cement in a batch-type mixer and poured into drums to harden. Few restrictions were imposed upon these packages other than a minimum density of 5.8 kg/liter of capacity in order to guarantee that they sink. Early in 1959, the volume and activity of radioactive waste reached a point where the continued use of 55 gallon drums for disposal became increasingly impractical. Larger packages were required to provide sufficient shielding and at the same time allow for larger payloads.

Three reinforced concrete casks were designed and fabricated to accommodate the various types and levels of radioactive wastes generated at BNL. Pertinent data for the three casks are given in Table I. These casks as designed in 1959 are currently used at BNL.

The Type III cask shown in Figure 2, is generally used for solidification of slurry wastes, baled paper and trash. Type I and II casks having thicker walls are used to reduce surface radiation levels and personnel exposures for more active gamma wastes. These casks are shown in Figure 3. The Brookhaven Overpack, a reusable steel protective outer container can be used with these casks to satisfy the requirements of 10CFR71 Appendix B, "hypothetical accident conditions" for the transport of larger than type A quantities of radioactive materials.

Waste slurry from the evaporator is solidified in the 15 cm wall concrete casks by use of a mixture of portland cement and vermiculite. The vermiculite acts as an absorber and as a cement diluent to reduce the heat evolved by cement hydration during curing. In the solidification procedure, portland cement and an agricultural grade vermiculite are first dry mixed in a hopper in the proportions of 1 part cement to 3 parts vermiculite by volume. This dry mixture is then transferred into the concrete cask by means of a conveyer belt as shown in Figure 4, to the lip level of the cask (Figure 2). The slurry is introduced into the cement-vermiculite mixture through a pipe 1.5-1.8m in length with a 1.3 cm I.D. situated in the center of the cask to a depth of about 2.5 cm from the bottom. Prior to solidification, the slurry is agitated for one day in the slurry tank to obtain a uniform mixture. This mixture is pumped into the cask using a gas operated centrifugal pump. At each pumping, samples are analyzed for total activity and isotopic content. A ball valve throttle is used to regulate the rate of slurry flow. Slurry is pumped into the cask until moisture is uniformly observed on the surface. Subsequently, a steel reinforcing bar grid is placed over the top and a concrete mix of the same formulation used in cask production is poured to seal the cask as shown in Figure 5.

The quantities of materials used to solidify evaporator slurry in a Type III cask are typically:

portland cement	0.91 m^3
vermiculite	2.7 m^3
slurry	$1.25x10^3$ liters

Based on the above proportions, the composite consists of 0.79 cm^3 of waste slurry/g mix. The solidified slurry waste has a total activity currently ranging from 0.87-2.3 Ci/batch.

Solid wastes are also packaged in these concrete casks for disposal. Contaminated machinery and compressed solid combustibles are placed in a cask which is then filled with a concrete mix. Ion exchange resins are normally received at the Waste Management Area in 55 gallon drums which are placed into a cask which is then filled with cement. For small resin volumes or resins in inadequate packaging, the resin may be mixed with the cement used to filled a cask.

A summary of all solid wastes processed at BNL for off-site shipment during the years 1954-1975 is shown in Table II.

SOLIDIFICATION OF SAVANNAH RIVER (SRP) WASTE IN CONCRETE WASTE

Concrete can be used for the solidification of intermediate- and low heat generating high-level wastes. Work was performed at BNL to investigate the properties of Savannah River Plant (SRP) high level waste incorporated into concrete(2-10).

SRP waste currently stored in underground tanks is in the form of sludge, supernate and salt cake (formed by evaporation of aged supernate). The sludge is composed principally of $Fe(OH)_3$ and MnO_2 while the salt cake and supernate contain $NaNO_3$, $NaNO_2$, NaOH, Na_2CO_3 and $NaAlO_2$. The primary sources of toxicity and heat generation in this waste are ^{137}Cs and ^{90}Sr. The bulk of the ^{90}Sr in the waste is adsorbed in the sludge while the majority of the ^{137}Cs is found in the supernate. The average rate of heat generation of this waste is approximately 0.008 W/ . In a conceptual solidification process, waste would be removed from tank storage by dissolving the salt cake with water and sluicing the sludge and salt-supernate solution from the tank. The sludge would be separated from the liquid fraction by centrifugation and filtration. ^{137}Cs would be removed from the solution by ion exchange and sorbed onto zeolite. The sludge would be washed to remove its salt content and dried. The forms of waste for a solidification process are then sludge, zeolite, and a salt solution containing relatively little activity. This salt solution could be evaporated to form a salt cake.

Simulated wastes of these types were solidified using portland type II and high alumina (Lumnite[a]) hydraulic cements. The leachability of these formulations was determined by a modification of the IAEA static leach test method(11). The modification consisted of exposing the entire external surface area of the specimen to the leachant (distilled water) rather than the top surface only. During the first two weeks, the leachant was removed daily for analysis and replaced by fresh leachant. Subsequently, sampling was done on a weekly basis. Cesium and strontium analyses were performed by atomic adsorption spectrophotometry; a colorimetric method was used for nitrate analysis. Leach rate data were calculated both as a fraction release, F_i, and bulk leach rate, L_B, where

$$F_i = \frac{a_n}{A_o} \qquad (1)$$

and

$$L_B = F_i\left(\frac{m}{S \cdot t}\right) \qquad (2)$$

[a]Trademark, Universal Atlas Cement, Division of United States Steel Corporation.

where a_n = amount of the species of interest leached from the composite during leach period n.

A_o = initial content of the species of interest in the composite.

m = composite mass, g.

S = geometric external surface area of the composite, cm^2.

t = leach time, days.

The bulk leach rate is expressed in units of $g/(cm^2\text{-day})$.

The strontium leachability of sludge-cement composites using high alumina and portland type II cements is shown in Table III. Increasing the sludge content of the composites results in decreasing strontium bulk leach rates. These leach rates represent the release of strontium from both the sludge and cement. Since the sludge adsorbs strontium, increasing the sludge content increases the probability that strontium being leached from the composite encounters a sludge particle and is adsorbed. The sludge has a strontium content of 367 ppm while the portland type II cement contains 720 ppm strontium and the high alumina cement 190 ppm. The leach rates for cement-water pastes given in Table IV are two orders of magnitude higher than for sludge-cement composites suggesting that the sludge also acts to sequester strontium from the cement matrix. As such, the rate at which strontium is leached from the sludge may be lower than suggested by Table III.

The release of cesium from Linde AW-500[b] zeolite incorporated in cement is a function of the zeolite content of the composite as shown in Table V. A decrease in the cesium bulk leach rate is noted as the zeolite content in the composite is increased.

---

[b]Union Carbide Corporation, New York, New York

Based on calculations, the relative amounts of sludge and cesium to be disposed are such that if combined in one composite formulation, there would be 16 parts of sludge to each part of zeolite by weight. A high alumina cement concrete composite formulation was determined using this ratio, incorporating as much sludge as possible while maintaining an adequate composite integrity (1,000 psi compressive strength). This formulation and its leach rate are shown in Table VI. Note that while the strontium bulk leach rate is comparable to that for sludge-cement composites, the cesium leach rate increased almost two orders of magnitude over that for a comparable zeolite-cement composite. The cause of this behavior is not immediately obvious, but apparently represents an interaction between the sludge and the zeolite. This suggests that the sludge and zeolite should be solidified separately.

The low level sodium nitrate waste from the SRP process can also be solidified in concrete. The leach behavior of portland type II and high alumina cements containing sodium nitrate was investigated(12-15). The bulk leach rate of $NaNO_3$ in portland type II cement composites varied from 2.5×10^{-4} to 1.3×10^{-2} g/(cm^2-day) for 5.0-30.0 wt.% $NaNO_3$ composites respectively. The leach rate was somewhat higher when high alumina cement was used for solidification. This is shown in Figure 6. This difference is attributed to a larger average pore size in the high alumina cement concrete.

POLYMER IMPREGNATED CONCRETE

Since concrete is an open cell structure as a result of the interconnected porosity formed during the cure stage, it is permeable to water and other fluids and therefore exposes a larger surface to leaching than is evidenced by the external geometric surface area. Techniques have been developed at BNL to impregnate this porosity with styrene monomer which is subsequently polymerized in situ(12-19). This produces a polymer impregnated concrete (PIC) which is essentially impermeable while its strength, durability, and resistance to chemical attack are significantly improved.

The process for producing polymer impregnated concrete is shown in Figure 7. Cement mixing and casting may be accomplished by a number of methods. Once the waste has been solidified in concrete, styrene monomer containing a polymerization catalyst is allowed to soak into the casting. After the concrete has been impregnated with monomer, it is heated to induce polymerization. Benzoyl peroxide and AIBN (2,2'-Azobis-[2-methyl propionitrile]) have been used as polymerization catalysts for styrene monomer at a concentration of approximately 0.5 wt.% in the monomer. Temperatures of 50-70^{o}C are used to induce polymerization. Styrene was chosen because of its low monomer viscosity which aids in the impregnation step and its excellent radiation resistance. The effect of polymer impregnation on cesium and strontium leach rates of cement concrete (CC) and polymer impregnated concrete (PIC) can be seen in Table VII. The first cement concrete formulation incorporates zeolite loaded with both cesium and strontium while in the second formulation zeolite contains cesium and the sludge contains strontium. Polymer loadings for these formulations averaged 8.4 wt.%. PIC specimens exhibited bulk leach rates for cesium and strontium at least two orders of magnitude lower than the respective cement concrete specimens. Most PIC leachant analyses were non-detectible (<0.01 ppm) accounting for the "less than" values in Table VII.

The durability of concrete matrix materials are considerably improved as a result of polymer impregnation. Polymer impregnated concretes typically exhibit compressive strengths of 12,000-20,000 psi. Failure due to freeze-thaw cycling is eliminated. The resistance of concrete to chemical attack is also greatly improved by polymer impregnation.

REFERENCES

1. F.P. Cowan and L. Gemmell, "Waste Management Operations at Brookhaven National Laboratory", Hearings on Industrial Radioactive Waste Disposal Problems held before the Special Sub-committee on Radiation of the Joint Committee on Atomic Energy, Jan. 28 - Feb. 3, 1959.

2-10. P. Colombo, et. al., _Savannah River Laboratory Long-Term Waste Storage Program_, Progress Reports 1-9, July 1973-April 1975.

11. Hespe, E.D., _At._ _Energy_ _Rev._ _9_(1), 195, (1971).

12-15. B. Manowitz, et. al., _Development of Durable Long-Term Radioactive Waste Composite Materials_, Progress Reports 3-6, June 1973-March 1974.

16-19. B. Manowitz, et. al., _Development of Durable Long-Term Radioactive Waste Composite Materials_, Progress Reports 7-10, April 1974-March 1975.

Table I
CONCRETE CASK DATA

Cask No.	Outside Dimensions (m)	Nominal Wall Thickness (cm)	Cask Volume (m^3)	Storage Capacity (m^3)	Cask Weight (kg)
I	1.2x1.2x2.4	43	3.6	0.18	8,120
II	1.5x1.2x2.4	30	4.5	1.02	8,390
III	1.5x1.5x1.8	15	4.3	2.27	4,760

Table II
Solid Wastes Processed at BNL for Off-Site Shipments

Calendar Year	No. of Containers	Type of Containers	Curie Content	Destination
1954	476	55 gal. drums	233	Sea disposal
1955	685	" " "	597	" "
1956	640	" " "	600	" "
1957	704	" " "	500	" "
1958	692	" " "	1,100	" "
1959	1,354	" " "	2,000	" "
	20	Concrete vaults	500	Oak Ridge
1960	92	Large pkgs.[a]	2,000	" "
1961	60	" "	1,300	" "
1962	55	" "	1,200	" "
1963	45	" "	980	West Valley, N.Y.
1964	38	" "	75	" " "
1965	32	Vaults, boxes, tanks [a]	152	" " "
1966	50	" " "	346	" " "
1967	31	" " "	4,846	" " "
1968	43	" " "	3,132	" " "
1969	None shipped			
1970	34	Vaults, boxes, tanks[b]	3,379	" " "
1971	34	Vaults and boxes	2,400	" " "
1972	16	" " "	653	" " "
1973	40	Vaults, boxes, tanks[b]	9,824	West Valley, N.Y. & Morehead, Kentucky
1974	47	Vaults, boxes and drums	35,504	Morehead, Kentucky
1975[c]	-	-	-	-

[a] Concrete vaults with 6", 12" and 17" shielding walls and a few sheet steel boxes for containing less active bulk gamma wastes that have been baled.

[b] Same concrete vaults and steel boxes plus 1,000 gal. oil tanks used for shipping solidified slurry.

[c] First six months only.

Table III
Strontium Leach for Sludge Type III - Cement Composites

Formulation, wt %			Specimen	Surface	Leach	Fraction	Bulk Leach Rate
Sludge	Cement	Water	Mass, g.	Area, cm^2	Time, days	Release	$g/(cm^2\text{-day})$
			HIGH ALUMINA CEMENT				
19.3	56.9	23.8	56.95	55.29	10	$<1.1 \times 10^{-4}$	$<1.1 \times 10^{-5}$
28.2	44.7	27.1	54.10	56.77	10	$<1.1 \times 10^{-4}$	$<1.1 \times 10^{-5}$
37.2	33.5	29.3	54.19	58.48	10	$<1.1 \times 10^{-4}$	$<9.9 \times 10^{-6}$
46.2	22.7	31.1	51.10	56.36	10	$<8.7 \times 10^{-5}$	$<7.9 \times 10^{-6}$
			PORTLAND TYPE II CEMENT				
20.0	55.7	24.3	59.75	56.77	10	6.3×10^{-4}	6.7×10^{-5}
30.0	42.6	27.4	54.00	55.99	10	3.5×10^{-4}	3.4×10^{-5}
40.0	29.5	30.5	53.70	56.36	10	$<2.1 \times 10^{-4}$	$<2.0 \times 10^{-5}$
50.0	16.4	33.6	49.90	55.54	10	$<8.3 \times 10^{-5}$	$<7.4 \times 10^{-6}$

Table IV
Strontium Leach for Cement-Water Pastes

Cement Type	Formulation wt % Cement	Water	Specimen Mass, g.	Surface Area, cm^2	Leach Time, Days	Fraction Release	Bulk Leach Rate $g/(cm^2\text{-day})$
Portland Type II	78.0	22.0	66.40	57.39	5	0.015	3.5×10^{-3}
High Alumina Cement (Lumnite)	78.0	22.0	63.20	56.96	5	0.022	4.9×10^{-3}

Table V
Cesium Leach for High Alumina Cement - Zeolite Composites

Formulation, wt % Zeolite	Cement	Water	Mass, g	Surface Area, cm^2	Leach Time, days	Cumulative Fraction Release	Bulk Leach Rate $g/(cm^2\text{-day})$
2.5	79.5	18.0	310.0	168.7	10	7.60×10^{-4}	1.40×10^{-4}
					31	1.36×10^{-3}	8.03×10^{-5}
3.9	76.1	20.0	320.5	167.2	10	6.53×10^{-4}	1.26×10^{-4}
					31	1.16×10^{-3}	7.17×10^{-5}
7.4	72.0	20.6	339.5	178.0	10	5.74×10^{-4}	1.09×10^{-4}
					31	1.05×10^{-3}	6.46×10^{-5}
11.3	66.0	22.7	370.7	187.4	10	4.34×10^{-4}	8.59×10^{-5}
					31	8.58×10^{-4}	5.48×10^{-5}
15.3	59.9	24.8	408.2	202.0	10	3.53×10^{-4}	7.13×10^{-5}
					31	8.18×10^{-4}	5.33×10^{-5}

Table VI
Cesium and Strontium Leach Rates For
Sludge-Zeolite-High Alumina Cement Composites

Composition, Wt.%				Mass,	Surface	Leach Time,	Cumulative Fraction Release		Bulk Leach Rate $g/(cm^2\text{-day})$	
Sludge	Zeolite	Cement	Water	g	Area, cm^2	Days	Cesium	Strontium	Cesium	Strontium
37.0	2.3	28.5	32.5	809.4	328.7	30	4.75×10^{-2}	8.86×10^{-5}	3.90×10^{-3}	7.27×10^{-6}

Strontium Content of Cement = 367 ppm

Cesium Loading of Zeolite = 1.0 meq/g

Table VII

Cesium and Strontium Leach Rates for Selected CC and PIC Formulations

Formulation, wt %					Polymer Loading wt %	Mass, g	Surface Area, cm^2	Leach Time, days	Bulk Leach Rate $g/(cm^2\text{-day})$	
Cement	Zeolite	Sludge	Sand	Water					Cesium	Strontium
35.0	12.5[a]	--	35.0	17.5	--	640.3	260.4	10	6.88×10^{-5}	2.07×10^{-4}
								31	2.27×10^{-5}	9.09×10^{-5}
								143	6.82×10^{-6}	2.50×10^{-5}
35.0	12.5[a]	--	35.0	17.5	8.69	702.0	279.4	10	$< 1.53 \times 10^{-6}$	$< 1.47 \times 10^{-6}$
								31	$< 4.72 \times 10^{-7}$	$< 4.56 \times 10^{-7}$
								143	$< 9.95 \times 10^{-8}$	9.61×10^{-8}
36.3	4.2[b]	8.3[c]	35.0	16.2	--	639.0	258.9	10	3.50×10^{-4}	4.65×10^{-4}
								31	1.83×10^{-4}	4.36×10^{-5}
								143	4.63×10^{-5}	9.27×10^{-7}
36.3	4.2[b]	8.3[c]	35.0	16.2	8.18	695.5	268.6	10	$< 1.60 \times 10^{-6}$	$< 1.49 \times 10^{-6}$
								31	$< 4.94 \times 10^{-7}$	$< 4.61 \times 10^{-7}$
								143	$< 1.04 \times 10^{-7}$	$< 9.72 \times 10^{-8}$

a. contains 0.11 meq cesium/g and 0.34 meq strontium/g

b. contains 0.32 meq cesium/g

c. contains 0.50 meq strontium/g

FIGURE NO.	TITLE
1	Flowsheet of Vapor Compression Evaporation Unit at BNL.
2	BNL Type III Concrete Cask.
3	BNL Type I (background) and Type II (foreground) Casks.
4	Filling a Type III Cask with the Dry 1:3 Portland Cement-Vermiculite Mix (by volume).
5	Capping a Filled Type III Cask.
6	Bulk Leach Rate as a Function of Sodium Nitrate Content for High Alumina and Portland Cement Composites (Averaged over First Ten Days).
7	Process Flow Diagram for the Fixation of Rad-Waste in Polymer Impregnated Concrete (PIC).

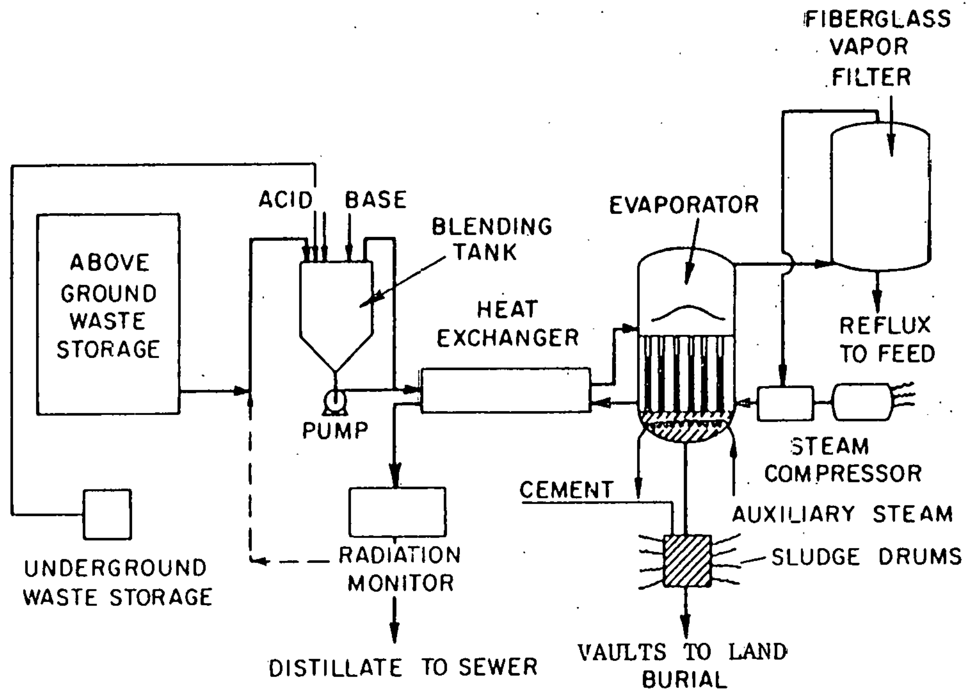

FIBERGLASS VAPOR FILTER
ACID
BASE
BLENDING TANK
EVAPORATOR
ABOVE GROUND WASTE STORAGE
HEAT EXCHANGER
REFLUX TO FEED
PUMP
STEAM COMPRESSOR
CEMENT
AUXILIARY STEAM
SLUDGE DRUMS
UNDERGROUND WASTE STORAGE
RADIATION MONITOR
DISTILLATE TO SEWER
VAULTS TO LAND BURIAL

Figure 1

Figure 2

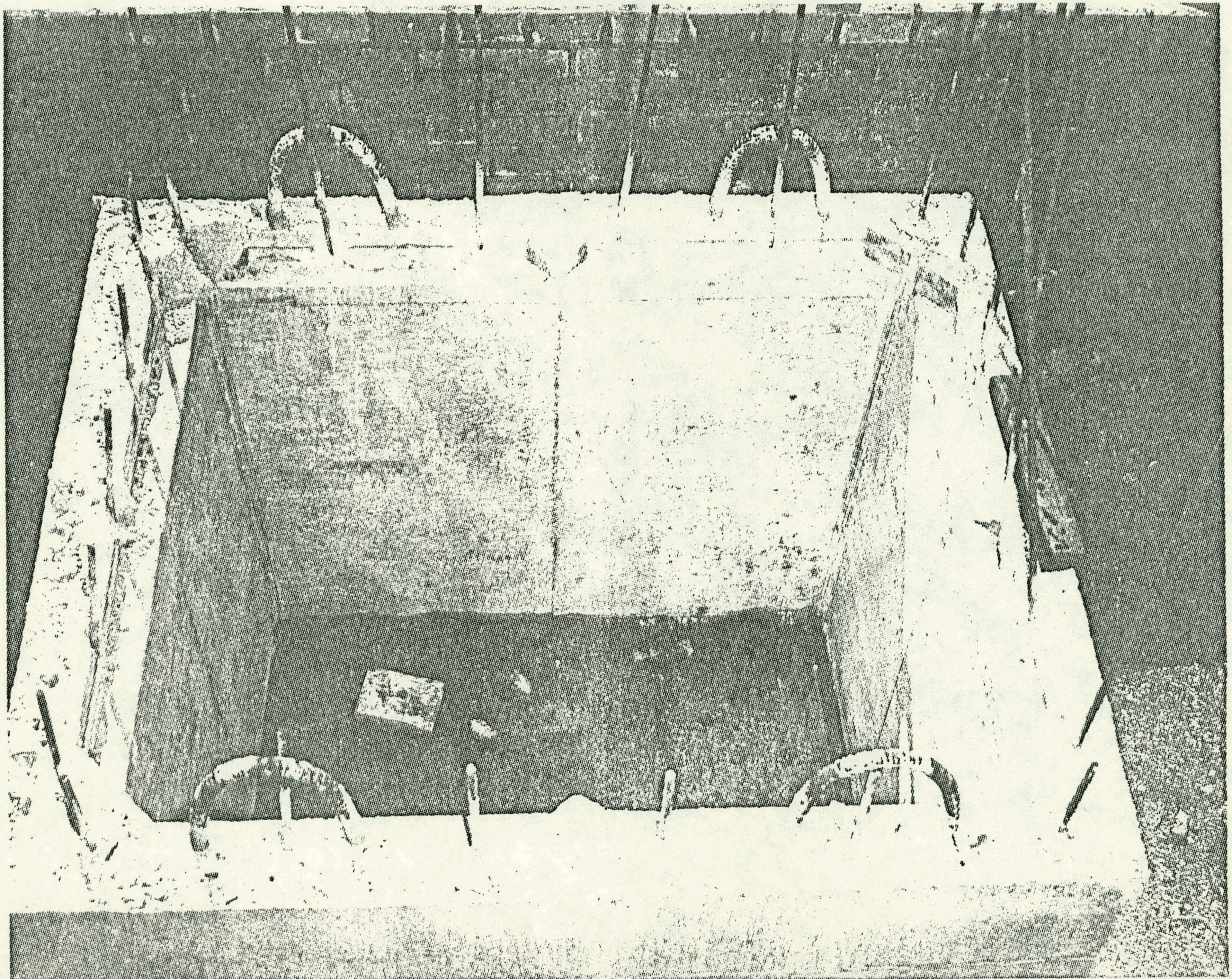


Figure 3

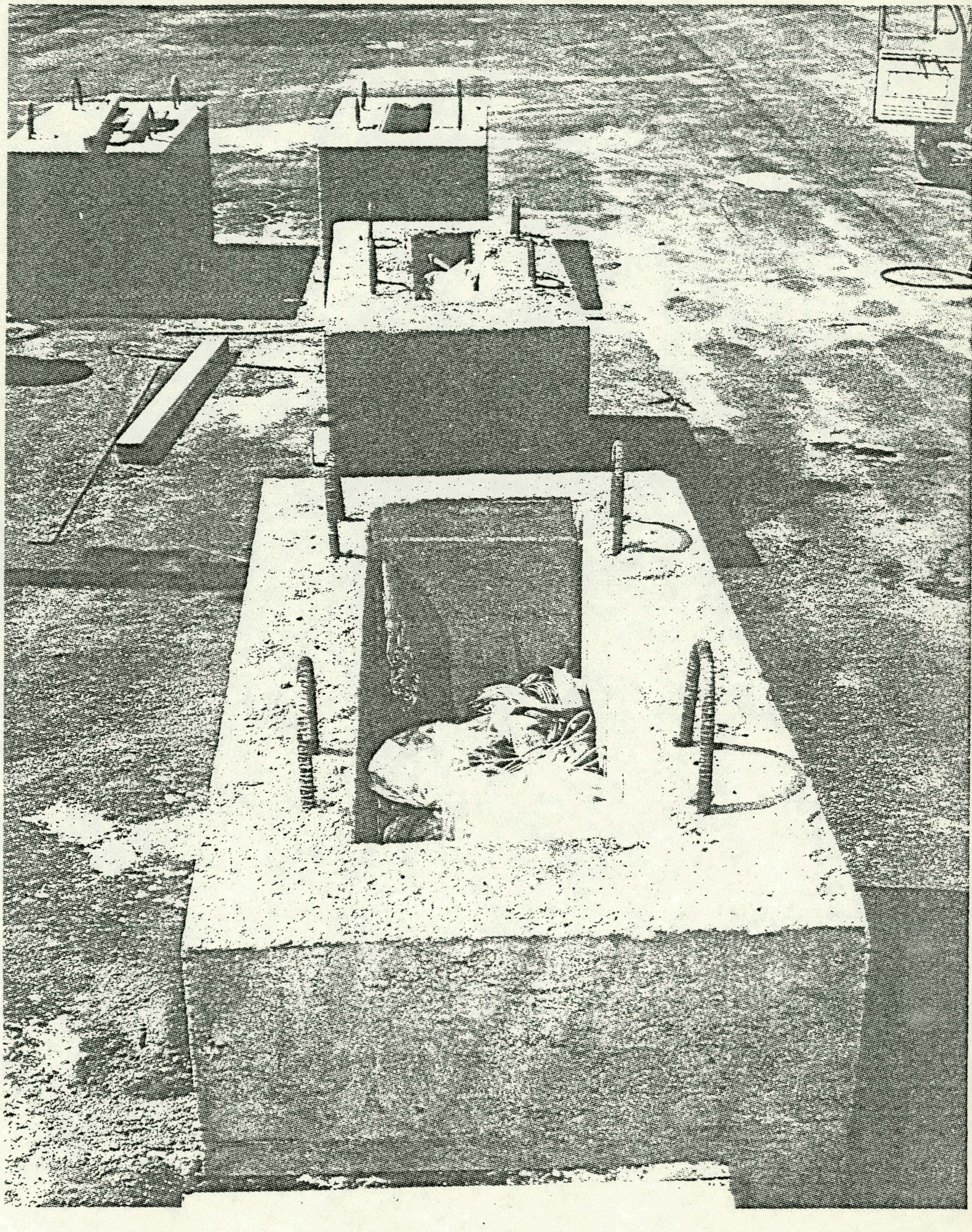


Figure 4

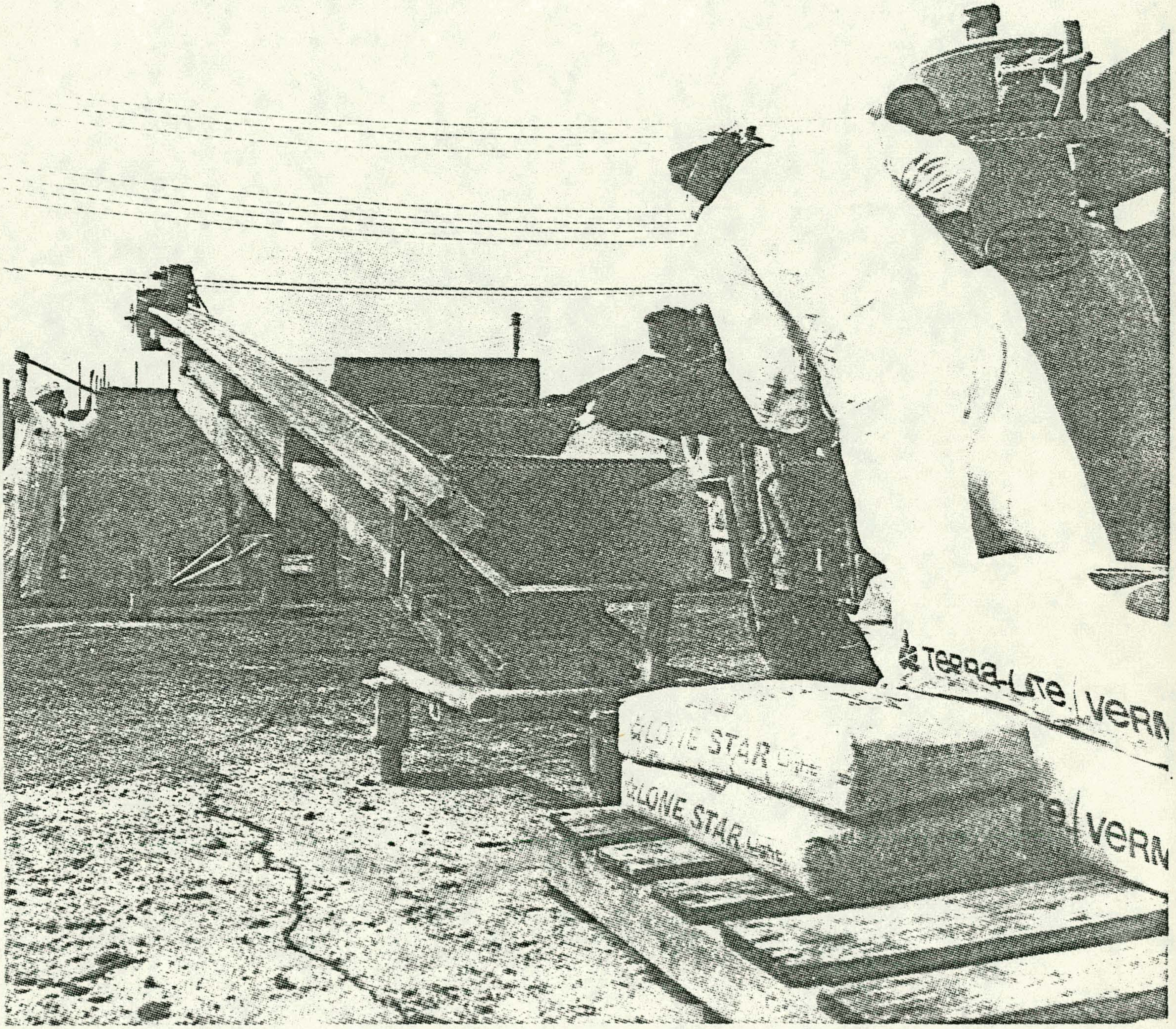
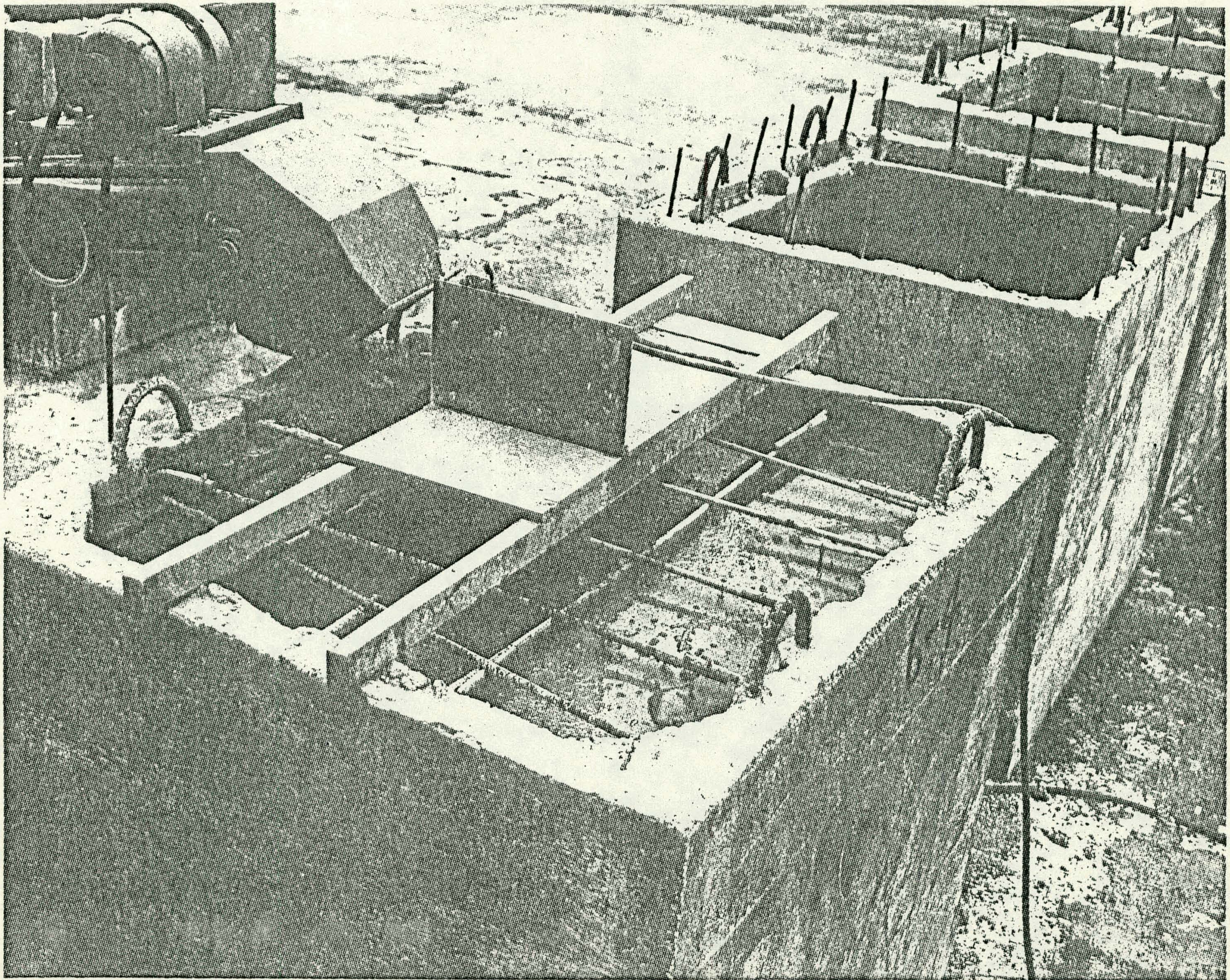


Figure 5



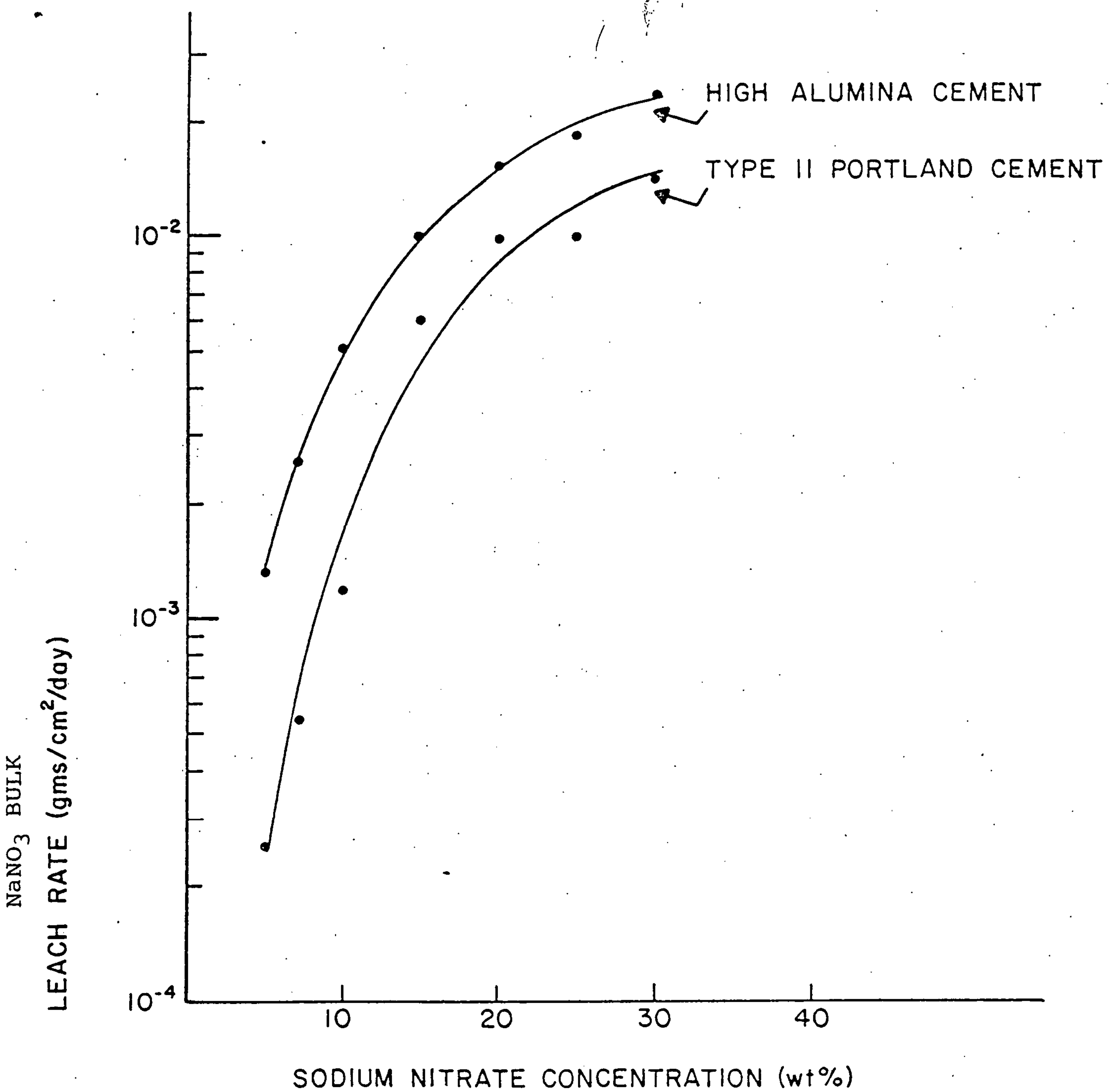
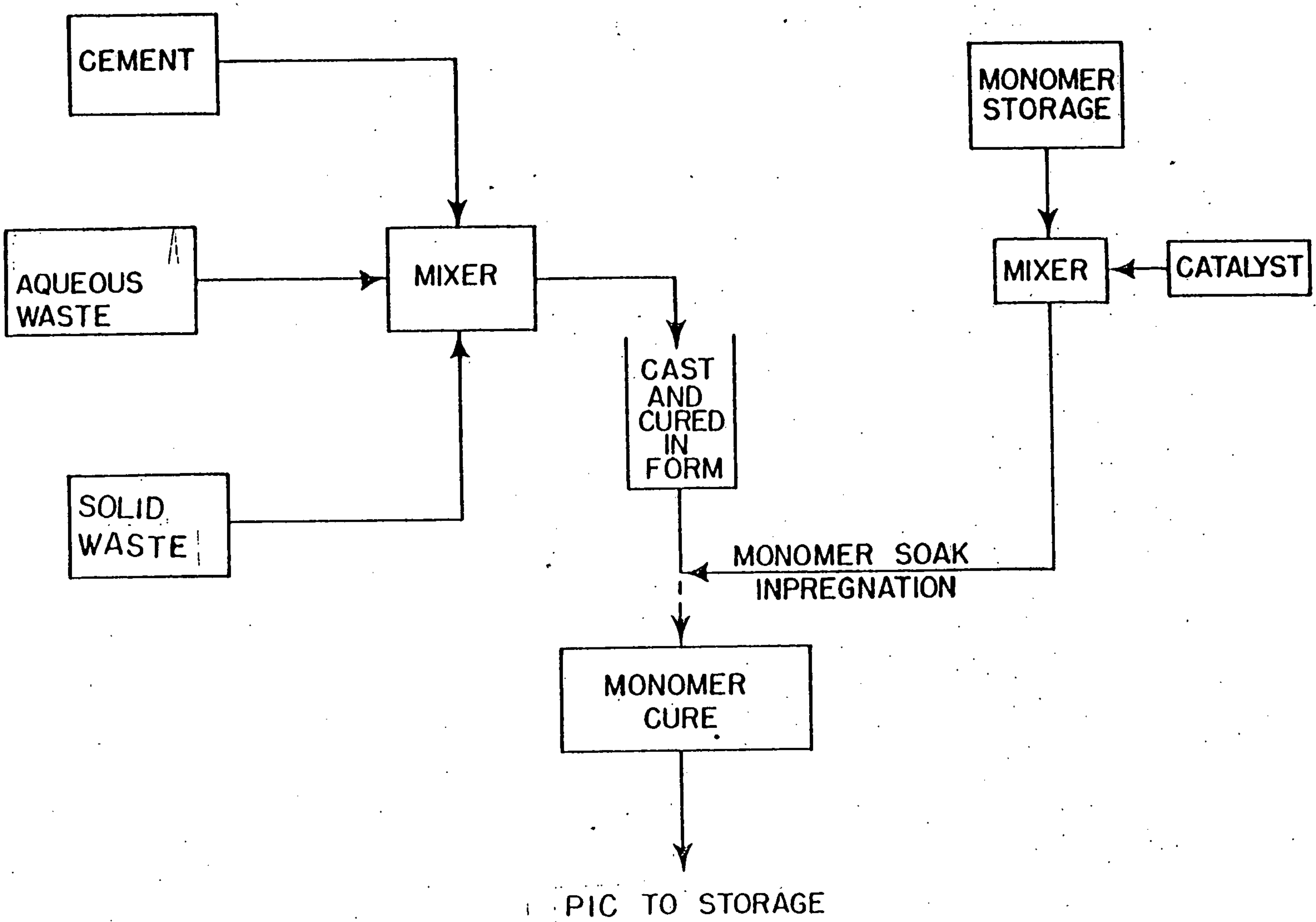

HIGH ALUMINA CEMENT
TYPE II PORTLAND CEMENT
10^{-2}
10^{-3}
10^{-4}
$NaNO_3$ BULK
LEACH RATE ($gms/cm^2/day$)
10
20
30
40
SODIUM NITRATE CONCENTRATION (wt%)

Figure 6

Figure 7


CEMENT
AQUEOUS WASTE
SOLID WASTE
MIXER
CAST AND CURED IN FORM
MONOMER STORAGE
MIXER
CATALYST
MONOMER SOAK INPREGNATION
MONOMER CURE
PIC TO STORAGE