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WELDON SPRING RAFFINATE PITS: EVALUATION OF CEMENT-BASED GROUTS AS A STABILIZATION OPTION

T. M. Gilliam
C. L. Francis

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OAK RIDGE NATIONAL LABORATORY
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EXECUTIVE SUMMARY

Solidification/stabilization technology has the potential to provide a regulatory acceptable and cost effective remedy for hazardous and/or low-level radioactive waste sites. Oak Ridge National Laboratory (ORNL) has conducted a study to assess the applicability of cement-based solidification/stabilization technology as a remedial action option for the Weldon Spring Raffinate Pits 1, 2, 3, and 4.

Three dry-solids blends were evaluated: (1) Blend A, consisting of 20 wt % Type II Portland cement and 80 wt % ASTM Class F fly ash, (2) Blend B, consisting of 40 wt % Type II Portland cement and 60 wt % ASTM Class F fly ash, and (3) Blend C, consisting of 60 wt % Type II Portland cement and 40 wt % ASTM Class F fly ash. The blends were combined with the raffinate pit sludge at mix ratios (grams of dry-solids blend per gram of waste) of 0.4, 0.6, and 0.8 g/g.

Waste forms were prepared with composite waste samples from pits 1, 2, 3, and 4 as well as composite samples diluted to 20 wt% solids content. All of the waste forms prepared with Blends B and C met the performance criteria of: (1) no drainable water within 28 d, (2) unconfined compressive strength of 60 psi and (3) resistance to thermal cycling. Volume increase (versus the original waste) was consistent for all three blends at any one mix ratio and were 22, 32, and 40 vol% at mix ratios of 0.4, 0.6 and 0.8 g/g, respectively.

Collectively, the data indicate that rate of set as determined by penetration resistance, drainable water and unconfined compressive strength can be controlled by minor changes in the dry-solids blend composition or mix ratio. In addition the effects of waste solids content on these properties can be controlled in the same manner. Thus these grouts (Blend B and C), using no proprietary additives, can accommodate expected variations in the waste composition or future more stringent performance criteria by the use of minor process operating changes (i.e., blend composition or mix ratio) which are well within the capability of standard commercially available technology.

Based on the available data, it is recommended that grouts prepared with Blend B at a mix ratio of 0.6 g/g be used as a reference formula for preliminary design and evaluation purposes. Waste forms prepared with this formula would be characterized by:

1. weight increase (versus the original waste) of 60%;
2. volume increase (versus the original waste) of 32%;
3. no free liquid within 21 d;
4. penetration resistance of 4000 psi within 14 d; and
5. unconfined compressive strength >200 psi.

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ABSTRACT

A proof-of-principal study was performed to assess the applicability of cement-based grout technology as a remedial action option for Weldon Spring Raffinate Pits 1, 2, 3, and 4. Grouts were prepared with actual waste samples and the resulting waste forms' drainable water, compressive strength, thermal cycling resistance, and volume increase were determined. The resulting data was then compared with available site performance criteria.

1. INTRODUCTION

In 1956, the Atomic Energy Commission (AEC) acquired about 89 hectares (220 acres) of the original Weldon Spring Ordnance Works property located in St. Charles County, Missouri, from the Department of Army for use as the Weldon Spring Uranium Feed Materials Plant (WSUFMP). The WSUFMP operated between 1957 and 1966, processing uranium ore concentrates and recycled scrap to produce pure uranium trioxide, uranium tetrafluoride, and uranium metal. An average of 16,000 tons of uranium materials were processed at this plant per year. In addition, thorium ore concentrates were also processed. These operations generated several chemical and radioactive waste streams, including raffinate streams from the refinery operation and the magnesium fluoride slurry streams (washed slag) from the uranium recovery process. These streams were slurried to four raffinate pits where the solids settled out and the supernatant liquids drained to the plant process sewer which drained off-site to a natural drainageway and ultimately to the Missouri River. The solids remaining in the pits consist of silica and other insolubles associated with the yellow cake ore feed materials, along with hydroxides and other precipitates formed from the pH neutralization of the raffinates with lime. Washed slag residues from the uranium metal production operation were also discharged to the pits. These pits contain an estimated 6 million cubic feet of waste sludge, including approximately 150 tons of uranium and 75 tons of thorium. The Department of Energy (DOE) has the responsibility for maintenance of the entire site including the 21-ha (52 acres) portion which contains the four raffinate pits.

Remedial action options for these raffinate pits are currently being evaluated. One option under consideration is stabilization/solidification.

Stabilization, as defined in the Waste Management Act, is "a chemical or thermal process in which materials or energy are added to the waste in order to reduce the possibility of migration of any hazardous constituents of the resulting stabilized waste" (115A.03, Subd. 32a). The goal of any stabilization process shall be to minimize the leaching of hazardous constituents from the waste. Stabilized wastes shall then be contained in a way so that the residuals do not pose a significant threat to human health or the environment.

Stabilization processes, through physical or chemical binding, limit the release of hazardous constituents contained in the waste by chemically altering the constituent to a more inert form, reducing the solubility of the constituent and/or reducing the accessibility of the constituent to the environment. As such, these processes include a broad spectrum of technologies, including glass, bitumen, polymer, and cement, as well as product consistency ranging from granular soil-like material to monoliths with properties similar to construction materials.

A previous evaluation of available stabilization/solidification technologies recommended that the glass and cement-based technologies be further evaluated for application to the Weldon Spring raffinate pits.[1] This recommendation was based on a general understanding of the processes and advantages/disadvantages of the host matrix material.

This report provides proof-of-principle information necessary to assess the merits of cement-based stabilization/solidification as a remedial action option applicable to the Weldon Spring raffinate pits.

In situ vitrification (glass) is being assessed by Pacific Northwest Laboratory (PNL) and will be reported separately.

2. DIRECTION FOR DEVELOPMENT EFFORTS

Preliminary scouting studies on two samples from the Weldon Spring raffinate pits were performed in 1985.[2] These samples, designated as 1-1 and 3-2, were obtained from pit 1 at sample point 1 and pit 3 at sample point 2, respectively.[3] Trace analyses of the samples are shown in Tables 1 and 2. Compressive strength data, on grouts prepared with these samples using two dry-solids blends: (1) 20 wt % Portland Type I cement, 80 wt % ASTM class F fly ash and (2) ASTM class C fly ash, are shown in Tables 3 and 4.[2] The compressive strength of the waste form utilizing the ASTM class C fly ash showed a decrease with time indicating a deterioration in the waste-form structure. It was hypothesized that this deterioration was due to the formation of a calcium aluminate hydrate such as $C3A \cdot 3CaSO_4 \cdot 31\text{-}32H_2O$ (i.e., ettringite).

The formation of this salt, with its large amount of water of crystallization and consequently large increase in volume, can be destructive to the grout product. If the ettringite is formed while the grout paste is still plastic, then the grout may be able to accommodate the expansive salt. However, if the ettringite forms after the grout has become rigid and "less forgiving," cracking will occur, which can significantly reduce the strength of the product. A discussion of ettringite is presented in Appendix A based on a literature search of textbooks, reports, and publications concerning cement chemistry and concrete research and development.[4-15]

As discussed in Appendix A, the chemistry of ettringite formation is complex. The majority of research on understanding the chemistry of ettringite has focused on neat cement pastes (i.e., cement and water). It is difficult to quantitatively extrapolate these data on ettringite to waste management applications because the synergistic effect of the waste components on cement chemistry is not well understood, and little research has been done in this area, particularly, in regard to the

Table 1. Trace analysis of Weldon Spring sample 1-1 after agitation and setting for 24 h

Element	Concentration Liquid (μg/mL)	 Solid (μg/g)
U	≤0.3	2,000
Th	≤0.3	100
Pb	≤0.1	≤10
Hg	≤0.1	≤10
Ba	-	30
Cd	≤0.5	≤20
Mo	1	5,000
Zr	-	20
Sr	2	50
As	-	100
Zn	0.6	1,000
Cu	0.2	100
Ni	≤0.1	-
Co	≤0.5	≤10
Fe	1	10,000
Y	-	20
Mn	≤0.03	500
Cr	0.6	30
V	0.1	10,000
Ca	>100	>100,000
K	50	500
Cl	10	1,000
S	100	10,000
P	0.4	2,000
Si	≤2	≤200
Al	0.2	500
Mg	5	10,000
Na	>100	8,000
F	≤0.2	>100,000
B	0.3	>100,000
Ce	-	≤4

Table 2. Trace analysis of Weldon Spring sample 3-2 after mixing and settling for 24 h

Element	Concentration Liquid (μg/mL)	Solid (μg/g)
U	0.6	8,000
Th	≤0.2	10,000
Pb	≤0.05	50
Hg	≤0.1	≤20
Ba	-	400
Sn	-	70
Cd	≤0.1	≤50
Mo	5	600
Nb	-	≤20
Zr	≤0.02	200
Y	-	60
Sr	0.7	50
Se	0.3	-
As	-	200
Zn	0.2	50
Cu	0.1	600
Co	0.2	≤5
Fe	0.3	>100,000
Mn	0.04	500
Cr	0.1	100
V	0.4	4,000
Ca	200	>100,000
K	40	500
Cl	4	700
S	100	700
P	0.4	7,000
Si	≤1	≤100
Al	>100	>100,000
Mg	>100	>100,000
Na	>100	>100,000
F	≤0.2	>100,000
B	0.7	>100,000
Ce	-	20

Table 3. Compressive strength of grout made with Weldon Spring sludge and a dry-solids blend of 20 wt% Portland Type I cement and 80 wt% ASTM Class F fly ash

Grout characteristics	Mix ratio of waste sample 1-1 (lb/gal)			Mix ration of waste sample 3-2 (lb/gal)		
	4	6	8	4[a]	6	8
7-d compressive strength, psi	22	157	650	39	145	225
28-d compressive strength, psi	562	235	977	147	119	951

Table 4. Compressive strength of grout made with Weldon Spring sludge and a dry-solids blend of ASTM Class C fly ash

Grout characteristics	Mix ratio of waste sample 1-1 (lb/gal)			Mix ration of waste sample 3-2 (lb/gal)		
	4	6	8	4[a]	6	8
7-d compressive strength, psi	39	72	257	45	123	212
28-d compressive strength, psi	65	148	195	15	44	107

Tables 3 and 4 formation of ettringite. However, it is clear that its presence in large quantities is undesirable.

For ettringite to form, two species must be present in some form: (1) aluminate and (2) sulfate. The waste characterization data from the raffinate pits had not been received at the time this study was initiated; thus, it is not clear if significant quantities of both of these species exist in the raffinate pits. Preliminary analyses (see Table 2) indicate that aluminum is present in large quantities; thus, the grout development studies presented in this report attempted to minimize ettringite formation as a precautionary measure.

Research on the basic chemistry of ettringite formation indicates that the potential for its formation is enhanced by the presence of excess lime, ASTM Class C fly ash, and the cement phase C3A. Thus, the cement-based matrix materials, lime and ASTM Class C fly ash were excluded from this study. In addition, Type II Portland cement was used in place of the more traditional Type I in order to control C3A content. A comparison of the major characteristics between Type I and II, as defined by ASTM C150-84, "Standard Specification for Portland Cement," are shown in Table 5. It should be noted that if the raffinate pit characterization data show that the sludge contains no significant quantities of sulfate, then Type I Portland cement could be used. In general, the use of Type I should show a perceptible increase in the wastes form's rate of set and final compressive strength as compared with Type II. Depending on the source of cement, the use of Type I may also result in a reduction of up to $20/ton in the cost of the cement. As discussed previously, Type II cement was used in this study in order to control the C3A content and, hence, summarize the potential for ettringite formation. The Type II cement used in these grout development studies was obtained from the Marquette Cement Co, a division of Lone Star Industries, located in St. Louis, Missouri.

In order to minimize the final volume increase (versus the waste) resulting from stabilization, it is desirable to substitute fly ash for the cement to the greatest extent possible. Previous scouting studies[2] indicated that ASTM Class F fly ash was acceptable for this purpose.

Table 5. Comparison of major characteristics between Type I and II Portland cement*

Cement Type	I	II
Silicon dioxide (SiO_2), min., %	NS	20.0
Aluminum oxide (Al_2O_3), max %	NS	6.0
Ferric oxide (Fe_2O_3), max., %	NS	6.0
Magnesium oxide (MgO), max., %	6.0	6.0
Sulfur trioxide (SO_3), max., %		
When (C_3A) is 8% or less	3.0	3.0
When (C_3A) is more than 8%	3.5	
Loss on ignition, max., %	3.0	3.0
Insoluble residue, max., %	0.75	0.75
Tricalcium aluminate (C_3A) max.,%		8.0

*See ASTM C150-84
NS - Not specified

Table 6. Major characteristics of ASTM Class F fly ash*

	ASTM Class F fly ash
Silicon dioxide (SiO_2) plus aluminum oxide (Al_2O_3) plus iron oxide (Fe_2O_3), min. %	70.0
Sulfur trioxide (SO_3), max., %	5.0
Moisture content, max., %	3.0
Loss on ignition, max., %	6.0

*See ASTM C618-85

Table 6 shows the major characteristics of ASTM Class F fly ash as defined by ASTM C618-85, "Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete." The material used in these grout development studies was obtained through the American Fly Ash Company. The fly ash is generated at Baldwin Station in Illinois and is presently being shipped through a terminal located in St. Louis, Missouri. The material characterization sheets for both the fly ash and cement that were received with the materials are shown in Appendix B.

The use of these materials ensures that the development effort will be performed using materials local to the Weldon Spring Site. Although other local sources may be available, it was beyond the scope of this development effort to evaluate sources of raw materials.

3. GROUT DEVELOPMENT DATA

Previous scouting studies[2] indicated that a product with desirable characteristics may be attainable with a dry-solids blend consisting of 20 wt % cement and 80 wt % fly ash. Other blends were used to assess the ability to control the product quality. The blends used were Blend A, consisting of 20 wt % Type II Portland cement and 80 wt % ASTM Class F fly ash; Blend B, consisting of 40 wt % Type II Portland cement and 60 wt % ASTM Class F fly ash; and Blend C, consisting of 60 wt % Type II Portland cement and 40 wt % ASTM Class F fly ash. The previous scouting studies also indicated that products with desirable characteristics could be obtained at low mix ratios (i.e., grams of dry-solids blend per gram of waste). Consequently, the mix ratios tested in this grout development effort were 0.4, 0.6, and 0.8 g/g.

3.1 DRY-SOLIDS BLEND PREPARATION

Predetermined weights of each blend component were added to a V-blender shown in Fig. 1. The materials were then tumbled for 4 h. The resulting blended material became the dry-solids blend to be added to the waste in the grout preparation step.

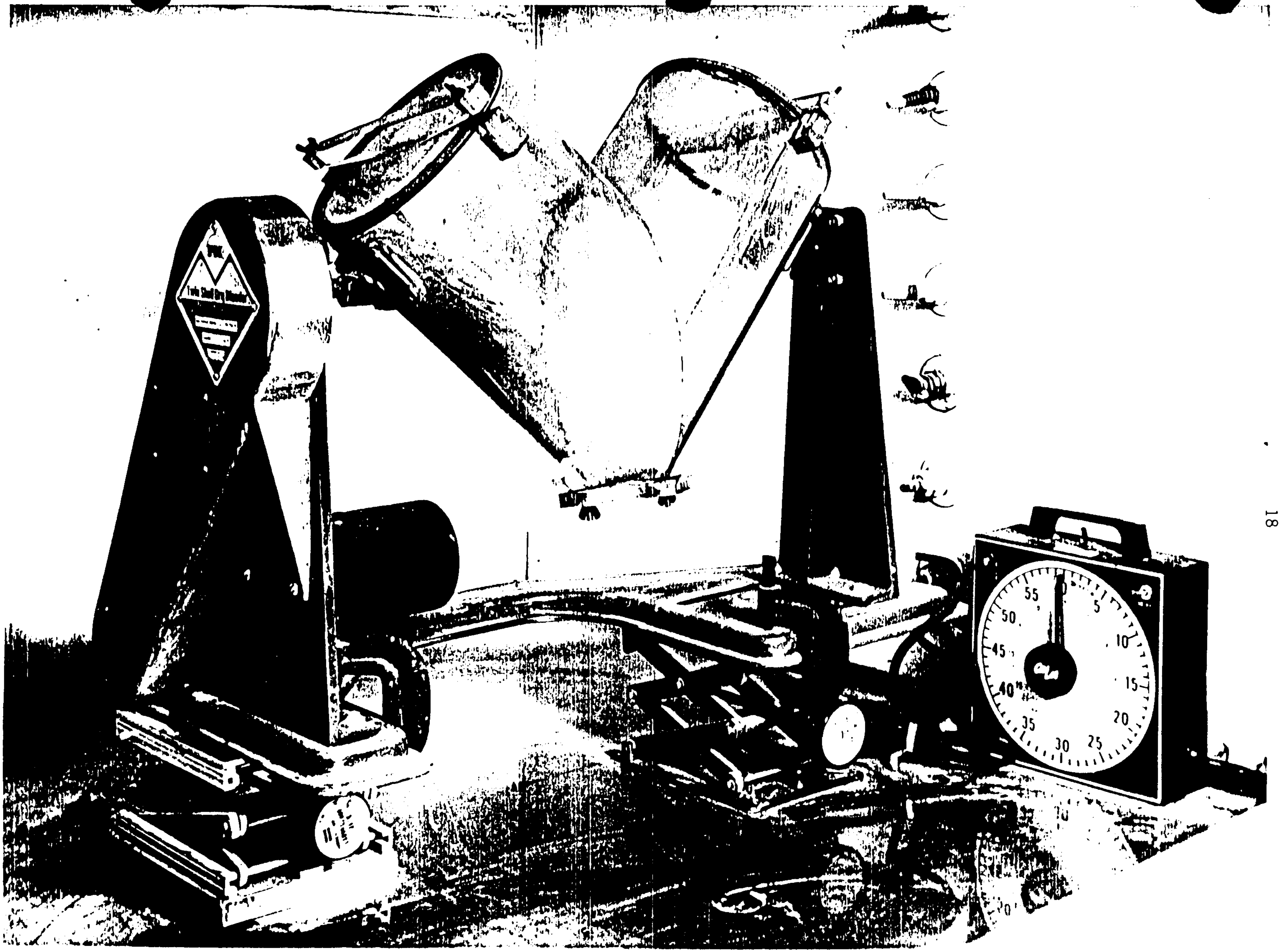

Fig 1. V-blender used in preparation of dry-solids blend

3.2 WASTE PREPARATION

Eighty-seven 5-gal buckets of raffinate pit sludge were received from the Weldon Spring Site. Due to sample acquisition and packaging difficulties, the samples did not readily lend themselves to grout preparation. Consequently, a composite sample was prepared for each of the raffinate pits. The appropriate samples were transferred to a 55-gal drum and the resulting liquid supernate decanted. The remaining sludge was redish-brown in color and gelatinous in nature. The sludge was stirred, as shown in Fig. 2, to homogenize the sample and to shear-thin the material, so that it could be poured into the appropriate containers for grout preparation. The solids content of the resulting composites, as determined by drying duplicate subsamples to a constant weight at 105°C, is shown in Table 7. A more detailed presentation of the preparation of the sludge composites is shown in Appendix C. The resulting stirred composite samples became the reference wastes which were added to the dry-solids blend in the grout preparation step.

The effects of moisture content were assessed by attempting to prepare grouts with waste at 35 and 20 wt% solids content (as compared with values in Table 7). The 20 wt% solids content waste, referred to hereafter as diluted waste, was prepared by diluting the reference waste with the decanted liquid supernate obtained during the waste composite step. The 35 wt% solids content waste was prepared by partially drying the reference waste in an oven.

3.3 GROUT PREPARATION

A predetermined weight of the waste was added to a Model N-50 Hobart Mixer (Fig. 3). The mixer was set to a low setting (~140 rpm) and a predetermined weight of dry-solids blend was added over a 10- to 15-s period and mixed for a total of 30 s at this setting. The mixer was then set to medium (~285 rpm) and mixing continued for an additional 30 s. The resulting freshly prepared grout was then poured or spooned into appropriate molds for further testing. After placement in the molds, they were vibrated for 30 s at a setting of 6.5 using a Model VP5101 Syntron vibrating table (Fig. 4). Grouts prepared with the three

Table 7. Solids content of composite waste used in grout development effort

Pit No.	Sample No.	Weight (g)		Solids content (wt %)
		Wet sludge	Dry sludge	
1	1	51.15	14.05	27.5
	2	52.36	14.40	27.5
2	1	47.24	13.12	27.8
	2	49.66	13.78	27.7
3	1	46.52	12.29	26.4
	2	45.82	12.08	26.4
4	1	49.70	15.19	30.6
	2	48.08	14.28	29.7

Fig. 3. Hobart mixer used in grout preparation

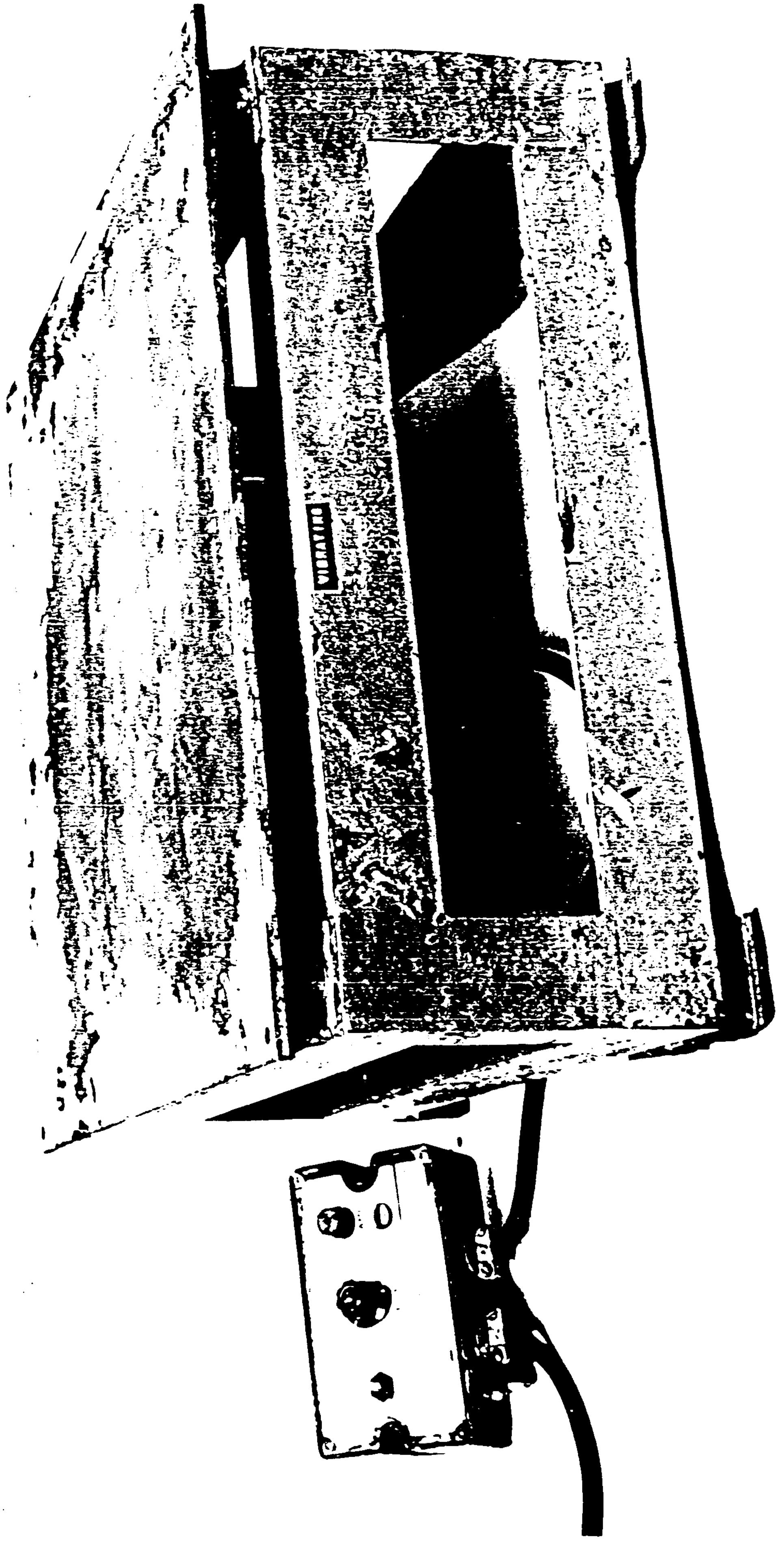

Fig 4. Vibrating table used in grout preparation

blends and reference waste at a mix ratio of 0.8 g/g were too thick to be placed into the testing molds. In addition, grouts prepared at all three mix ratios with the waste containing 35 wt% solids content (Fig. 5) were too thick to be placed into the molds. Consequently, no data could be obtained on grouts prepared at these conditions. It should be noted that, based on visual observation, the grouts prepared with waste at 35 wt% solids content were thoroughly mixed in the Hobart. However, the resulting freshly prepared grouts were too thick and sticky to provide uniform and consistent samples with the laboratory-scale molds. Based on these observations, it is believed that grouts prepared at these conditions could be handled with field-scale equipment.

3.4 DRAINABLE WATER

One of the performance criterion for an acceptable grout product is that it exhibit no drainable or free water within 28 d after it is poured. Drainable water or phase separation was determined by pouring a freshly prepared grout into a sealed, graduated container and then measuring observed surface water at 1, 2, 7, 14, 21, and 28 d. The resulting data are shown in Tables 8 and 9.

3.5 PENETRATION RESISTANCE

Penetration resistance is a measure of set, or the stiffening, of the grout (ASTM C403-85, "Time of Setting of Concrete Mixtures by Penetration Resistance"). Initial set, is the elapsed time, after initial contact of the dry-solids blend and waste, required to reach a penetration resistance of 500 psi. Final set, is the elapsed time, after initial contact of the dry-solids blend and waste, required to reach a penetration resistance of 4000 psi. Although no substitute for calorimetry data, penetration resistance does provide a quick and easy method for assessing the extent to which the cementitious reactions have occurred, as well as a means of comparing the effects of variables such as dry-solids blend composition, mix ratio, and waste composition.

In this study, freshly prepared grouts were poured into cylindrical plastic molds (2.4-in diam by 2-in high) and then stored in

Table 8. Phase separation data (vol %) obtained from grouts prepared with reference raffinate pit sludge

		Mix Ratio (g/g)					
		Blend A		Blend B		Blend C	
Day	Pit No.	0.4	0.6	0.4	0.6	0.4	0.6
1	1	0	0	0	0	0	0
	2	0	0	0	0	0	0
	3	0	0	0	0	0	0
	4	0.2	0.3	0	0	0	0
2	1	0	0				
	2	0	0				
	3	0	0				
	4	0	0.1				
7	1	0	0				
	2	0	0				
	3	0	0				
	4	0	0				

Table 9. Phase separation data (vol %) obtained from grouts prepared with reference raffinate pit sludge diluted to 20 wt% solids content

		Mix Ratio (g/g)								
		Blend A			Blend B			Blend C		
Day	Pit No.	0.4	0.6	0.8	0.4	0.6	0.8	0.4	0.6	0.8
1	1	1.2	0.8	2.2	2.2	0.7	0	1.0	0.6	0
	2	1.1	0.4	1.9	1.4	0.1	0	1.1	0.2	0
	3	1.8	0.2	1.9	0.5	0.1	0	0.6	0.1	0
	4	5.6	3.3	4.4	4.5	3.2	1.1	4.9	2.8	1.5
2	1	0.8	0.5	1.8	1.7	0.4	0	0.6	0.1	0
	2	0.7	0	1.4	0.8	0	0	0.7	0	0
	3	1.0	0	1.2	0	0	0	0	0	0
	4	4.4	2.0	3.5	3.5	2.2	0	4.0	1.8	0.5
7	1	0.6	0	0.8	0.4	0		0	0	0
	2	0	0	0.4	0.1	0		0	0	0
	3	0.5	0	0	0	0		0	0	0
	4	4.1	1.4	2.0	2.8	1.0		3.0	0.5	0
14	1	0	0	0	0	0		0	0	
	2	0	0	0	0	0		0	0	
	3	0	0	0	0	0		0	0	
	4	3.4	0.4	0.6	2.3	0.3		1.7	0.4	
21	1	0	0	0	0	0		0	0	
	2	0	0	0	0	0		0	0	
	3	0	0	0	0	0		0	0	
	4	3.0	0	0	1.6	0		0	0	
28	1	0			0					
	2	0			0					
	3	0			0					
	4	2.6			1.2					
56	1	0			0					
	2	0			0					
	3	0			0					
	4	1.6			0					

Fig. 5. Waste at 35 wt% solids content

a humidity cabinet (Fig. 6) at 27°C and a relative humidity of 98%. The samples were removed from the cabinet at selected time intervals (1, 2, 7, 14, 21, and 28 d); penetration resistance measurements were obtained; and the samples were then returned to the cabinet. Penetration resistance data were obtained using an Acme Penetrometer (Fig. 7) with needles having 0.05 and 0.11 sq in surface areas at the point of penetration. A vertical force downward on the apparatus is applied until the needle penetrates the grout to a depth of 1 in. Penetration resistance is determined by dividing the force required to penetrate the grout to a depth of 1 in by the surface area of the needle at the point of contact with the grout. Resulting data are presented in Tables 10 through 17, and shown graphically in Figs. 8 through 22. It should be noted that a value of 8000 psi represents the upper limit of the penetrometer's measuring capability.

3.6 UNCONFINED COMPRESSIVE STRENGTH

Unconfined compressive strength [ASTM C 109-80, "Compressive Strength of Hydraulic Cement Mortars (Using 2-in or 50-mm Cube Specimens)"] is a measure of the ability of the waste form to withstand applied loads such as would occur from the trench overburden or stacked containers (e.g., drums) during storage or final disposal. Thus unconfined compressive strength is an important parameter which addresses the concern of overburden subsidence and maintaining structural integrity of the final waste form. The desired unconfined compressive strength is dictated by the site specific storage and disposal scenario. At the time of this study, the optimum storage and disposal scenario for the raffinate pits had not been finalized. As such, the unconfined compressive strength performance criterion for this study was 60 psi, which is the minimum value recommended by the Nuclear Regulatory Commission (NRC).[18]

In this study, freshly prepared grouts were poured or spooned into 2-in cube molds conforming to ASTM C 109-80 specifications and then placed in a humidity cabinet maintained at 27°C and 98% relative humidity. 28 d after being placed in the molds, the cured grouts were

Table 10. Penetration resistance data (psi) from grouts prepared with reference sludge from raffinate pit 1

	Mix Ratio (g/g)					
	Blend A		Blend B		Blend C	
Day	0.4	0.6	0.4	0.6	0.4	0.6
1	0	0	340	780	600	1800
2	240[1]	480	620	1540	1120	2800
7	400	1160	1600	4400	3000	6920
14	740	2640	2880	7680	5480	8000
21	1160	2960	3480	8000	7320	
28	1680	4120	4880		8000	
56	2280	5080				

[1] Data taken at 3 d.

Table 11. Penetration resistance data (psi) from grouts prepared with reference sludge from raffinate pit 2

	Mix Ratio (g/g)					
	Blend A		Blend B		Blend C	
Day	0.4	0.6	0.4	0.6	0.4	0.6
1	0	0	400	1400	1120	2800
2	240	760	900	2100	2520	5760
7	740	1900	2800	5920	5000	8000
14	1600	4720	4320	8000	6840	
21	2680	6480	5080		8000	
28	2880	7320	8000			
56	4040	8000				

Table 12. Penetration resistance data (psi) from grouts prepared with reference sludge from raffinate pit 3

	Mix Ratio (g/g)					
	Blend A		Blend B		Blend C	
Day	0.4	0.6	0.4	0.6	0.4	0.6
1	0	0	240	760	920	2920
2	80	360	600	1660	1960	6000
7	160	920	1200	4600	4160	8000
14	320	1440	3080	8000	5880	
21	760	2960	3720		8000	
28	640	3160	4920			
56	1080	4600				

Table 13. Penetration resistance data (psi) from grouts prepared with reference sludge from raffinate pit 4

	Mix Ratio (g/g)					
	Blend A		Blend B		Blend C	
Day	0.4	0.6	0.4	0.6	0.4	0.6
1	0	0	0	760	560	2200
2	0	200	440	1560	1520	5160
7	320	1320	1760	6080	4080	8000
14	880	2880	3480	8000	6560	
21	1000	5520	4240			
28	1520	8000	5600			
56	3520					

Table 14. Penetration resistance data (psi) from grouts prepared with reference sludge from raffinate pit 1 diluted to 20 wt% solids content

	Mix Ratio (g/g)								
	Blend A			Blend B			Blend C		
Day	0.4	0.6	0.8	0.4	0.6	0.8	0.4	0.6	0.8
1	0	320	0	0	400	640	160	480	1840
2	200	440	480	220	900	1700	240	720	3400
7	520	1640	1300	760	1760	4280	840	2080	8000
14	1000	3200	3200	1440	4040	8000	1640	3840	
21	1320	4640	4680	1960	5720		2280	6200	
28	1640	6320	5080	2400	7920		2680	8000	
56	2880	8000	7440	4280	8000		4520		

Table 15. Penetration resistance data (psi) from grouts prepared with reference sludge from raffinate pit 2 diluted to 20 wt% solids content

	Mix Ratio (g/g)								
	Blend A			Blend B			Blend C		
Day	0.4	0.6	0.8	0.4	0.6	0.8	0.4	0.6	0.8
1	0	360	0	0	440	1480	180	780	2720
2	200	660	600	400	1380	2140	360	1180	5200
7	720	2120	1760	840	2480	5320	1040	3280	8000
14	1280	3880	4000	1560	4720	8000	1640	6320	
21	1960	4480	5440	2280	6280		2360	8000	
28	2080	6720	6280	2520	8000		3000		
56	2960	8000	8000	4120			4720		

Table 16. Penetration resistance data (psi) from grouts prepared with reference sludge from raffinate pit 3 diluted to 20 wt% solids content

	Mix Ratio (g/g)								
	Blend A			Blend B			Blend C		
Day	0.4	0.6	0.8	0.4	0.6	0.8	0.4	0.6	0.8
1	0	0	0	0	0	820	160	600	2880
2	120	440	400	320	480	1780	280	960	5920
7	400	1680	1200	720	2440	5320	1400	3280	8000
14	1080	3680	2920	1680	4960	8000	2520	7040	
21	1760	6160	4920	2720	8000		2560	8000	
28	1600	7360	5560	2600[1]			3600		
56	2800	8000	7320	4120			5840		

[1] Suspect data point due to sample cracking during data acquisition.

Table 17. Penetration resistance data (psi) from grouts prepared with reference sludge from raffinate pit 4 diluted to 20 wt% solids content

	Mix Ratio (g/g)								
	Blend A			Blend B			Blend C		
Day	0.4	0.6	0.8	0.4	0.6	0.8	0.4	0.6	0.8
1	0	0	0	0	0	400	0	0	1080
2	0	280	220	0	360	1600	80	260	2720
7	280	1240	1480	480	1880	5720	600	1480	6680
14	840	3440	4840	1080	4040	8000	1600	2600	8000
21	1640	5920	5960	2080	6080		2320	2880	
28	2360	7040	8000	2560	6600		3080	4440[1]	
56	4160	8000		4880	8000		5720		

[1] Suspect data point due to sample cracking during data acquisition.

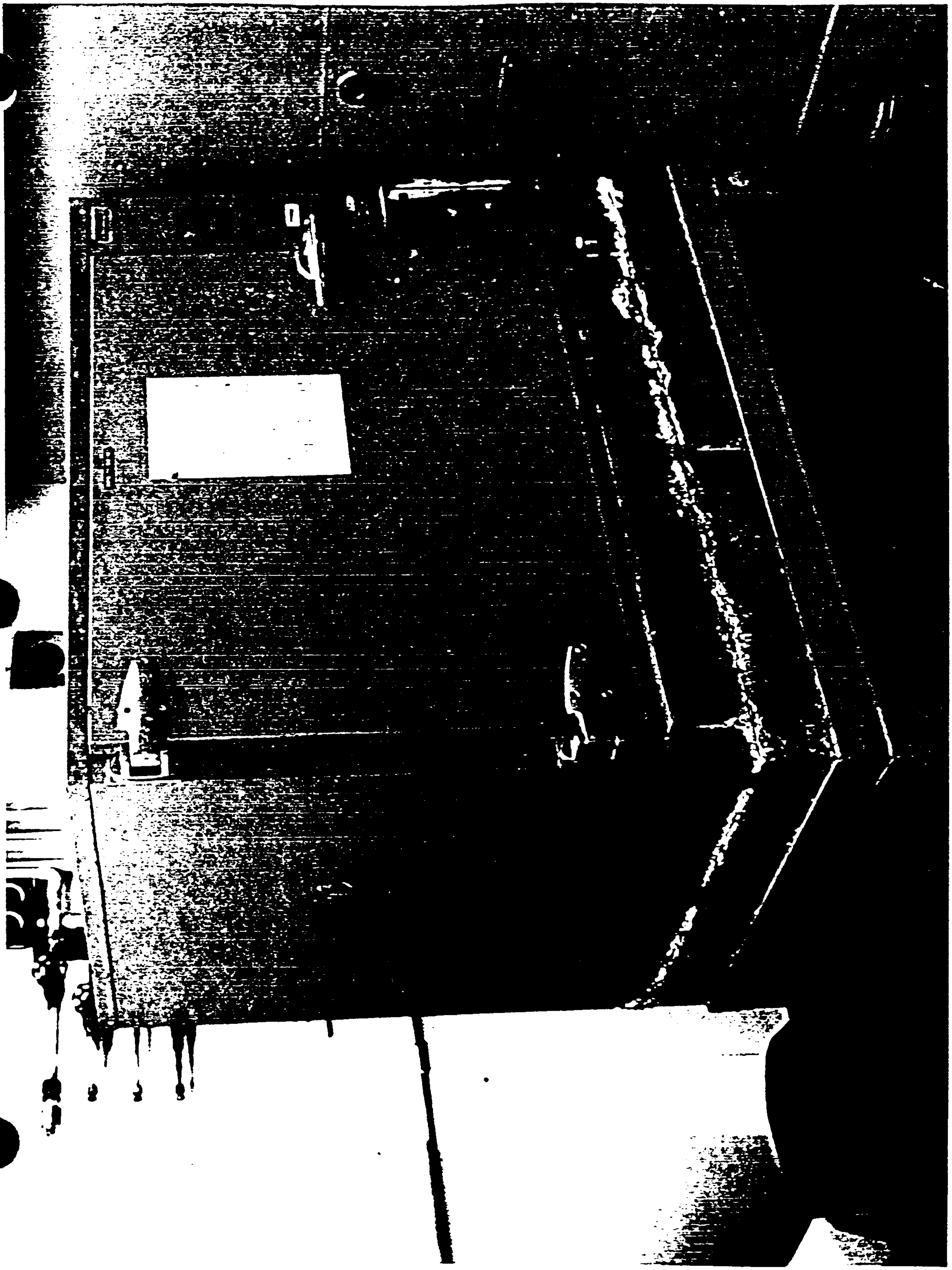

Fig. 6. Humidity cabinet for sample storage and cure

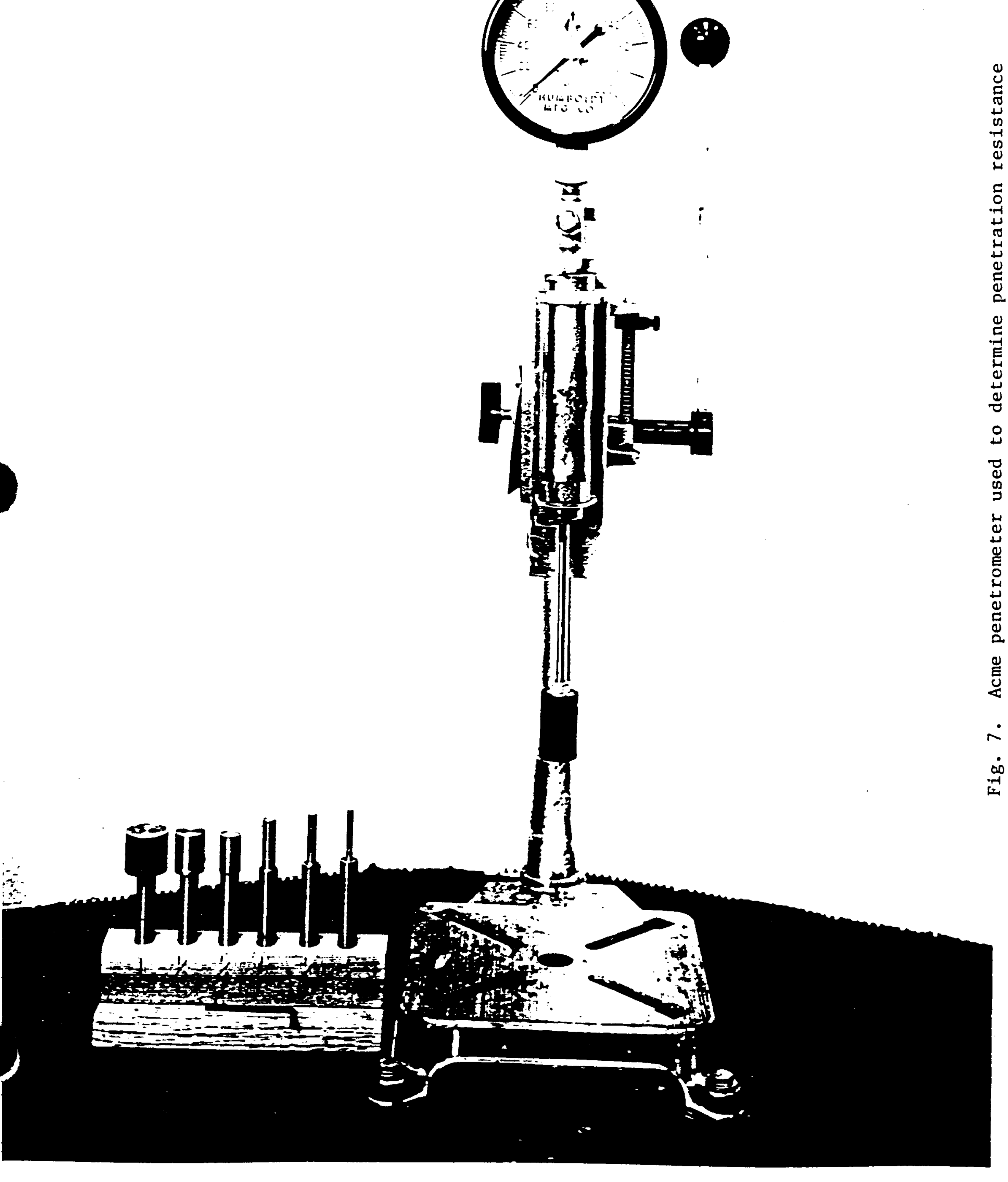

Fig. 7. Acme penetrometer used to determine penetration resistance

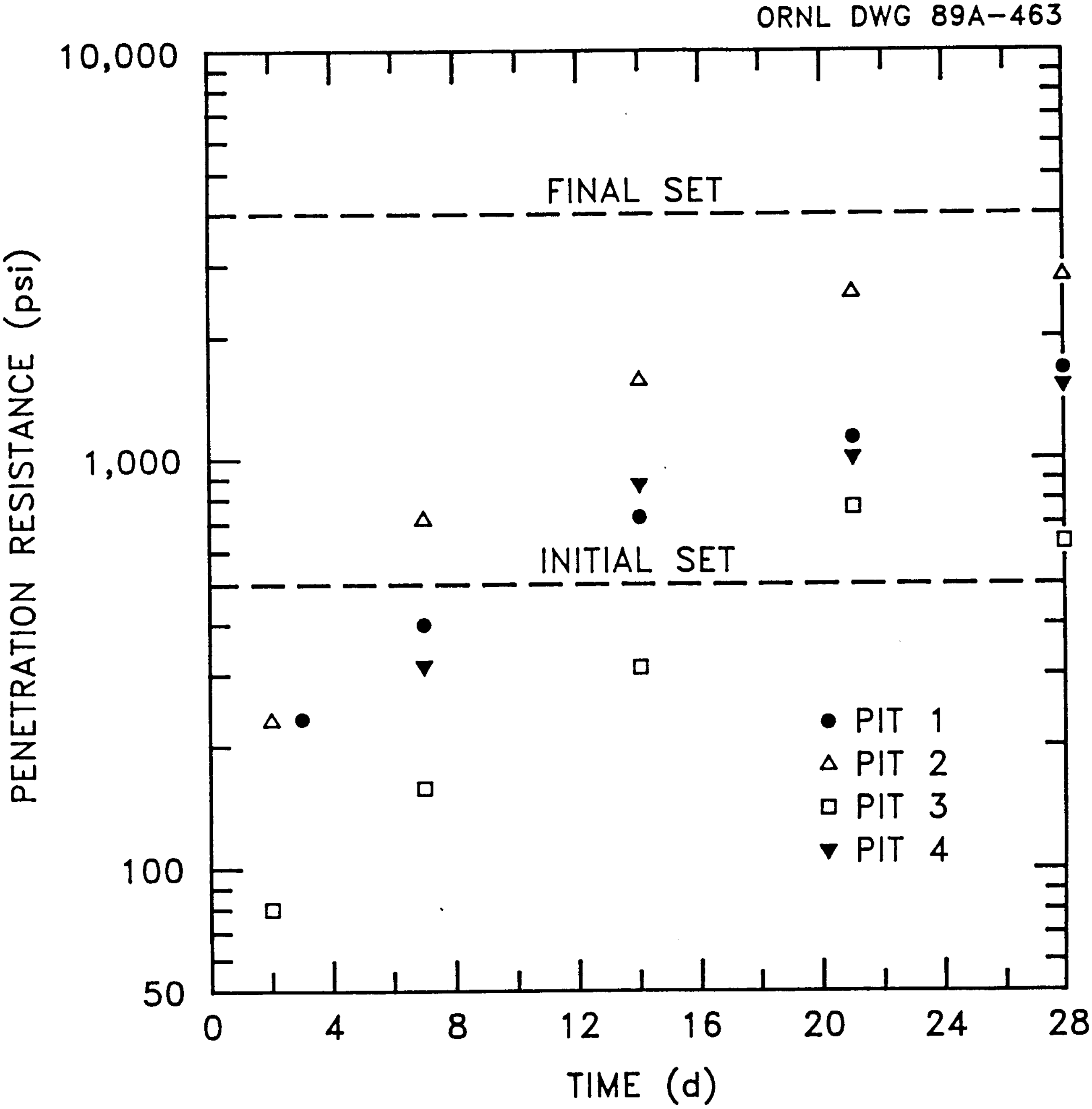

Fig 8. Penetration resistance (psi) as a function of time for grouts prepared with reference waste and Blend A at a mix ratio of 0.4 g/g

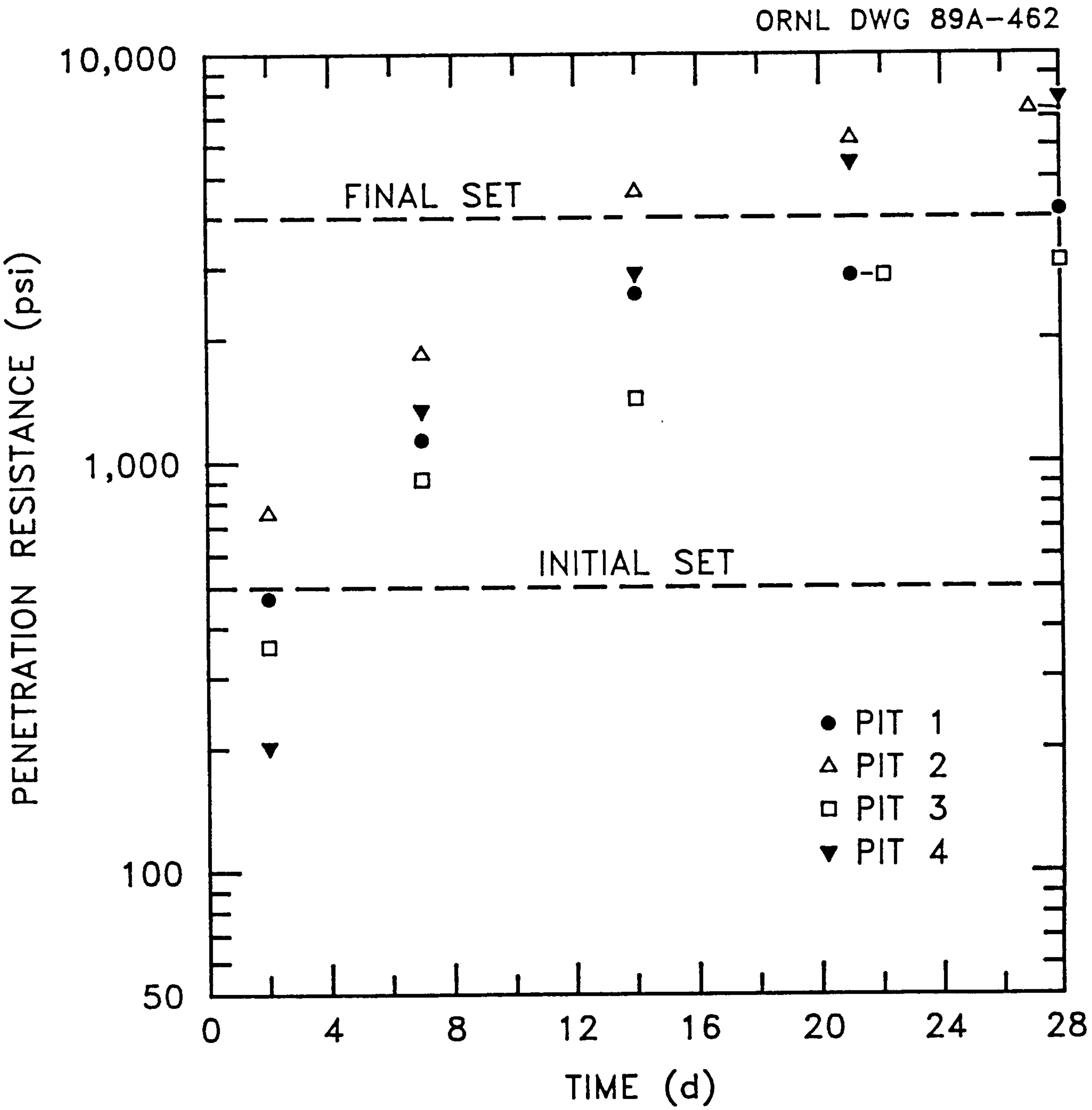

Fig 9. Penetration resistance (psi) as a function of time for grouts prepared with reference waste and Blend A at a mix ratio of 0.6 g/g

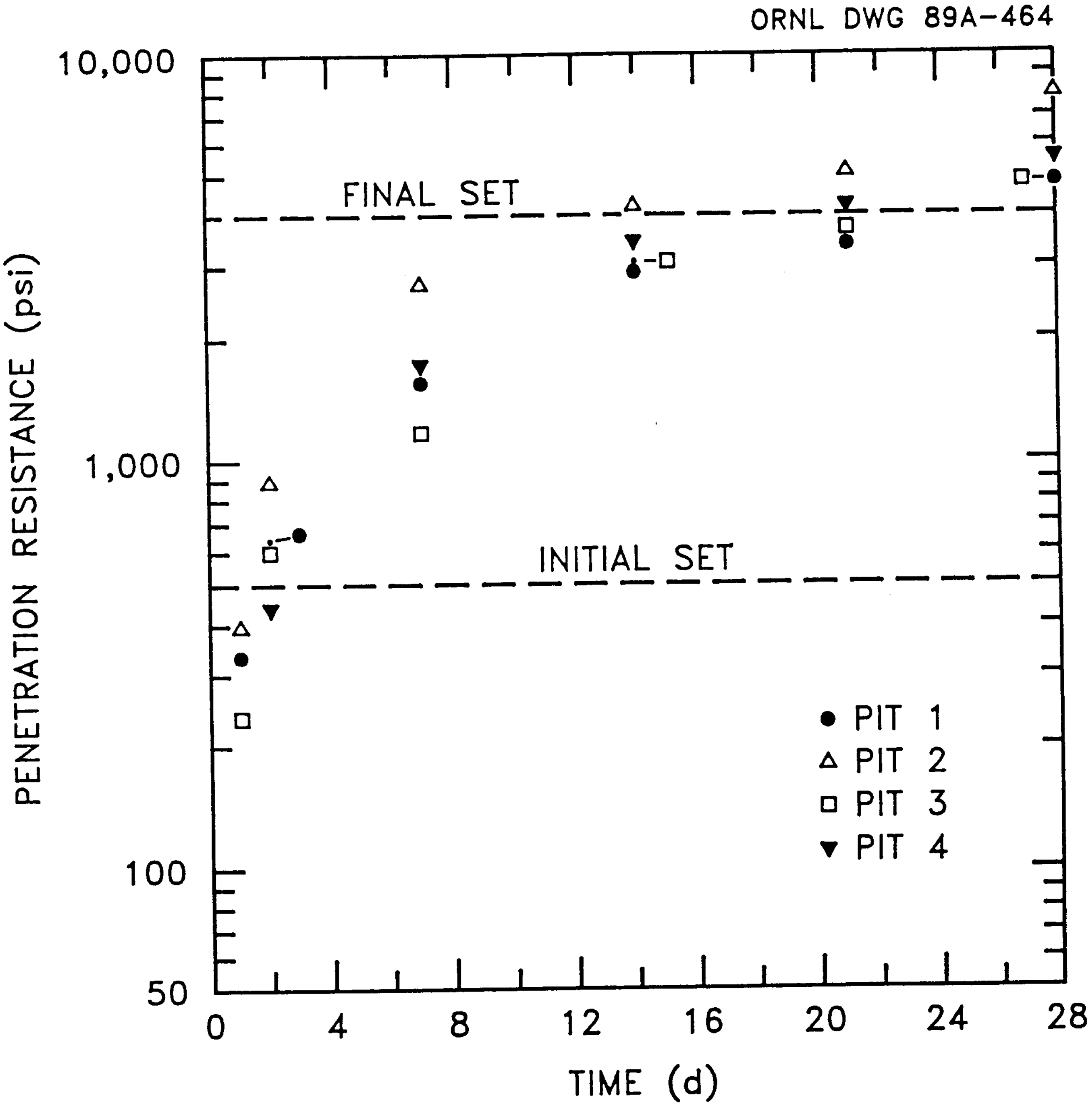

Fig 10. Penetration resistance (psi) as a function of time for grouts prepared with reference waste and Blend B at a mix ratio of 0.4 g/g

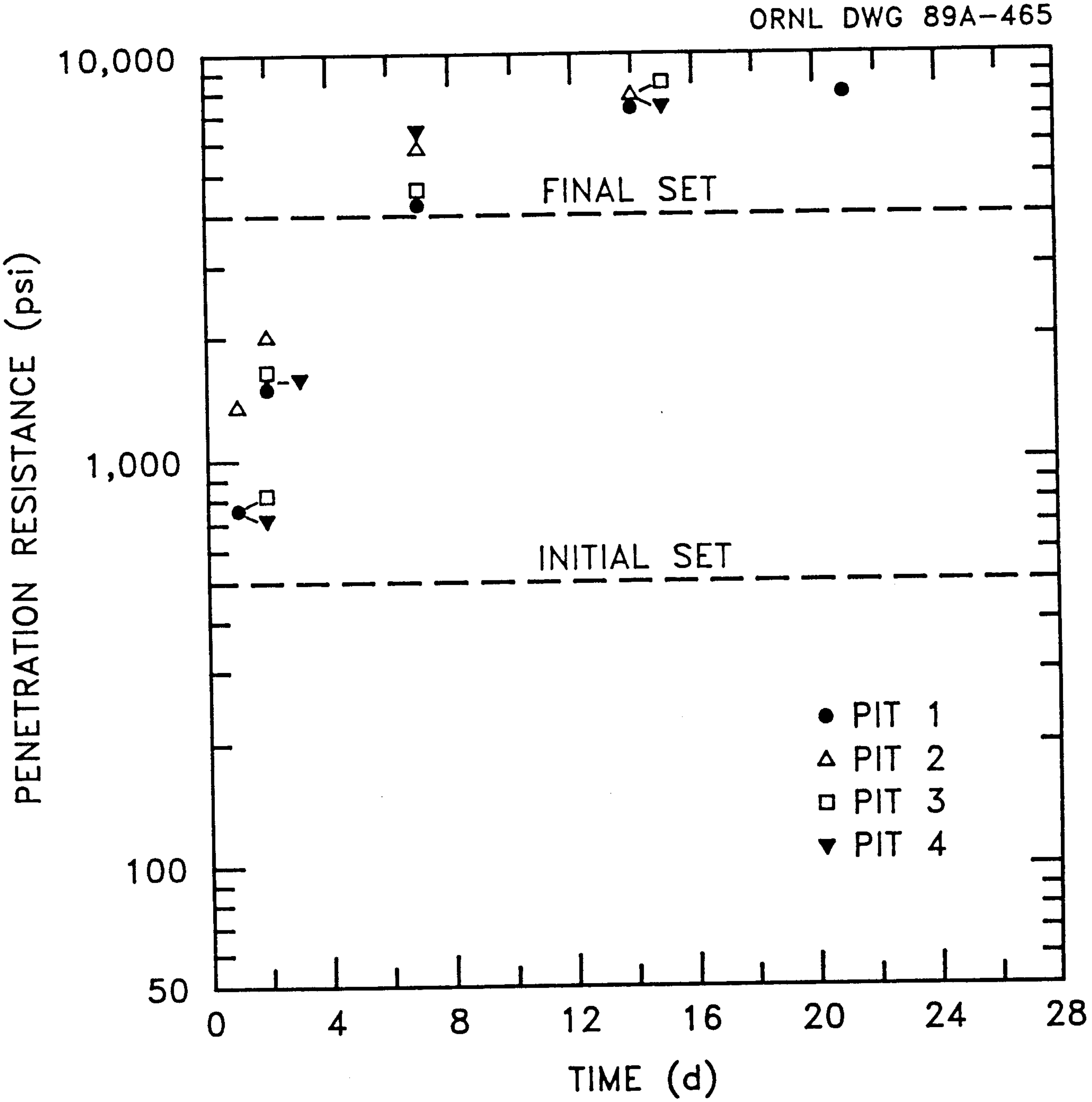

Fig. 11. Penetration resistance (psi) as a function of time for grouts prepared with reference waste and Blend B at a mix ratio of 0.6 g/g

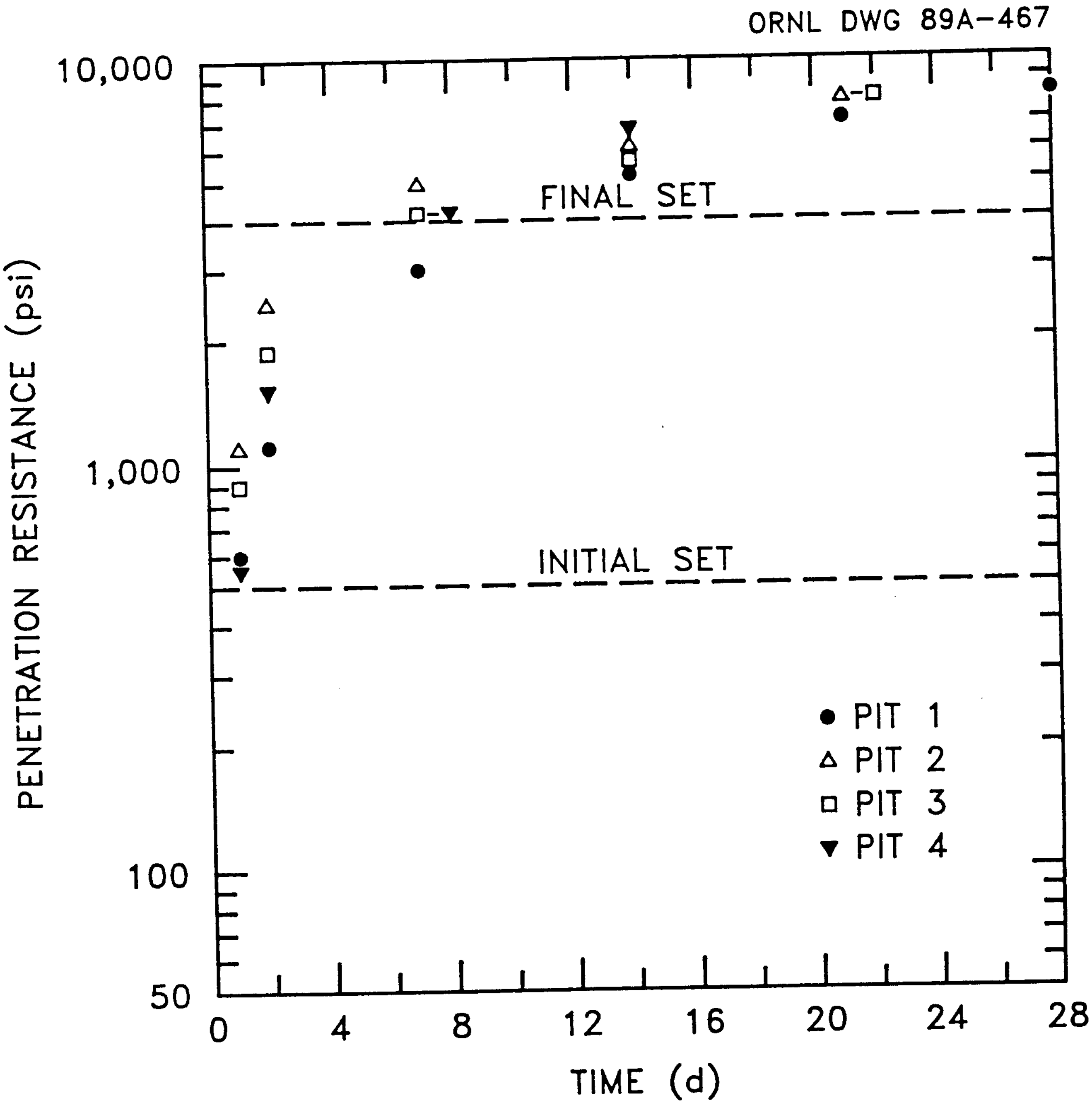

Fig 12. Penetration resistance (psi) as a function of time for grouts prepared with reference waste and Blend C at a mix ratio of 0.4 g/g

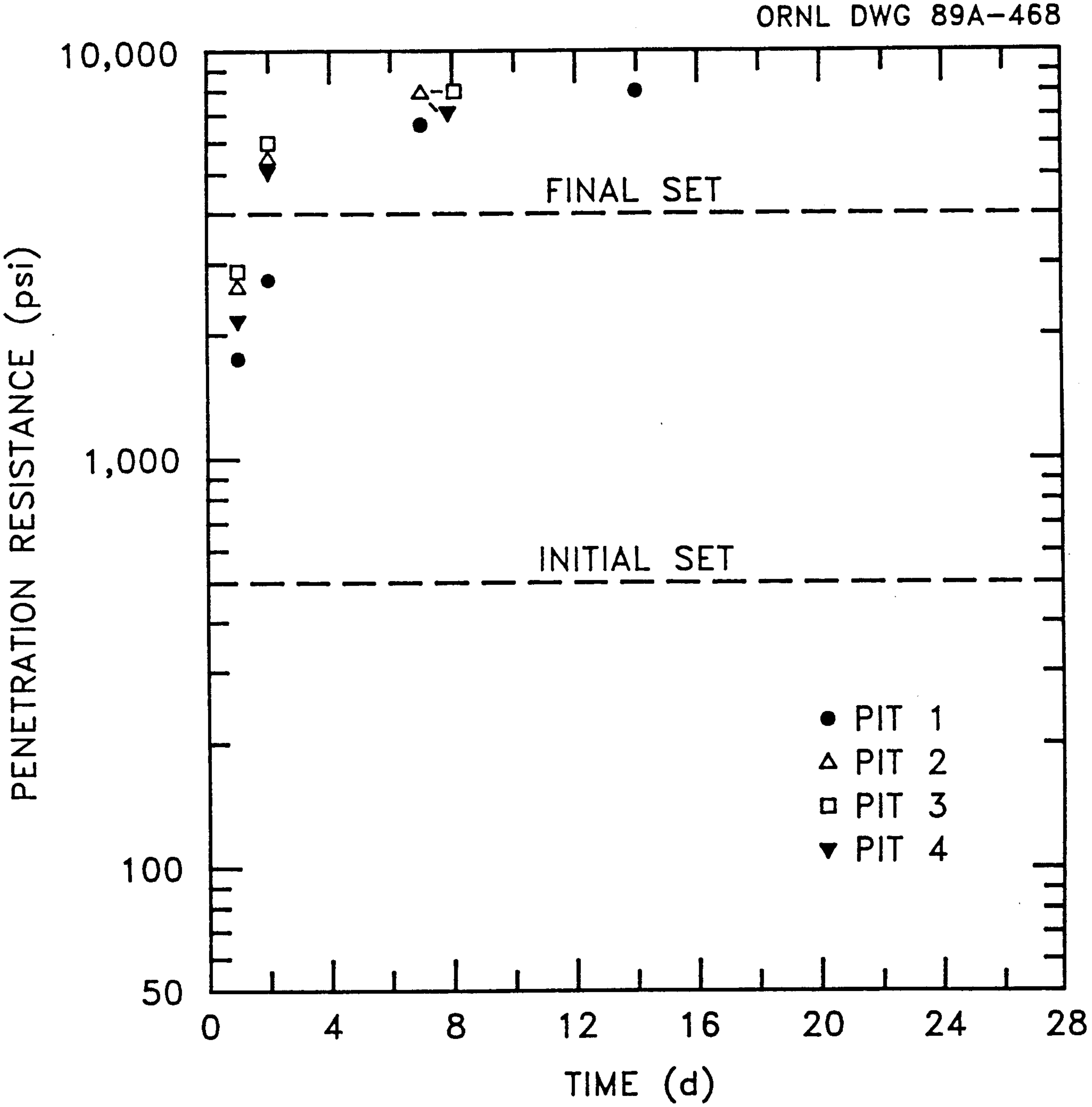

Fig 13. Penetration resistance (psi) as a function of time for grouts prepared with reference waste and Blend C at a mix ratio of 0.6 g/g

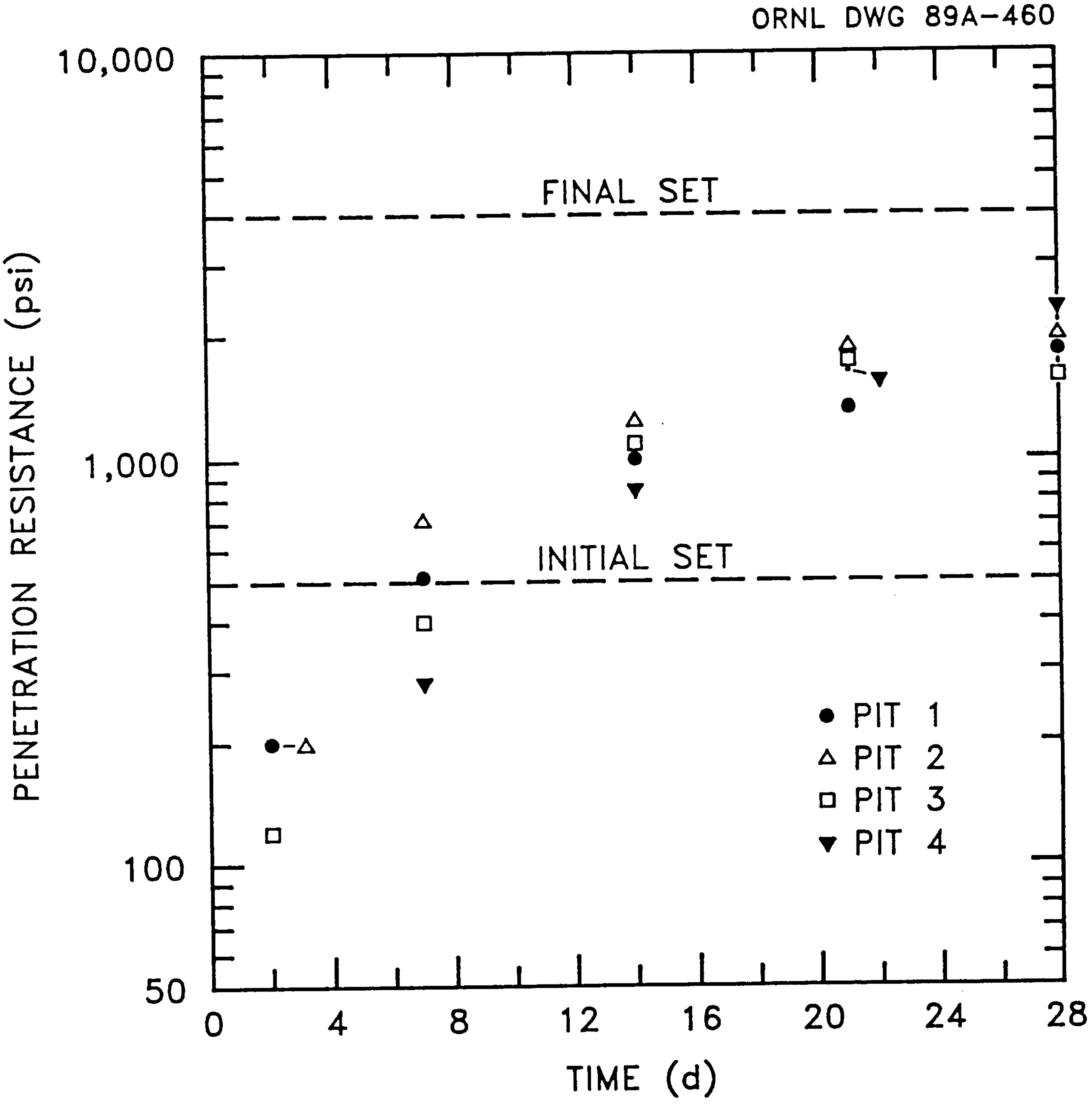

Fig 14. Penetration resistance (psi) as a function of time for grouts prepared with sludge diluted to 20 wt% solids content and Blend A at a mix ratio of 0.4 g/g

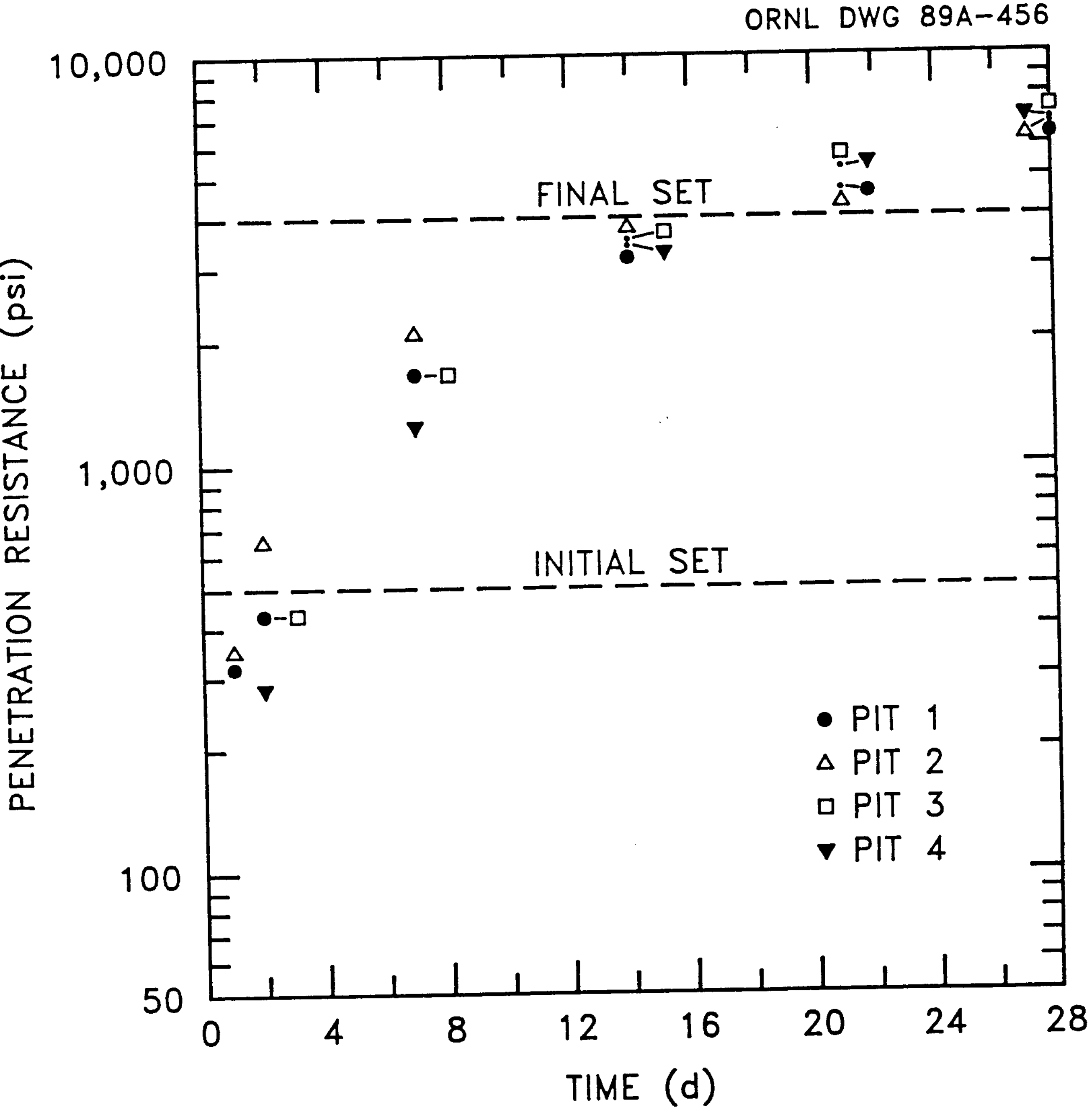

Fig 15. Penetration resistance (psi) as a function of time for grouts prepared with sludge diluted to 20 wt% solids content and Blend A at a mix ratio of 0.6 g/g

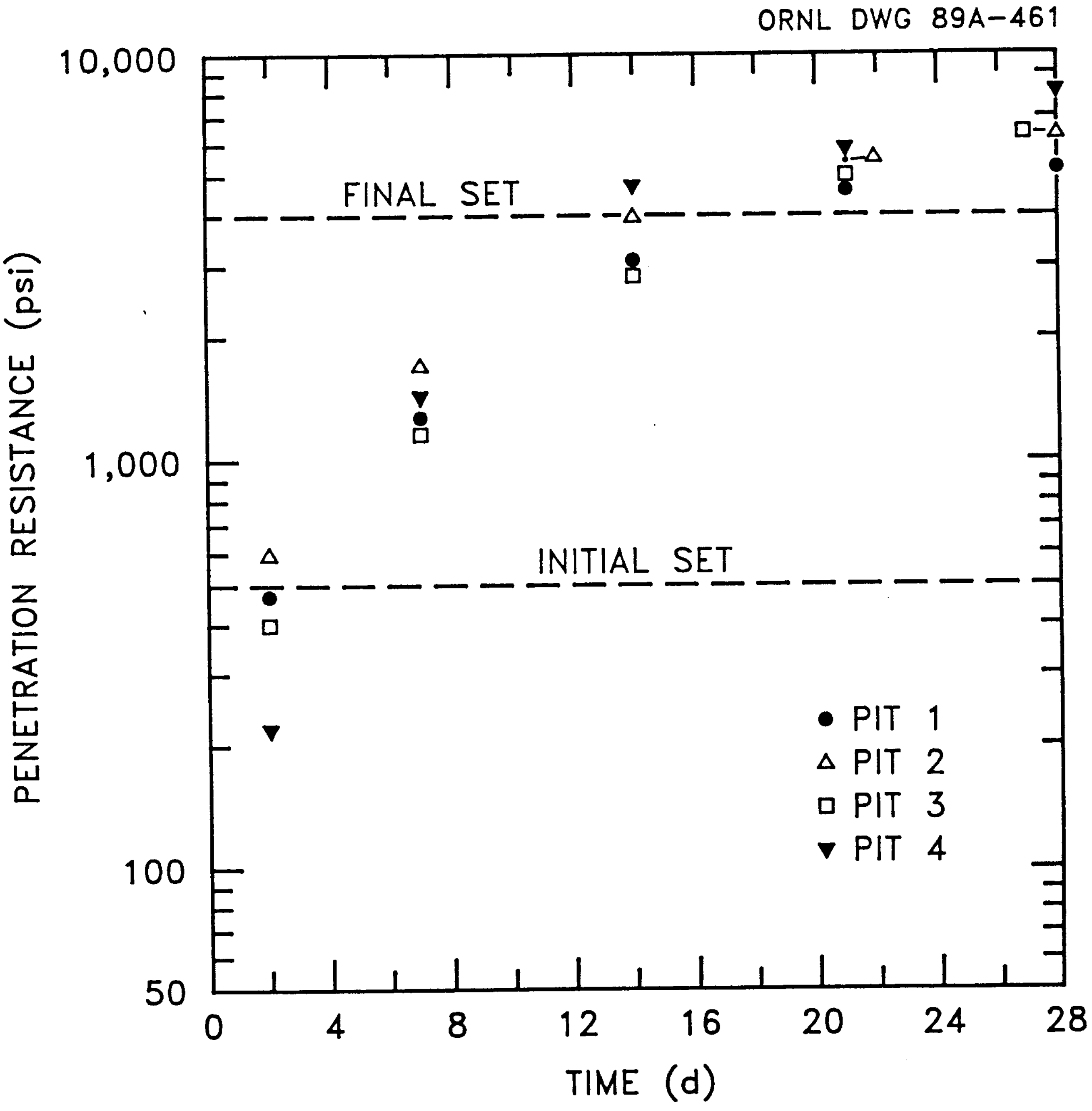

Fig 16. Penetration resistance (psi) as a function of time for grouts prepared with sludge diluted to 20 wt% solids content and Blend A at a mix ratio of 0.8 g/g

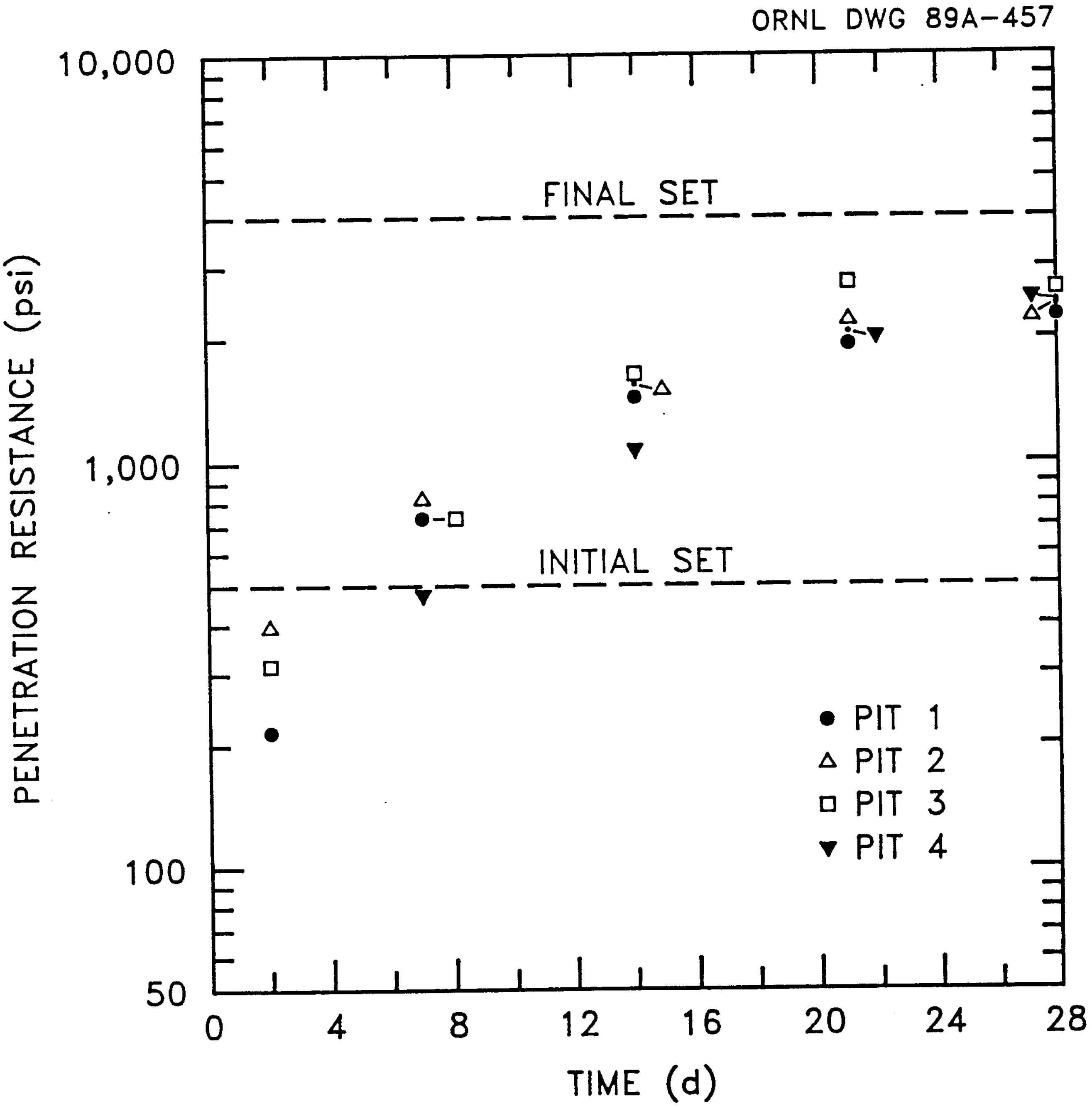

Fig 17. Penetration resistance (psi) as a function of time for grouts prepared with sludge diluted to 20 wt% solids content and Blend B at a mix ratio of 0.4 g/g

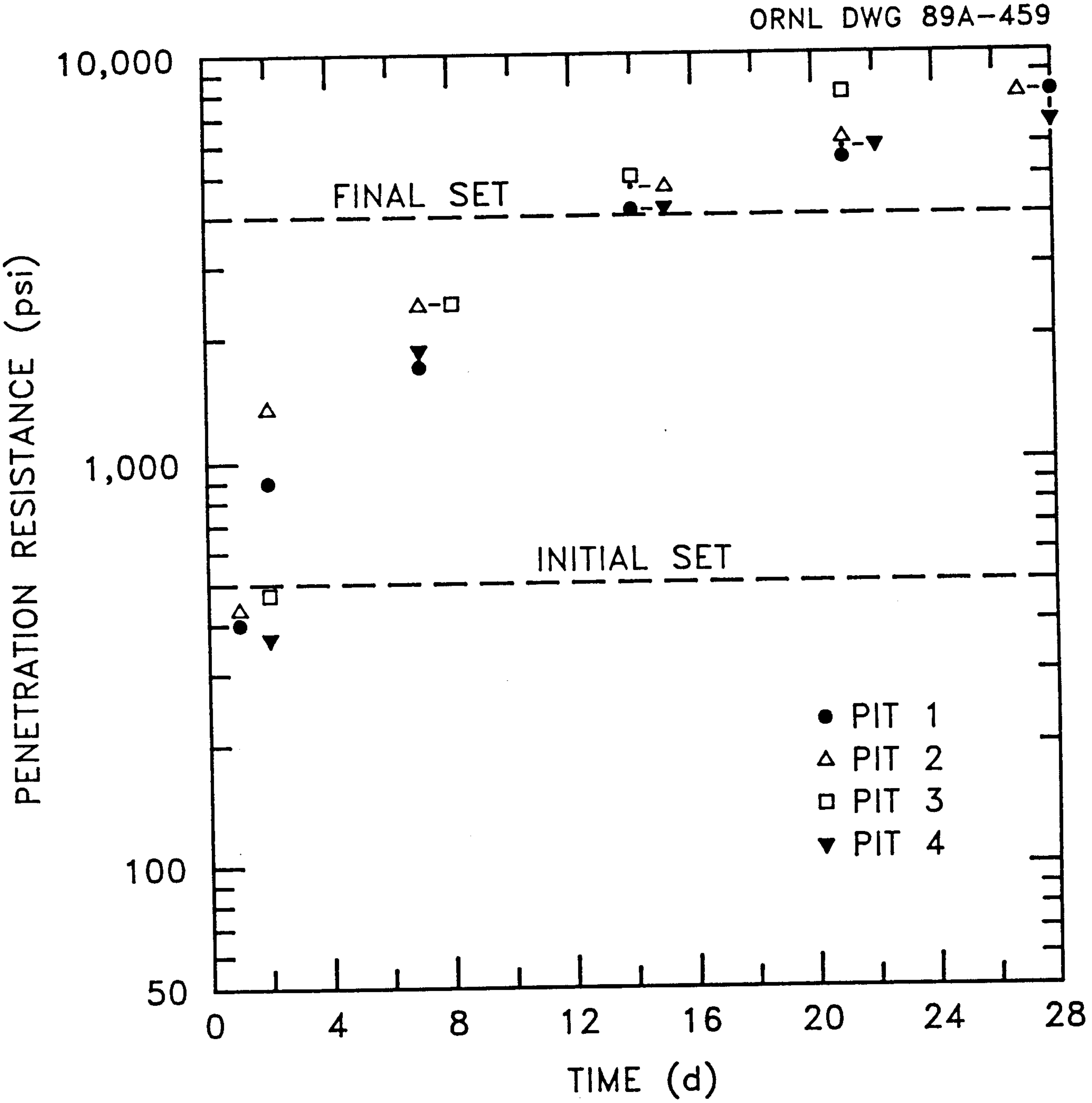

Fig 18. Penetration resistance (psi) as a function of time for grouts prepared with sludge diluted to 20 wt% solids content and Blend B at a mix ratio of 0.6 g/g

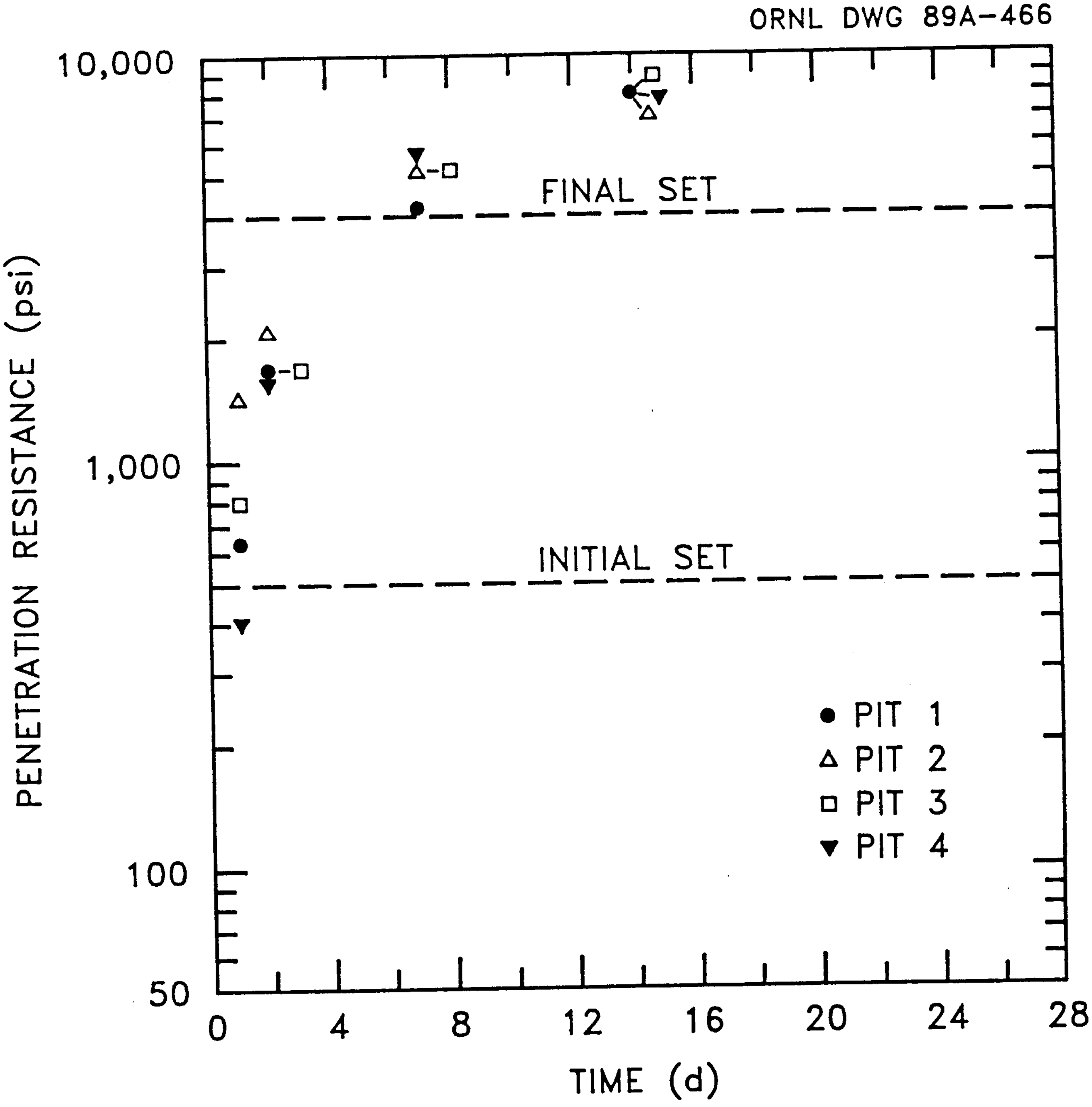

Fig 19. Penetration resistance (psi) as a function of time for grouts prepared with sludge diluted to 20 wt% solids content and Blend B at a mix ratio of 0.8 g/g

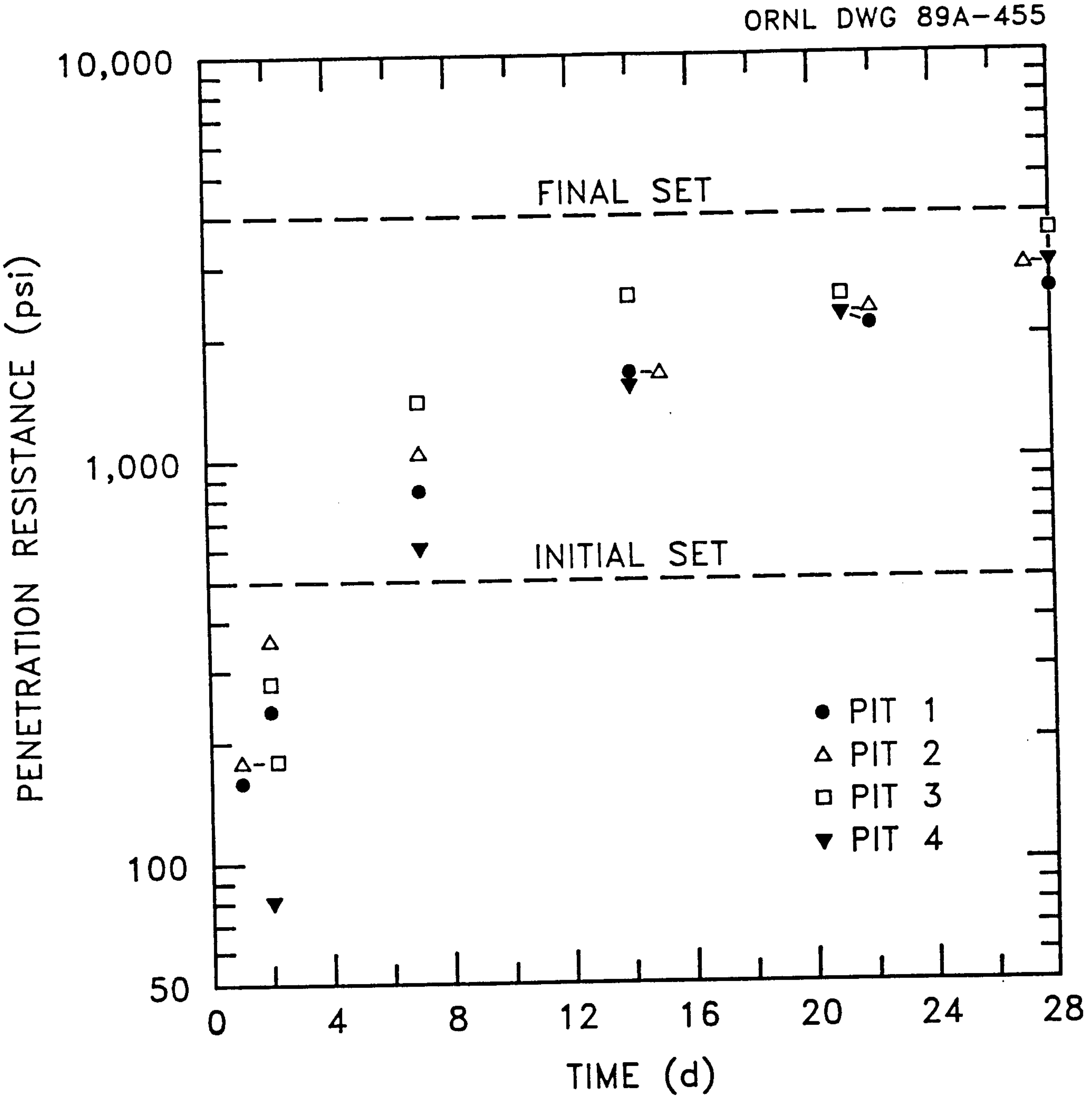

Fig 20. Penetration resistance (psi) as a function of time for grouts prepared with sludge diluted to 20 wt% solids content and Blend C at a mix ratio of 0.4 g/g

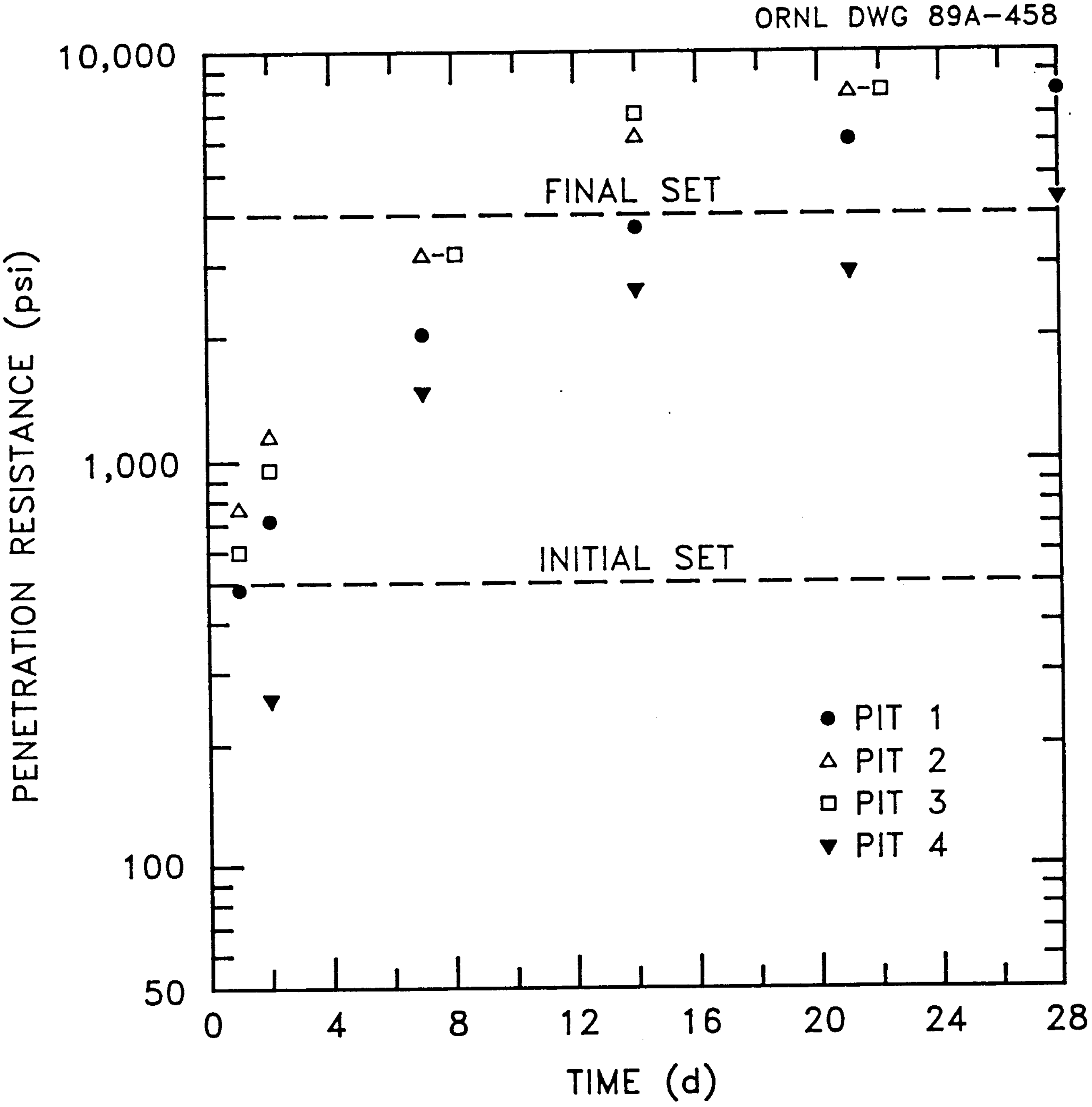

Fig 21. Penetration resistance (psi) as a function of time for grouts prepared with sludge diluted to 20 wt% solids content and Blend C at a mix ratio of 0.6 g/g

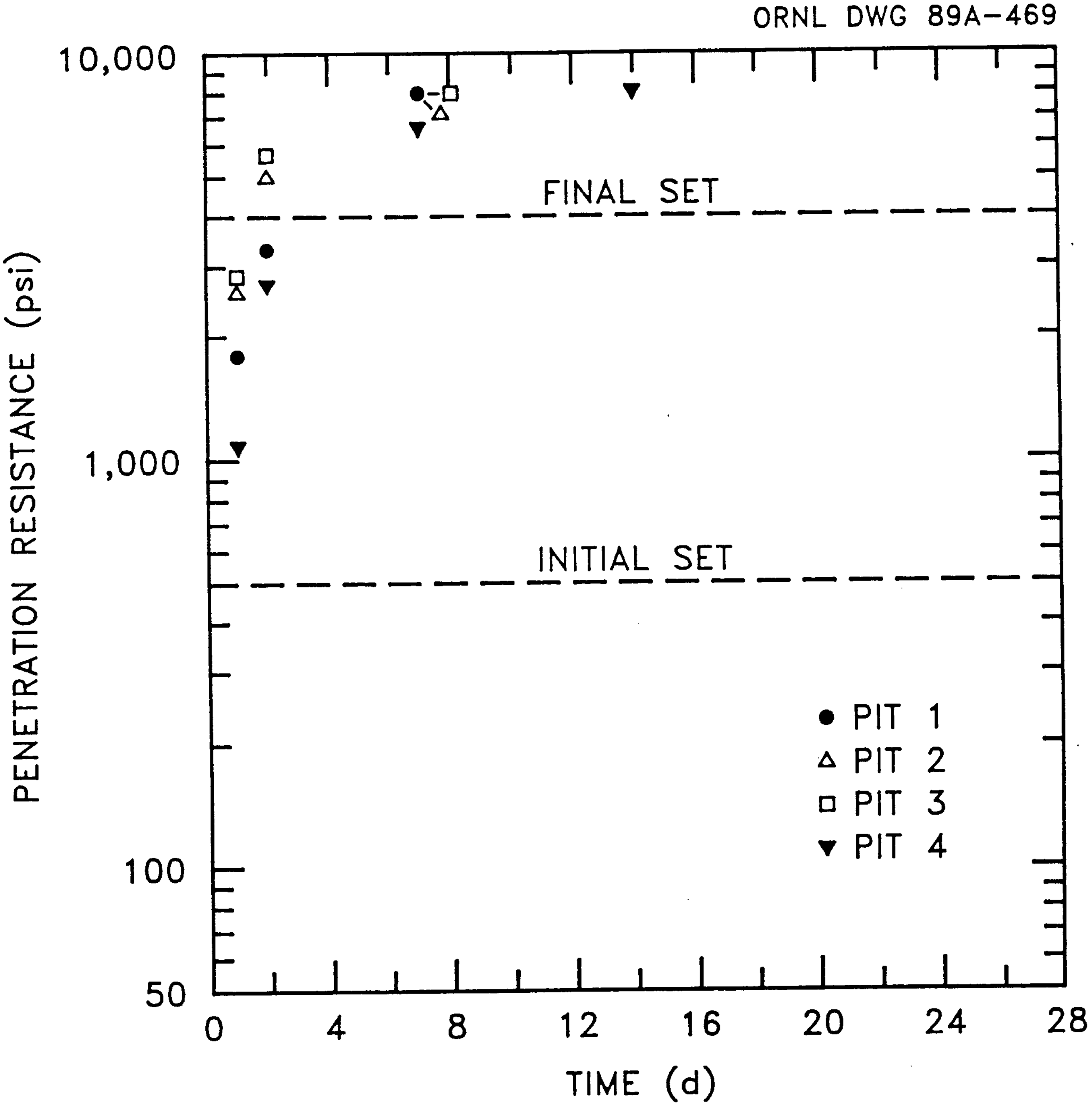

Fig 22. Penetration resistance (psi) as a function of time for grouts prepared with waste diluted to 20 wt% solids content and Blend C at a mix ratio of 0.8 g/g

removed and the unconfined compressive strength determined using a Tinius Olsen Super L Universal Testing Machine (Fig. 23). Results are shown in Tables 18 and 19.

3.7 THERMAL CYCLING

One of the performance criterion of this grout development effort was for the products to be resistant to exposure to thermal cycling. Resistance to freeze-thaw cycles is a measure of the capability of a waste form to withstand the natural temperature variation at a disposal or storage site. This resistance is particularly important during interim storage or for waste disposal above ground. Temperature variations experienced by waste disposed below the frost line should be minor.

In this study, freshly prepared grouts were poured into 2-in cube molds and then stored in a humidity cabinet at 27°C and a relative humidity of 98%. The cured grout samples were removed at 56-d and subjected to thermal cycling using a test method involving modifications to ASTM B553, "Standard Test Method for Thermal Cycling for Electroplated Plastics," For this test, 2-in cube samples were sealed inside glass jars. The cubes were placed on platforms to raise them above any water condensed during testing. The jars were placed in a Ransco Environmental Chamber (Fig. 24) and subjected to 30 thermal cycles between temperature extremes of 60 and -40°C. Each thermal cycle consists of:

1. Ramp from 20 to 60°C.
2. Hold at 60°C for 1 h.
3. Ramp from 60 to 20°C.
4. Hold at 20°C for 1 h.
5. Ramp from 20 to -40°C.
6. Hold at 40°C for 1 h.
7. Ramp from -40 to 20°C.
8. Hold at 20°C for 1 h.

The ramping time varied between 45 and 60 minutes. After being subjected to this thermal cycling, the samples were subjectively

Table 18. 28-d unconfined compressive strength data (psi) from grouts prepared with reference sludge from Weldon Spring Raffinate Pits

Pit No.	Blend	Mix Ratio (g/g)	28-d unconfined compressive strength[1] (psi)
1	A	0.4	98 ± 24
		0.6	167 ± 20
2	A	0.4	106 ± 4
		0.6	272 ± 2
3	A	0.4	45 ± 2
		0.6	147 ± 6
4	A	0.4	72 ± 5
		0.6	228 ± 16
1	B	0.4	209 ± 8
		0.6	509 ± 17
2	B	0.4	293 ± 10
		0.6	587 ± 39
3	B	0.4	213 ± 13
		0.6	633 ± 4
4	B	0.4	216 ± 10
		0.6	588 ± 16

---

[1] Unconfined compressive strength values are an average of measurements taken on three replicate samples and error bars are based on one standard deviation.

Table 18. 28-d unconfined compressive strength data (psi) from grouts prepared with reference sludge from Weldon Spring Raffinate Pits (cont.)

Pit No.	Blend	Mix Ratio (g/g)	28-d unconfined compressive strength[1] (psi)
1	C	0.4	370 ± 9
		0.6	813 ± 55
2	C	0.4	473 ± 9
		0.6	951 ± 29
3	C	0.4	444 ± 4
		0.6	1049 ± 97
4	C	0.4	438 ± 4
		0.6	1085 ± 41

---

[1] Unconfined compressive strength values are an average of measurements taken on three replicate samples and error bars are based on one standard deviation.

Table 19. 28-d unconfined compressive strength data (psi) from grouts prepared with reference sludge from Weldon Spring Raffinate Pits diluted to 20 wt% solids content

Pit No.	Blend	Mix Ratio (g/g)	28-d unconfined compressive strength[1] (psi)
1	A	0.4	97 ± 4
		0.6	266 ± 2
		0.8	188 ± 22
2	A	0.4	94 ± 3
		0.6	282 ± 5
		0.8	236 ± 2
3	A	0.4	98 ± 4
		0.6	312 ± 4
		0.8	214 ± 15
4	A	0.4	78 ± 2
		0.6	270 ± 2
		0.8	226 ± 25
1	B	0.4	115 ± 4
		0.6	292 ± 5
		0.8	660 ± 12
2	B	0.4	119 ± 5
		0.6	299 ± 23
		0.8	775 ± 19
3	B	0.4	128 ± 4
		0.6	384 ± 11
		0.8	882 ± 10
4	B	0.4	96 ± 5
		0.6	302 ± 2
		0.8	571 ± 35

---

[1] Unconfined compressive strength values are an average of measurements taken on three replicate samples and error bars are based on one standard deviation.

Table 19. 28-d unconfined compressive strength data (psi) from grouts prepared with reference sludge from Weldon Spring Raffinate Pits diluted to 20 wt% solids content (cont.)

Pit No.	Blend	Mix Ratio (g/g)	28-d unconfined compressive strength[1] (psi)
1	C	0.4	138 ± 3
		0.6	431 ± 29
		0.8	937 ± 43
2	C	0.4	123 ± 5
		0.6	510 ± 4
		0.8	1044 ± 15
3	C	0.4	198 ± 12
		0.6	625 ± 8
		0.8	1406 ± 88
4	C	0.4	144 ± 1
		0.6	410 ± 14
		0.8	1122 ± 64

---

[1] Unconfined compressive strength values are an average of measurements taken on three replicate samples and error bars are based on one standard deviation.

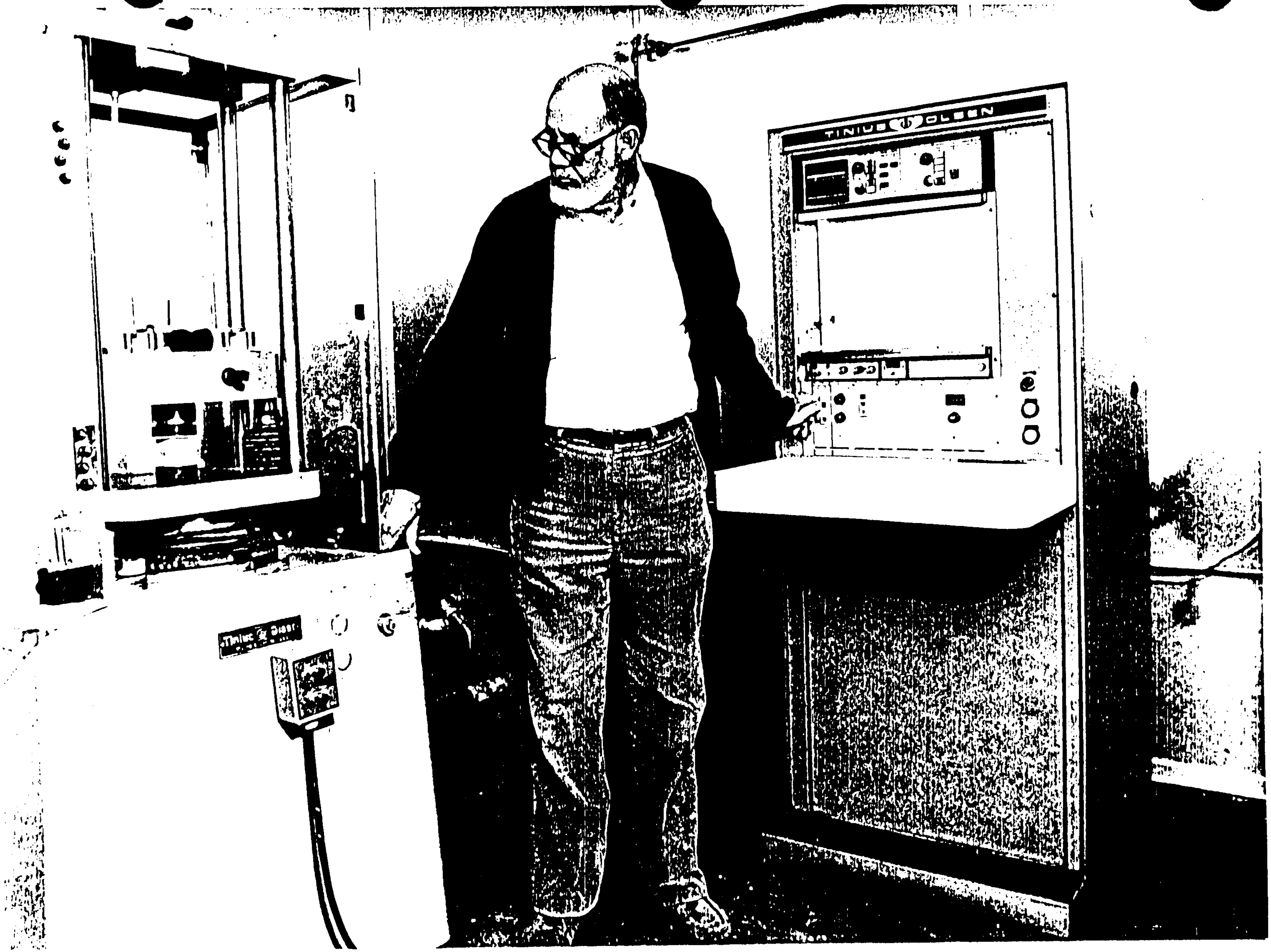

Fig 23. Tinium Olsen Super L Universal Testing Machine used to determine unconfined compressive strength

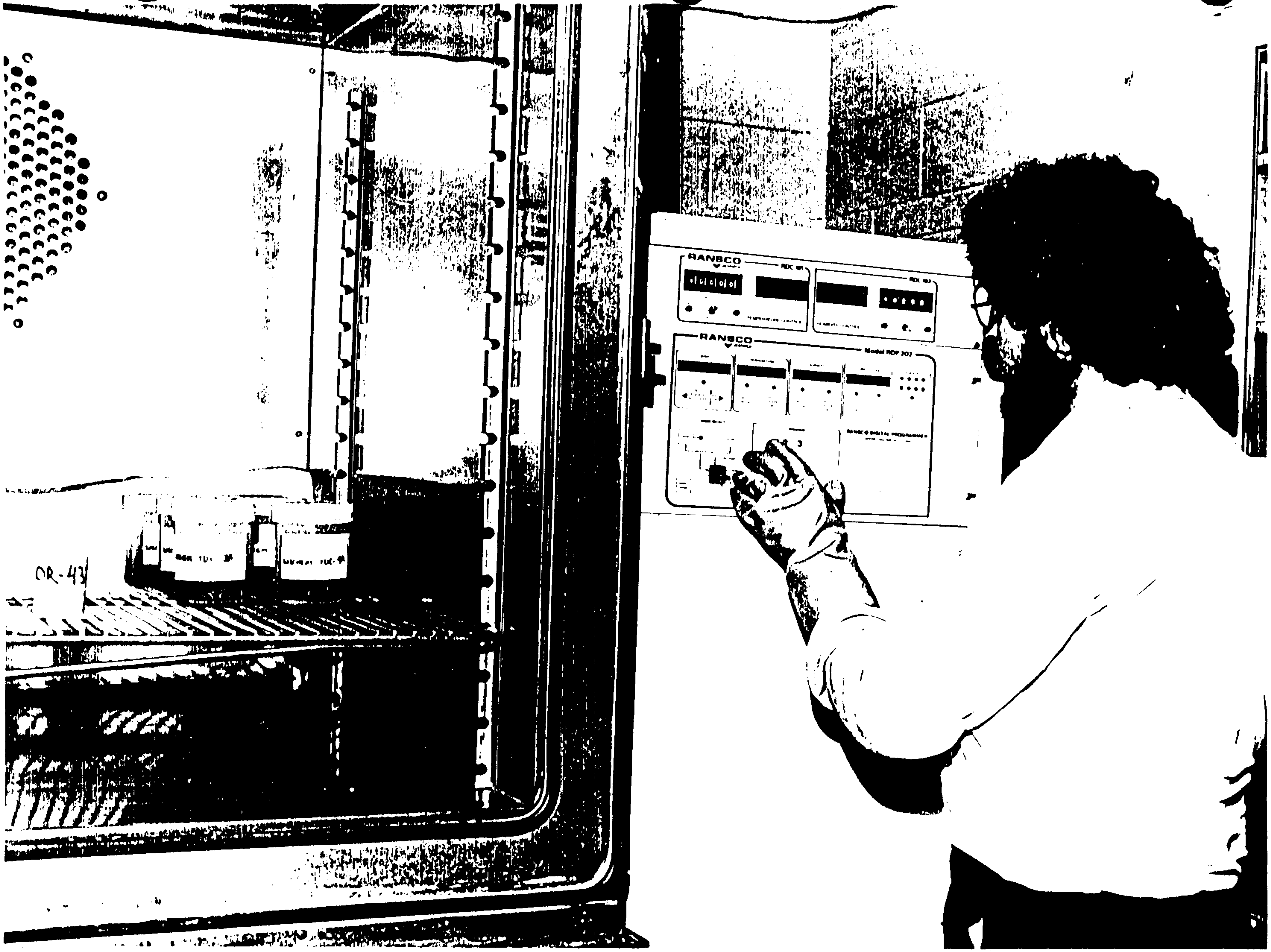

Fig 24. Instrumentation used for control of thermal cycling

evaluated for degradation and were submitted for measurement of their unconfined compressive strengths for comparison with the value obtained at 56-d before freeze-thaw testing. Resulting data are shown in Tables 20 and 21.

3.8 VOLUME INCREASE

One of the performance criterion of this grout development effort was to maximize waste loadings and, hence, summarize volume increase resulting from the cementitious reactions. Volume increase is determined by:

$$VI = \frac{\text{weight waste + weight additives}}{\text{weight waste}} * \frac{\text{density of waste}}{\text{density of waste form}}$$

where VI = the ratio of final waste-form volume to the volume of waste contained in the waste form.

For this study, the density of the final waste form was determined by weighing the 2-in cubes used for unconfined compressive strength determination and dividing by the volume of the cube. The density of the waste sludge was determined by placing a known weight of sludge into a graduated cylinder and then dividing the weight by the resulting volume. The waste densities were 1.22, 1.20, 1.20, and 1.22 g/cm^3 for reference sludge contained in pits 1, 2, 3, and 4, respectively.

The densities for waste diluted to 20 wt% solids content were 1.16, 1.14, 1.19, and 1.15 g/cm^3 for raffinate pits 1, 2, 3, and 4, respectively. The calculated volume increase is shown in Tables 22 and 23.

4.0 DISCUSSION

4.1 DRAINABLE WATER

As shown in Table 8, all grouts prepared with the reference wastes met the performance criterion of no drainable water within 28-d after pouring. Indeed this performance criterion was met within 1-d with the exception of those prepared with Blend A using reference waste from pit 4. However, in this case, the criterion was met within 7-d.

Table 20. Effect of thermal cycling on grouts prepared with reference sludge from Weldon Spring raffinate pits

Pit No.	Blend	Mix ratio (g/g)	56-d unconfined compressive strength (psi)[1] thermal cycling before	after
1	A	0.4	99 ± 4	68 ± 15
		0.6	243 ± 8	105 ± 35
2	A	0.4	158 ± 26	164 ± 23
		0.6	374 ± 11	405 ± 27
3	A	0.4	58 ± 8	59 ± 1
		0.6	183 ± 9	183 ± 8
4	A	0.4	103 ± 6	118 ± 0
		0.6	413 ± 20	392 ± 12
1	B	0.4	306 ± 16	185 ± 90[2]
		0.6	788 ± 39	697 ± 273[3]
2	B	0.4	401 ± 25	355[4]
		0.6	995 ± 39	961 ± 69[5]
3	B	0.4	309 ± 6	257 ± 35[5]
		0.6	1085 ± 87	799 ± 122
4	B	0.4	312 ± 14	343 ± 103[6]
		0.6	749 ± 77	828 ± 12

---

[1] Unconfined compressive strength values are an average of measurements taken on three replicate samples unless otherwise noted. Error bars are based on one standard deviation.

[2] Average of two values. One test specimen was unsuitable for compressive strength determination, one specimen was unaffected, and one specimen showed evidence of crumbling (weight loss approximately 23%) but was still amenable to compressive strength determination.

[3] Average of three values, but one specimen showed evidence of crumbling with a weight loss of ~12 wt%.

[4] Single value. Two specimens were unsuitable for compressive strength determination.

[5] Average of two values. One specimen was unsuitable for compressive strength determination.

[6] Average of three values, but one specimen showed evidence of crumbling with a weight loss of ~16 wt%.

Table 20. Effect of thermal cycling on grouts prepared with reference sludge from Weldon Spring raffinate pits (cont.)

Pit No.	Blend	Mix ratio (g/g)	56-d unconfined compressive strength (psi)[1] thermal cycling	
			before	after
1	C	0.4	529 ± 5	461 ± 16[7]
		0.6	1047 ± 110	1184 ± 181[8]
2	C	0.4	634 ± 40	627 ± 28[8]
		0.6	1278 ± 77	1273 ± 47
3	C	0.4	609 ± 37	452 ± 73[9]
		0.6	1329 ± 123	1114 ± 200
4	C	0.4	507 ± 24	520 ± 30
		0.6	1071 ± 148	1185 ± 117

---

[7] Average of three values, but one specimen showed evidence of crumbling wIth a weight loss of 16 wt%.

[8] Average of three values, but one specimen showed evidence of surface cracking.

[9] Average of three values, but one specimen showed evidence of crumbling with a weight loss of ~7 wt%.

Table 21. Effect of thermal cycling on grouts prepared with reference sludge diluted to 20 wt% solids content from Weldon Spring raffinate pits

Pit No.	Blend	Mix ratio (g/g)	56-d unconfined compressive strength (psi)[1] thermal cycling before	after
1	A	0.4	138 ± 5	90 ± 23[2]
		0.6	364 ± 27	410 ± 110[3]
		0.8	274 ± 5	298 ± 18
2	A	0.4	149 ± 2	104 ± 44[4]
		0.6	429 ± 1	391 ± 105[5]
		0.8	301 ± 8	265 ± 13
3	A	0.4	136 ± 2	115 ± 26
		0.6	471 ± 19	425 ± 20
		0.8	295 ± 17	255 ± 13
4	A	0.4	146 ± 8	150 ± 10
		0.6	463 ± 23	581 ± 50
		0.8	402 ± 3	394 ± 73
1	B	0.4	186 ± 7	154 ± 73[6]
		0.6	583 ± 31	507 ± 184[7]
		0.8	1210 ± 161	1150 ± 181
2	B	0.4	187 ± 24	147 ± 37
		0.6	689 ± 38	633 ± 66
		0.8	1293 ± 81	1200 ± 83
3	B	0.4	192 ± 6	138 ± 48[8]
		0.6	702 ± 13	550 ± 74
		0.8	1442 ± 73	1471 ± 43

---

[1] Unconfined compressive strength values are an average of measurements taken on three replicate samples unless otherwise noted. Error bars are based on one standard deviation.

[2] Average of three measurements but one sample showed evidence of cracking with a 4 % weight loss.

[3] Average of three measurements but one sample showed evidence of cracking with a 14% weight loss.

[4] Average of three measurements but one sample showed evidence of cracking with no weight loss.

[5] Average of three measurements but one sample showed evidence of cracking with a 9% weight loss.

[6] Average of three measurements but one sample showed evidence of cracking with a 6% weight loss.

[7] Average of three measurements but one sample showed evidence of cracking with a 20% weight loss.

[8] Average of three measurements but two samples showed evidence of cracking with weight losses of 10 and 15 wt %, respectively.

Table 21. Effect of thermal cycling on grouts prepared with reference sludge diluted to 20 wt% solids content from Weldon Spring raffinate pits (cont.)

Pit No.	Blend	Mix ratio (g/g)	(psi)[1]	56-d unconfined compressive strength thermal cycling	
				before	after
4	B	0.4		252 ± 28	241 ± 21
		0.6		544 ± 26	572 ± 37
		0.8		956 ± 61	983 ± 17
1	C	0.4		204 ± 5	
		0.6		660 ± 13	
		0.8		1441 ± 146	1580 ± 120
2	C	0.4		215 ± 10	
		0.6		873 ± 22	
		0.8		1565 ± 88	1454 ± 81
3	C	0.4		293 ± 9	
		0.6		900 ± 27	
		0.8		1993 ± 39	1595 ± 103
4	C	0.4		273 ± 6	
		0.6		615[e]	
		0.8		913 ± 46	1411 ± 48

---

[e] Single value. Two specimens were unsuitable for compressive strength determination.

Table 22. Volume of waste forms prepared with reference waste compared with volume of waste sludge contained in the waste form

Pit No.	Blend	Mix ratio (g/g)	Waste form density (g/cm³)	Volume increase ratio[1]
1	A	0.4	1.42	1.20
		0.6	1.50	1.30
2	A	0.4	1.44	1.17
		0.6	1.48	1.30
3	A	0.4	1.39	1.21
		0.6	1.47	1.30
4	A	0.4	1.48	1.16
		0.6	1.41	1.38
1	B	0.4	1.43	1.20
		0.6	1.50	1.30
2	B	0.4	1.43	1.18
		0.6	1.48	1.30
3	B	0.4	1.41	1.19
		0.6	1.49	1.29
4	B	0.4	1.38	1.23
		0.6	1.39	1.40

---

[1] Ratio of final waste form volume to volume of waste contained in the waste form.

Table 22. Volume of waste forms prepared with reference waste compared with volume of waste sludge contained in the waste form (cont.)

Pit No.	Blend	Mix ratio (g/g)	Waste form density (g/cm^3)	Volume increase ratio[1]
1	C	0.4	1.39	1.23
		0.6	1.47	1.33
2	C	0.4	1.32	1.27
		0.6	1.41	1.36
3	C	0.4	1.37	1.23
		0.6	1.45	1.32
4	C	0.4	1.26	1.36
		0.6	1.37	1.43

---

[1] Ratio of final waste form volume to volume of waste contained in the waste form.

Table 23. Volume of waste forms prepared with reference waste diluted to 20 wt% solids content compared with volume of waste sludge contained in the waste form

Pit No.	Blend	Mix ratio (g/g)	Waste form density (g/cm^3)	Volume increase ratio[1]
1	A	0.4	1.36	1.19
		0.6	1.48	1.25
		0.8	1.52	1.37
2	A	0.4	1.38	1.16
		0.6	1.45	1.26
		0.8	1.54	1.33
3	A	0.4	1.29	1.29
		0.6	1.40	1.36
		0.8	1.50	1.43
4	A	0.4	1.20	1.34
		0.6	1.28	1.44
		0.8	1.49	1.38
1	B	0.4	1.36	1.19
		0.6	1.46	1.27
		0.8	1.55	1.34
2	B	0.4	1.36	1.17
		0.6	1.44	1.27
		0.8	1.52	1.35
3	B	0.4	1.37	1.22
		0.6	1.47	1.30
		0.8	1.52	1.41
4	B	0.4	1.39	1.16
		0.6	1.31	1.40
		0.8	1.35	1.52

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[1] Ratio of final waste form volume to volume of waste contained in the waste form.

Table 23. Volume of waste forms prepared with reference waste diluted to 20 wt% solids content compared with volume of waste sludge contained in the waste form (cont.)

Pit No.	Blend	Mix ratio (g/g)	Waste form density (g/cm^3)	Volume increase ratio[1]
1	C	0.4	1.36	1.19
		0.6	1.45	1.28
		0.8	1.51	1.39
2	C	0.4	1.35	1.18
		0.6	1.45	1.26
		0.8	1.43	1.44
3	C	0.4	1.36	1.23
		0.6	1.44	1.32
		0.8	1.49	1.44
4	C	0.4	1.24	1.30
		0.6	1.36	1.35
		0.8	1.42	1.46

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[1] Ratio of final waste form volume to volume of waste contained in the waste form.

Increasing the liquid content of the reference sludge (i.e., decreasing the solids content to 20 wt%) produced a corresponding increase in observed drainable water (Table 9). The exception being grouts prepared at a mix ratio of 0.8 g/g using Blends B and C, which showed no drainable water within 1-d for diluted waste from pits 1, 2, and 3. All grouts prepared with diluted waste met the performance criterion within 21-d with the exception of grouts prepared with diluted waste from pit 4 using Blends A and B at a mix ratio of 0.4 g/g. In both of these cases, the performance criterion of no drainable water within 28-d was not met but was achieved within 56-d for Blend B.

As seen in Tables 8 and 9, grouts prepared with sludge (reference and diluted) from raffinate pit 4, consistently exhibited more drainable water than similar grouts prepared with sludge from pits 1, 2, and 3. Visual observation indicates that the sludge from pit 4 was easier to stir than the other three, even though it had the highest solids content (Table 7). Apparently, the solids contained in pit 4 have less ability to sorb water than those contained in the other pits.

Beyond the ability of the solids present in the waste to sorb water, it is the cement which plays the major role in controlling drainable water. This is due to the progression of the cementicious reactions and the waters of hydration associated with these reactions. Although less significant, the fly ash does aid in control of drainable water. This is illustrated by comparing drainable water observed for grouts prepared with diluted waste from pit 4 using Blend A at a mix ratio of 0.8 g/g with grouts prepared with diluted waste from pit 4 using Blend B at a mix ratio of 0.4 g/g (Table 9). For these two cases, the cement content (on a per gram of waste bases) is identical at 0.16 g/g, but the fly ash content is 0.64 and 0.24 g/g, respectively. The grout with the higher fly ash content resulted in no drainable water between 14 and 21-d, while the grout with the lower fly ash content achieved zero drainable water between 28 and 56-d. It is clear from the data that drainable water can readily be controlled to desired specifications by either minor changes in the dry solids blend content or the mix ratio.

4.2 PENETRATION RESISTANCE

As shown in Figs. 8 through 13, grouts prepared with reference waste generally behaved as expected with regard to rate of set as determined by penetration resistance (that is, for a given waste and dry solids blend composition, the rate of set increased with increasing mix ratio; and for a given waste and mix ratio, the rate of set increased with the cement content of the dry solids blend).

As shown in Fig. 8, all grouts prepared with Blend A and reference waste at a mix ratio of 0.4 g/g failed to achieve a penetration resistance of 4000 psi (final set) within 28-d. Initial set (penetration resistance of 500 psi) was achieved within 7-d for grouts prepared with reference sludge from pit 2; within 14-d for grouts prepared with reference sludge from pits 1 and 4; and within 21-d for grouts prepared with reference sludge from pit 3. It was observed that the grouts cracked and crumbled easily as penetration data were being detained. This is a strong indication that the durability of these grouts are suspect. Conversely, it is also an indication that the grouts would be recoverable from the disposal site by conventional earth-moving equipment.

Increasing the mix ratio to 0.6 g/g using Blend A resulted in an increased rate of set (Fig. 9), as compared with a mix ratio of 0.4 g/g. Final set was achieved within 14-d for grouts prepared with reference sludge from pit 2; within 21-d for grouts prepared with reference sludge from pit 4; and within 28-d for grouts prepared with reference sludge from pit 1. Grouts prepared with reference sludge from pit 3 did not achieve final set within 28-d but did within 56-d (Table 16). Initial set was achieved within 2-d for grouts prepared with reference sludge from pit 2 and within 7-d for all grouts.

As shown in Fig. 10, all grouts prepared with reference sludge at a mix ratio of 0.4 g/g using Blend B achieved final set within 28-d. All grouts achieved initial set within 2-d, with the exception of those prepared with reference sludge from pit 4 which achieved initial set within 7-d. Significantly, measurable penetration resistance is achieved within 1-d for all grouts with the exception of those prepared with reference sludge from pit 4.

All grouts prepared with reference waste at a mix ratio of 0.6 g/g using Blend B (Fig. 11) achieved initial set within 1-d and final set within 7-d.

As shown in Fig. 12, all grouts prepared with reference waste and Blend C at a mix ratio of 0.4 g/g achieved initial set within 1-d. Final set was achieved within 7-d for all grouts with the exception of those prepared with reference sludge from pit 1 which achieved final set within 14-d. Increasing the mix ratio to 0.6 g/g (Fig 13) accelerated the rate at which final set was achieved (compared with a mix ratio of 0.4 g/g). At this mix ratio, final set was achieved within 2-d for all grouts within 2-d, with the exception of those prepared with reference sludge from pit 1 which achieved final set within 7-d.

It should be noted that grouts prepared with Blend B at a mix ratio of 0.6 g/g and those prepared with Blend C at a mix ratio of 0.4 g/g had identical cement content (0.24 g of cement per g of waste) but differing fly ash contents (0.36 and 0.16 g/g, respectively). A comparison between their respective rates of set (Figs. 11 and 12) illustrates the beneficial role of fly ash on rate of set as determined by penetration resistance. As seen in the figures, final set was achieved more rapidly with increased fly ash content (Blend B at a mix ratio of 0.6 g/g). Fly ash can affect the rate of set by a number of mechanisms including: (1) ASTM Class F fly ash has the physical consistency of noncompressible glass balls which can increase the matrix's resistance to penetration, (2) the glass balls can fill pore voids resulting from the cementitious reactions which can increase the matrix's resistance to penetration, (3) fly ash reduces the $Ca(OH)_2$ (a by-product of the cementitious reactions) concentration of the matrix and thus accelerate the cementitious reactions and (4) fly ash, being a pozzolance material, can participate in the cementitous reactions.

As shown in Fig. 14 through 22, grouts prepared with diluted waste generally showed a perceptible decrease in rate of set as compared with those prepared with reference waste (Figs. 8 through 13). None of the grouts prepared with diluted waste and Blend A at a mix ratio of 0.4 g/g (Fig. 14) achieved final set within 28-d. Initial set was achieved within 7-d for grouts prepared with diluted waste from pits 1 and 2 and within 14-d for grouts prepared with diluted waste from pits 3 and 4. Increasing the mix ratio to 0.6 g/g (Fig. 15) resulted in all grouts achieving final set within 21-d. Initial set was achieved within 7-d for all grouts and within 2-d for grouts prepared with diluted waste from pit 2. Further increasing the mix ratio to 0.8 g/g (Fig. 16) accelerated the rate at which final set was achieved for grouts prepared with diluted waste from pits 2 and 4.

Fig. 17, which presents penetration resistance data for grouts prepared with diluted waste and Blend B at a mix ratio of 0.4 g/g, provides one of the more obvious illustrations of the reduction in rate of set as compared with similar grouts prepared with reference waste (Fig. 10). As shown in Fig. 17, none of the grouts prepared with diluted waste achieved final set within 28-d, while all grouts prepared similarly with reference waste (Fig. 10) did achieve final set within 28-d. It should be noted that these grouts prepared with diluted waste did achieve final set within 56-d (Tables 14 through 17). Increasing the mix ratio to 0.6 g/g (Fig. 18) resulted in all grouts prepared with diluted waste and Blend B achieving final set within 14-d. Further increasing the mix ratio to 0.8 g/g (Fig. 19) results in all grouts prepared with diluted waste and Blend B achieving final set within 7-d.

As shown in Fig. 20, none of the grouts prepared with diluted waste and Blend C at a mix ratio of 0.4 g/g achieved final set within 28-d. However, as shown in Tables 14 through 17, final set was achieved within 56-d. Increasing the mix ratio to 0.6 g/g (Fig. 21) resulted in all grouts prepared with diluted waste and Blend C achieving final set within 28-d, with grouts prepared with diluted waste from pits 1, 2, and 3 achieving final set within 14-d. Further increasing the mix ratio to 0.8 g/g (Fig. 22) results in all grouts prepared with diluted waste and Blend C achieving final set with 7-d or less.

Significantly all grouts prepared with reference waste which achieved final set also achieved final set when prepared with diluted waste but at a perceptibly slower rate. Collectively the data contained in Tables 8 through 17 show that the delay in set experienced with diluted waste corresponds to an increase in drainable water. This point is more easily illustrated by noting when a penetration resistance of 8000 psi (the instrument's maximum measurement) is achieved. For example, grouts prepared with reference waste and Blend B at a mix ratio of 0.6 g/g resulted in no drainable water within 1-d (Table 8). These grouts achieved a penetration resistance of 8000 psi within 7 through 21-d (Tables 10 through 13). Conversely similar grouts prepared with diluted waste resulted in no drainable water within 2-d for pits 2 and 3, within 7-d for pit 3 and within 21-d for pit 4 (Table 9). These grouts containing diluted waste achieved a penetration resistance of 8000 psi within 21 to 28-d for pits 1, 2, and 3 and within 56-d for pit 4 (Tables 14 through 17). There is an approximate difference of 21-d between zero drainable water and a penetration resistance of 8000 psi.

It is not clear whether the presence of drainable water (and hence its unavailability for cement hydration) is the cause of the delay or if both measurements are evidence of a more fundamental change in the cementitious reactions. What is clear is that penetration resistance (and thus rate of set) can be controlled by minor changes in blend content or mix ratio even at significant waste dilutions.

4.3 UNCONFINED COMPRESSIVE STRENGTH

All 28-d unconfined confined compressive strengths met the performance criterion of 60 psi with the exception of grouts prepared with reference waste from pit 3 at a mix ratio of 0.4 g/g using Blend A (Tables 18 and 19). The data clearly indicate that unconfined compressive strengths of several hundred psi can be achieved with Blends B and C at the mix ratios studied.

As shown in Table 19, grouts prepared with diluted waste resulted in a waste form with a lower unconfined compressive strengths than similar grouts prepared with reference waste (Table 18). This is to be expected since the increased liquid content of the diluted waste results in a waste form with pore voids filled with a more compressible material (liquid versus waste solids).

In general, for a specific blend and waste, the unconfined compressive strength increased as the mix ratio was increased from 0.4 to 0.8 g/g. This is due principally to the corresponding increase in cement content.

It should be noted that unconfined compressive strength is not dictated solely by the cement content. This is illustrated by comparing results obtained with Blend C at a mix ratio of 0.4 g/g and Blend B at a mix ratio of 0.6 g/g. In both cases, the cement content is the same on a per gram of waste basis. However, the compressive strengths are higher for Blend B than those obtained using Blend C. Clearly the increased fly ash content of Blend B (on a per gram of waste basis) is playing a beneficial role in both the final strength and its rate of development.

Significantly grouts prepared with diluted waste and Blend A did not follow the general trend of increasing strength with increasing mix ratio. As shown in Table 19, grouts prepared with diluted waste and Blend A consistently had a lower unconfined compressive strength at a mix ratio of 0.8 g/g than at 0.6. Although determining the cause of this phenomenon is beyond the scope of this study, it is clear that the strength is being adversely affected by the waste dilution. Thus, the chemical interaction between this blend and the waste is too sensitive to be considered for use in the field.

4.4 THERMAL CYCLING

As shown in Tables 20 and 21, 56-d unconfined compressive strengths are consistently higher than those observed at 28-d (Tables 18 and 19). It is well known that grouts continue to cure well beyond the standard 28-d reporting period. There is also little evidence of strength reduction upon exposure to the thermal cycles.

As noted in the tables, there was evidence on some samples of surface cracking and crumbling upon exposure to the thermal cycles. This is believed to be due to the testing methodology. During the thermal cycles, these samples were contained in each jar. The bottom sample was raised above the glass by a 1 mm wire. In many cases, it was observed that the bottom and sometimes middle sample had sorbed condensed water. It is those samples which experienced the surface degradation.

4.5 VOLUME INCREASE

In general, the volume increases resulting from solidification (versus the original waste) were consistent for all blends at any given mix ratio for both the reference and diluted waste (Tables 22 and 23). Average volume increase for all grouts prepared at mix ratios of 0.4, 0.6, and 0.8 g/g were 22, 32, and 40 vol%, respectively.

It should be noted that there was significant deviation from these average values for grouts prepared with waste from pit 4. Average volume increase for all grouts prepared with waste from pit 4 at mix ratios of 0.4, 0.6, and 0.8 g/g were 26, 40, and 45 vol%, respectively.

These volume increases and the associated waste-form densities (Tables 22 and 23) can be used to estimate final disposal and/or transportation volume and weight requirements. They can also be used to identify potential disposal scenarios. For example, these increases can be compared with available space within the raffinate pits to assess the potential of the in situ option or possibly consolidating the solidified waste from the four pits into pit 4 (the largest).

4.6 EP-TOXICITY CALCULATIONS

Under the RCRA, a waste form is classified as hazardous if it exhibits any of the characteristics of EP-Toxicity, corrosivity, reactivity, or ignitability as defined by testing protocols described in Environmental Protection Agency (EPA) SW-846, *Test Methods for Evaluating Solid Waste*. For monolithic waste forms, the only characteristic of potential concern (as defined by test methods in EPA SW-846) is EP-Toxicity. The characteristic of EP-Toxicity is determined by Method 1310, *Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test*.

This extraction procedure involves the placement of a 100 g waste-form specimen in a pH 5 acetic acid solution for 24 h and then determining the concentration of the species of interest in the extraction fluid. If these concentrations are above established threshold limits, then the waste form is EP-Toxic and is hazardous as per this characteristic.

In this test, the extraction fluid is made in the following manner: (1) Type II water is added at 16 times the weight of the waste form, (2) a 0.5 N acetic acid solution is added to maintain the pH of the extraction fluid at 5 ± 0.2, and (3) the maximum allowable acetic acid addition is 4 ml per gram of waste form. The extraction of cement-based waste forms generally requires the maximum allowable addition of acetic acid due to the buffering capacity of the waste form [$Ca(OH)_2$ is a by-product of the cement reactions]. Thus, the total amount of extraction fluid used in this case is approximately 20 times the waste-form weight or approximately 20 ml of extraction fluid per gram of waste form.

Using the 20 ml/g value and substituting the EP-Toxicity threshold concentration of each species of interest allows the calculation of the minimum waste-form concentration required to achieve these EP-Toxicity threshold concentrations. If the actual waste-form concentration is below these calculated values, then the waste form does not contain sufficient quantities of the species of interest to exceed the EP-Toxicity limits. It must be noted that this evaluation involves two unrealistic, yet conservative, assumptions: (1) that all of the species of interest contained in the waste form is immediately and completely soluble in the extraction fluid and (2) the waste-form matrix does not impede the release of the constituent of interest from the waste (i.e., the source of the contaminants in the waste form). Thus, it must be recognized that waste-form concentrations above the calculated value may not necessarily exhibit the characteristic of EP-Toxicity, but waste-form concentrations below the calculated value cannot exhibit this characteristic.

The results of these calculations are shown in Table 24. The calculated waste-form concentrations were determined by the following simple relationship:

$$C_w = 20 \frac{\underline{ml}}{g} \times C_t \qquad \text{Eq. (1)}$$

where

C_w = the minimum waste form-concentration (g/g) required to achieve the characteristic of EP-Toxicity

C_t = the EP-Toxicity threshold concentration, g/ml

If one assumes that the principal source of the species of interest is the waste contained in the waste form, then the calculated waste-form threshold concentrations can be extrapolated to actual waste concentrations by multiplying the waste-form threshold concentration by the ratio of the waste-form weight to the weight of waste contained in the waste form:

$$C_o = \frac{\underline{W_w}}{W_o} \cdot \underline{C_w} \qquad \text{Eq. (2)}$$

where

C_o = the minimum waste concentration required to achieve characteristic of EP-Toxicity after solidification or stabilization;

W_w = weight of waste form; and

W_o = weight of waste contained in the waste form.

At mix ratios of 0.4, 0.6, and 0.8 g/g, the waste-threshold concentration would be calculated by multiplying the values in Table 24 by 1.4, 1.6, and 1.8, respectively. The resulting values can then be compared directly with actual waste concentrations.

Analysis of the site characterization data (including analyses of individual samples used to prepare the composite reference wastes used in this study) had not been received at the time this study was performed. The methodology described in this section can be applied to those analyses as they become available in order to identify species of potential concern in regard to EP-Toxicity.

Table 24. Minimum waste-form concentrations required to achieve the characteristic of EP-Toxicity

Constituent	EP-Toxicity threshold concentration (mg/l)	Waste-form threshold concentration[a] (μg/g)
Arsenic	5	100
Barium	100	2000
Cadmium	1	20
Chromium[b]	5	100
Lead	5	100
Mercury	0.2	4
Selenium	1	20
Silver	5	100

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[a] Minimum waste-form concentration required to achieve the characteristic of EP-Toxicity.

[b] Although total chromium is used here, only chromium (VI) is addressed in the test.

One of the performance criterion of this grout development effort was that the waste forms should not be more hazardous than the original waste. This was addressed by using only additives which are nonhazardous (i.e., Portland cement and ASTM Class F fly ash). The ability of cement-based waste forms to sequester the species listed in Table 24 is well established[17,18] and the EPA has accepted the use of solidification/stabilization as a remedial action to be implemented at several superfund sites. A recent literature search has identified 16 NPL sites at which this technology is the recommended remedial action as defined in the ROD for each of the sites[19].

Based on the established ability of cement-based waste forms to sequester the species of concern in Table 24 and the lack of available site characterization data, EP-Toxicity testing was not a criterion for this proof-of-principal effort. If this technology is chosen as the remedial action option for the raffinate pits, then the methodology discussed in this section can be applied to the final selected grout recipe (combined with the site characterization data) to identify the worst case conditions in regard to EP-Toxicity. EP-Toxicity testing could then be performed at these worst case conditions in order to demonstrate waste-form acceptability.

4.7 COST ESTIMATES

It was beyond the scope of this study to provide cost estimates of applying the cement-based stabilization/solidification option to the raffinate pits. However, a recently completed study by ORNL on application of this technology to a DOD hazardous waste remedial action site provided generic cost information which can be used to estimate order-of-magnitude costs for application to the Weldon Spring site.

In the related study, commercial vendors of this technology were contacted and cost ranges for use of portable processing equipment were obtained. Based on the throughput capacity of the commercially available equipment, the time required to treat the 36,000 yd^3 site was calculated and support labor costs were estimated. The resulting cost estimate of $2-3 million did not include project closeout costs of capping the site, monitoring well installation, etc. Nor does this estimate include the cost of containers (e.g., drums or vaults) since the in situ option was being evaluated.

Based on this cost estimate and assuming a total waste volume of 6 million cu ft (a factor of 6 increase over the DOD site), it is estimated that application of this technology to the four Weldon Spring raffinate pits would cost $12-18 million using commercially available portable equipment.

5. SUMMARY

Data from the grout development effort have been presented. Available data clearly indicate the viability of utilizing cement-based grout as a remediation option for the sludge contained in the Weldon Spring Raffinate Pits 1, 2, 3, and 4.

Three dry-solids blends were evaluated: (1) Blend A, consisting of 20 wt % Type II Portland cement and 80 wt % ASTM Class F fly ash, (2) Blend B, consisting of 40 wt % Type II Portland cement and 60 wt % ASTM Class F fly ash, and (3) Blend C, consisting of 60 wt % Type II Portland cement and 40 wt % ASTM Class F fly ash. The blends were combined with the raffinate pit sludge at mix ratios of 0.4, 0.6, and 0.8 g/g.

Waste forms were prepared with composite waste samples from pits 1, 2, 3, and 4 as well as composite samples diluted to 20 wt% solids content. All of the waste forms prepared with Blends B and C met the performance criteria of: (1) no drainable water within 28 d, (2) unconfined compressive strength of 60 psi and (3) resistance to thermal cycling. Volume increase (versus the original waste) was consistent for all three blends at any one mix ratio and were 22, 32, and 40 vol% at mix ratios of 0.4, 0.6 and 0.8 g/g, respectively.

Collectively, the data indicate that rate of set as determined by penetration resistance, drainable water and unconfined compressive strength can be controlled by minor changes in the dry-solids blend composition or mix ratio. In addition the effects of waste solids content on these properties can be controlled in the same manner. Thus these grouts (Blend B and C), using no proprietary additives, can accommodate expected variations in the waste composition or future more stringent performance criteria by the use of minor process operating changes (i.e., blend composition or mix ratio) which are well within the capability of standard commercially available technology.

Based on the available data, it is recommended that grouts prepared with Blend B at a mix ratio of 0.6 g/g be used as a reference formula for preliminary design and evaluation purposes. Waste forms prepared with this formula would be characterized by:

1. weight increase (versus the original waste) of 60%;
2. volume increase (versus the original waste) of 32%;
3. no free liquid within 21 d;
4. penetration resistance of 4000 psi within 14 d; and
5. unconfined compressive strength >200 psi.

5.1 RAFFINATE PIT 4

Throughout this report it was noted that grouts prepared with waste from raffinate pit 4 consistently behaved differently from those prepared with waste from the other three pits. Grouts containing waste from pit 4 were characterized by more drainable water, larger volume increases, and spurious compressive strengths. Visual observation indicates that this waste is less viscous and easier to stir than the other wastes and has components which are more sandy-silt in nature. Based on these observations it is recommended that special attention be given to the characterization of pit 4.

6. REFERENCES

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7. DOCUMENTATION

This report contains a summary of all data pertinent to the study. Additional raw data are contained in ORNL Technical Notebook No. A103101-G, pp. 1-80.

APPENDIXES

Appendix A: Formation of Ettringite

This appendix contains information on the formation of ettringite compiled by J. L. Kasten.

A. FORMATION OF ETTRINGITE

A discussion of ettringite is presented based on a literature search of textbooks, reports, and publications concerning cement chemistry and concrete research and development.[1-14]

A.1 CEMENTITIOUS REACTIONS OF PORTLAND CEMENT

Portland cement consists essentially of crystalline compounds (minerals) of calcium combined with silica, alumina, iron oxide, and sulfate. The main compounds of Portland cement are found in Table A.1. Typically, the approximate composition and amounts of the principal minerals present are C_3S - 50%. C_2S -25%, C_3A - 10%, C_4AF - 8%, CSH_2 - 5%. These minerals are unstable in water and begin to undergo dissolution at various rates as soon as water is added to cement.[6]

Table A.1. Main compounds of Portland cement

Name of compound	Oxide composition	Abbreviation
Tricalcium silicate	$3CaO \cdot SiO_2$	C_3S
Dicalcium silicate	$2CaO \cdot SiO_2$	C_2S
Tricalcium aluminate	$3CaO \cdot Al_2O_3$	C_3A
Tetracalcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_3O_3$	C_4AF

The chemical reactions of cement with water can generally be described as the hydration process. This hydration process is much more complex than the simple attachment of water molecules (or OH ions) to the original cement compounds. The complex processes of dissolution and precipitation result in a reorganization of the constituents of the original compounds to form new hydrated compounds. It is recognized that all reactive phases continue to react with an available water supply throughout the hydration process. The reactions of the aluminates in particular, and the aluminoferrites, to a lesser degree, significantly affect the very early stages of the hydration process, while the silicates play a dominant role in the late (hardening) stages.[4]

When water is added to cement, the minerals begin to ionize, and the ionic species form hydrated products of low solubility which precipitate out of the solution. The volume of the hydration product formed is less than the sum of the volumes of cement and water which react to form it. Due to the lower density of the hydration products as compared to the anhydrous minerals, the formation and deposition of these hydration products into previously water-filled space leads first to a progressive decrease in consistency. Hydration of the cement matrix proceeds until either the cement is completely hydrated or the available space within the matrix is completely filled. Thus, the setting of the cement results in the progressive decrease in porosity.[6]

It is expected that calcium silicate compounds and/or their derivatives will comprise the major fraction of a cement matrix at any stage of hydration. The hydration of the bulk of these calcium silicate compounds takes place, however, after the setting period has occurred.

The main product of hydration of the silicate minerals in Portland cement is a calcium silicate hydrate (C-S-H) of colloidal dimensions. By using a scanning electron microscope, it has been shown that, at an early age, C-S-H usually shows up as an aggregation of acicular particles, or often as very fine grains partly intergrown together. It is highly cementitious and constitutes about 60 to 65% of the total solids in a fully hydrated Portland cement. It is the properties of the hydrated calcium silicates that produce the ultimate strength-giving structure of the hardened-cement matrix.

C-S-H either grows around solid particles or stops growing in that particular direction when it meets such obstacles. Thus, the hydration of the calcium silicates is not accompanied by an increase in the total volume of the paste. The hydration products will only occupy space that is available to them within the paste, which is the volume originally occupied by the mix water. If this space is filled before complete hydration has occurred, further hydration will virtually cease.

The other major product of hydration of the silicate minerals is about 20% calcium hydroxide (CH), which usually occurs as large hexagonal crystals, and contributes little to the cementitious properties of the system. Also, being relatively more soluble and alkaline than the other hydration products, it is easily subjected to attack by water or acidic solutions, thus reducing the durability of Portland cement systems to such environments.[4,5,6]

A.2 ETTRINGITE

The various phases present in cement each have distinct compositions and properties. Some of the phases produced by cement hydration is sufficiently crystalline to permit detection by structure-sensitive techniques such as X-ray powder diffraction. One such phase is designated AFt; A, F, and t representing aluminum (Al), iron (Fe), and trisulfate, respectively. The AFt phase, which is a calcium sulfoaluminate hydrate, is referred to as ettringite. The correct name for ettringite is 6-calcium aluminate trisulfate-32-hydrate, chemically written as

$$(Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O).$$

The formula for ettringite is often written $C_3A \cdot 3CS \cdot H32$. Ettringite is also the name given to a naturally occurring mineral of the same composition. Ettringite is synthesized on a large scale as white coating for paper.

The basic structure of ettringite consists of hexagonal columns built of alternating triclusters of $Ca(OH)_8$ polyhedra linked by $Al(OH)_6$ groups. The chain may be compared with a linear string of beads, the bulky triclusters comprising the "beads" and the linking single $Al(OH)_6$ groups the "string." The columns are rather widely spaced parallel to the 10.7 A c axis, and the space between channels is occupied by the remaining H_2O molecules, as well as by sulfate ions which balance the positive charge on the columns.

The trisulfate hydrate, ettringite, is usually the first product to precipitate out of the system, and is mostly responsible for the initial set and very early strength (up to three days) in Portland cement. Subsequently, depending on the content and reactivity of the sulfate, alkali, and aluminate-bearing phases in the cement, either a monosulfate hydrate (C_4ASH18) or a mixture of monosulfate and calcium aluminate hydrate (C_4AH19) may also form. Hydration of the ferrite phase (C_4AF) in Portland cement is somewhat slower than C_3A and produces iron analogs of ettringite, monosulfate, and calcium aluminate hydrate. It is important to note here that the reaction products of the aluminate-sulfate interaction, namely ettringite, monosulfate hydrate, calcium aluminate hydrates and their iron analogs, are capable of contributing strength to cement matrix.[8]

The behavior of ettringite when it is formed from C_3A or the ferrite phase is quite the contrary to that of C-S-H. Ettringite crystals will make space for themselves when their crystal growth is impeded by solid material.[5]

A.2.1 Formation of Ettringite

In Portland cement, the hydration of C_3A involves reactions with sulfate ions which are supplied by the dissolution of gypsum. The reactions and subsequent formation of hydration products from C_3A are shown in Table A.2.[5]

Table A.2. Formation of hydration products from C_3A

CSH_2/C_3A Molar Ratio	Hydration products formed
3	Ettringite
3.0-1.0	Ettringite + monosulfoaluminate
1.0	Monosulfoaluminate
<1.0	Monosulfoaluminate solid solution
0	Hydrogarnet

Ettringite is a stable hydration product only while there is an ample supply of sulfate available. If all the sulfate is consumed before the C_3A has completely hydrated, then ettringite transforms to another calcium sulfoaluminate hydrate containing less sulfate:

$$2C_3A + C_6AS3H32 + 4H = 3C_4ASH12$$

This second product is called tetracalcium aluminate monosulfate-12-hydrate, or simply monosulfoaluminate. It is often written $C_3A \cdot CS \cdot H12$. Monosulfoaluminate may sometimes form before ettringite if C_3A reacts more rapidly with the sulfate ions than they can be supplied by the gypsum to the mix water. A certain concentration of sulfate ions is required for the formation of ettringite.[5]

The reaction of C_3A alone with water is immediate. The ions go into solution, and the formation of a crystalline hydrate occurs rapidly with liberation of a large amount of heat. Thus, both steps in the hydration of C_3A[4,5,6] are exothermic. The relative heats of hydration of cement compounds are shown in Table A.3.

Table A.3. Heats of complete hydration of individual compounds

Anhydrous compound	Product	Heat of hydration (cal/g anhydrous compounds)
C_3S	C_3S+3H_2O	120
C_2S	C_2S+2H_2O	62
C_3A	$C_3A \cdot 6H_2O$	207
C_3A	$C_3A \cdot 6H_2O$	214
C_3A	$C_3A \cdot 8H_2O$	235
C_3A	$C_3A \cdot 10 \cdot 2H_2O$	251
C_3A	$C_3A \cdot 11 \cdot 6H_2O$	261
C_3A	$C_3A \cdot 3CaSO_4 \cdot 32H_2O$	347
C_4AF		100
CaO	$Ca(OH)_2$	278-9

In Portland cement, unless this violent reaction of C_3A is moderated by some means, flash-set occurs. With gypsum present as a retarder, the gypsum and C_3A, in solution, react to form a relatively insoluble sulfoaluminate coating on the C_3A phases, which slows down the reaction.

The formation of ettringite slows down the hydration of C_3A by creating a diffusion barrier around C_3A analogous to the behavior of C-S-H during the hydration of the calcium silicates. This barrier is broken down during the conversion to monosulfoaluminate and allows C_3A to react rapidly again. Thus, the calorimeter curve for hydrating C_3A looks qualitatively much like the curve for C_3S, although the underlying reactions are quite different and the amount of heat evolved is much greater.

Ettringite formation is favored in a lime-rich solution. Its formation is depressed with increasing alkali concentrations due to the resulting decrease in the solubility of lime. The hydration reaction of C_3A with gypsum in a strongly alkaline solution (1 N NaOH) depresses ettringite formation and accelerates that of calcium hydroxide. Tetracalcium aluminate hydrate forms, which is rapidly carbonated, and calcium hydroxide precipitates.[8]

The formation of monosulfoaluminate occurs because of a deficiency of sulfate ions necessary to form ettringite from all the available aluminate ions. When monosulfoaluminate is brought into contact with a new source of sulfate ions, then ettringite can be formed once again.

A.3 FLY ASH

Fly ashes can be divided into two categories:

1. The low-calcium fly-ash category, containing less than 5% analytical CaO, is generally a product of combustion of anthracite and bituminous coals;
2. The high-calcium fly-ash category, containing 15 to 35% analytical CaO, generally is the product of combustion of lignite and subbituminous coals.

The ASTM Standard Specification for Mineral Admixtures (C618-85, "Standard Specification for Fly Ash and RAN or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete") does not differentiate fly ashes on the basis of calcium content, although this objective is achieved indirectly by requiring a minimum of 70% of major noncalcium oxides (silica + alumina + iron oxide) for Class F fly ash and 50% for Class C fly ash, since the latter is high in calcium.

The low-calcium fly ashes, due to the high proportions of silica and alumina, consist principally of aluminosilicate glass. Researchers have confirmed that the principal crystalline minerals in low-calcium fly ashes are alpha quartz, mullite, sillimanite, hematite, and magnetite which are nonreactive at ordinary temperatures in the Portland cement solution phase. Their presence in large proportions, at the cost of the noncrystalline component or glass, reduces the reactivity of the ash.

The principal crystalline mineral in high-calcium fly ash is generally C_3A, which is known to be the most reactive mineral present in Portland cement. Crystalline C_4A_3S, CS, and free CaO have been detected, in addition to C_3A, in high-calcium fly ashes, which readily react to form cementitious calcium aluminates and sulfoaluminate hydrates (ettringite). The quick setting behavior of some ASTM Class C fly ashes, due to the rapid formation of C_4AH13, C_4AH18, and ettringite has been observed by researchers.[6] In addition, the formation of ettringite around high-calcium fly-ash particles has also been observed.[8]

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LONE STAR INDUSTRIES, INC.

2524 S. Sprigg Street, Cape Girardeau, MO 63701
314 335-5591

MILL TEST REPORT

DATE SHIPPED	06/13/88	FOR:	MR. MIKE GILLIAN OAK RIDGE NAT. LAB P.O. BOX 2003 OAK RIDGE, TN 37831-7273
CEMENT TYPE	II/LOW HEAT		

This Portland cement complies with Current ASTM C 150, AASHTO M-85 and Federal SS-C-1960/3b Specifications.

The data presented below is the average of the silo or bin from which this cement was shipped.

CHEMICAL DATA

	Test Value, %
SiO_2	24.10
Al_2O_3 —	2.60
Fe_2O_3 —	3.24
CaO —	61.95
MgO —	3.54
SO_3 —	2.76
Loss on Ignition —	0.90
Insoluble Residue —	0.12
C_3S —	39.07
C_3A —	1.41
Na_2O Equiv. —	0.50

PHYSICAL DATA

	Test Value
Fineness, Blaine — cm.^{2}/gm.	3230
Wagner	
Soundness, Autoclave — %	0.08
Time of Set, Vicat — Minutes — Initial	160
Final	275
Air Content — %	9.2
Compressive Strength:	
1 day — psi	910
3 day — psi	1980
7 day — psi	2870
28 DAY - PSI	5000

Remarks:

TYPICAL ANALYSIS

By:

D.DOBSON - QUALITY SUPERVISOR

APPENDIX C: PREPARATION OF REFERENCE SLUDGE COMPOSITE

This appendix contains the makeup of the reference sludge composites referred to in the text. As such, it provides the documentation required to relate the composite to the individual samples received from the Weldon Spring site.

Table C.1. Makeup of reference sludge composite for Weldon Spring raffinate pit 1

Sample ID[1]	Visual Description	Weight (g)
SD-3105-0002-B-C	Red Mud	10,206
SD-3103-0406-B-C	Red Mud	8,618
SD-3104-0810-B-C	Red Mud	7,938
SD-3103-0810-B-C	Red Mud	4,627
SD-3104-0406-B-C	Red Mud	6,940
SD-3103-0608-B-C	Red Mud	8,981
SD-3103-0406-B-C	Red Mud	7,348
SD-3103-0608-B-C	Red Mud	5,398
SD-3104-0204-B-C	Red Mud	8,074
SD-3104-0002-B-C	Red Mud	7,031
SD-3104-0608-B-C	Red Mud	5,443
SD-3104-0204-B-C	Red Mud	5,126
SD-3104-0406-B-C	Red Mud	3,856
SD-3105-0204-B-C	Red Mud	8,755
SD-3105-0406-B-C	Red Mud	3,992
SD-3104-0608-B-C	Red Mud	6,759
SD-3103-0810-B-C	Red Mud	6,124
SD-3103-0204-B-C	Red Mud	6,904
SD-3103-0204-B-C	Red Mud	5,443
SD-3104-0002-B-C	Red Mud	5,670
SD-3104-0810-B-C	Red Mud	7,031

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[1] ID of sample received from Weldon Spring site

Table C.2. Makeup of reference sludge composite for Weldon Spring raffinate pit 2

Sample ID[1]	Visual Description	Weight (g)
SD-3201-0002-B-C	Red Mud	5,851
SD-3201-0002-B-C	Red Mud	6,396
SD-3205-0608-B-C	Red Mud	4,082
SD-3202-0608-B-C	Red Mud	5,443
SD-3205-1012-B-C	Red Mud	4,808
SD-3205-0406-B-C	Red Mud	4,355
SD-3202-0810-B-C	Red Mud	5,579
SD-3205-0810-B-C	Red Mud	5,851
SD-3202-0204-B-C	Red Mud	5,670
SD-3202-1012-B-C	Red Mud	3,674
SD-3202-0406-B-C	Red Mud	5,443
SD-3201-0204-B-C	Red Mud	6,396
SD-3205-0002-B-C	Red Mud	5,851
SD-3201-0204-B-C	Red Mud	7,938
SD-3201-0406-B-C	Red Mud	5,443
SD-3202-0002-B-C	Red Mud	4,763
SD-3201-0406-B-C	Red Mud	3,629
SD-3205-0204-B-C	Red Mud	5,670

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[1] ID of sample received from Weldon Spring site

Table C.3 Makeup of reference sludge composite for Weldon Spring raffinate pit 3

Sample ID[1]	Visual Description	Weight (g)
SD-3313-0406-B-C	Red Mud	6,804
SD-3307-0608-B-C	Red Mud	3,992
SD-3307-0204-B-C	Red Mud	5,715
SD-3313-0002-B-C	Red Mud	5,715
SD-3308-0406-B-C	Red Mud	6,350
SD-3312-0608-B-C	Red Mud	5,988
SD-3309-0810-B-C	Red Mud	5,262
SD-3308-0204-B-C	Red Mud	5,761
SD-3312-0810-B-C	Red Mud	5,670
SD-3309-0002-B-C	Red Mud	1,225
SD-3312-0002-B-C	Red Mud	5,716
SD-3309-0204-B-C	Red Mud	9,208
SD-3312-0406-B-C	Red Mud	7,122
SD-3307-0002-B-C	Red Mud	7,212
SD-3312-0204-B-C	Red Mud	3,085
SD-3313-0204-B-C	Red Mud	7,122
SD-3309-0406-B-C	Red Mud	6,260
SD-3307-0406-B-C	Red Mud	4,899
SD-3308-0608-B-C	Red Mud	7,575
SD-3308-0810-B-C	Red Mud	8,618
SD-3308-0002-B-C	Red Mud	9,299
SD-3309-0608-B-C	Red Mud	7,031

---

[1] ID of sample received from Weldon Spring site

Table C.4. Makeup of reference sludge composite for Weldon Spring raffinate pit 4

Sample ID[1]	Visual Description	Weight (g)
SD-3406-0204	Red Mud	2,975
SD-3418-0002-B-C	Red Mud	3,892
SD-3406-0002-B-C	Red Mud	2,693
SD-3406-0204-B-C	Red Mud	2,852
SD-3406-0002-B-C	Red Mud	5,389
SD-3410-0002-B-C	Brown Mud	5,353
SD-3419-0002-B-U	Brown Sandy Material	4,763

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[1] ID of sample received from Weldon Spring site