PROGRESS REPORT

Feasibility Evaluation of the Implementation of Concrete Polymers for Bridge Deck

State Study 76-09-2

School of
CHEMICAL ENGINEERING
and
MATERIALS SCIENCE

The University of Oklahoma

202 West Boyd
Room 23
Norman, Oklahoma 73069

PROGRESS REPORT

Feasibility Evaluation of the Implementation of Concrete Polymers for Bridge Deck

State Study 76-09-2

To

Oklahoma Department of Transporation

by

Carl E. Locke
University of Oklahoma

January 5, 1977

Introduction

This report summarizes the work done on the project to date. The work has been divided into three phases: polymer concrete - (use of polymer and aggregate with no portland cement), polymer impregnated concrete, and a literature survey. All work during this period has involved laboratory phases only.

Polymer Concrete

Investigations have been conducted on the curing times of methyl methacrylate and polyester-styrene as a function of initiator, promoter, cross link agent, and flexiblizer concentrations and types. Since the polymerization of both methyl methacrylate and polyester-styrene is exothermic, measurement of the batch temperature as a function of time has been used as the method of detection of curing. All room temperature studies were done with the monomer mix in a "pie pan" sitting on an aluminum plate in which a thermocouple was imbedded. Results from the curing time experiments with each of the polymer types will be discussed separately.

Methyl Methacrylate

Table 1 lists the initiators, promoters, crosslinkers, and flexiblizers used with the methyl methacrylate.

Table 1

Materials Used in Methyl Methacrylate Curing Studies

Initiators

- Benzoyl Peroxide, BP
- Lauroyl Peroxide, LP

Promoters/Accelerators

- Dimethyl Para-Toluidene, DMPT
- Dimethyl Aniline, DMA

Table 1 continued

Cross Linking Agents

Trimethylol Propane Trimethacrylate, TMPTMA
1,3-Butylene Dimethacrylate, BDMA

Flexiblizers

Butyl Acrylate, BA

Monomer

Methyl Methacrylate, MMA
(10 ppm polymerization inhibitor)

The initiators are compounds that decompose to produce free radicals that attack the monomer which starts the polymerization. The promoters/accelerators cause the initiators to decompose at room temperature and below. The initiators will spontaneously decompose when the temperature is raised to 50-60°C. The cross linking agents tie all the polymer chains together which lowers or retards the creep and increases strength of the resulting polymer. In addition, the curing time is lowered by use of these compounds. In some formulations, these materials are necessary for the mixture to polymerize to a hard solid. The flexiblizers increase the impact strength of the resulting polymer.

Table 2 summarizes all the room temperature experiments run with methyl methacrylate. The formulation of each experiment, curing time, and maximum temperature reached by the polymer are listed. The times listed are the times from mixing of the reaction mixture until the maximum temperature (curing temperature) is reached. In addition to this information, a qualitative description of the reaction product is given. Batches were run in the "pie pan" as described above, some with the formulation only and others with sand as a filler.

There are a few tentative conclusions to be reached from these

CURING TIME STUDIES AT ROOM TEMPERATURE

Methyl Methacrylate

Initiator	Accelerator	Cross-Linker	Curing Time	Curing Temp.	Comments
1% BP	1% DMPT		36 min	47.4°C	
1% BP	0.25% DMA 0.27% DMPT		1 hr 38 min	41.3°C	thin syrup
1% BP	0.25% DMA 0.27% DMPT	5% TMPTMA	41 min	94°C	hard with shrinkage
1% BP	0.25% DMA 0.27% DMPT	5% TMPTMA	44 min	32.25°C	w/sand, w/evap., hard
2% BP	1% DMA		2 hrs 7 min	53.6°C	hard bottom, soft to liquid on top
2% BP	1% DMA		1 hr 52 min	52.5°C	hard bottom, liquid top
2% BP	1% DMA	5% BDMA	1 hr 12 min	94°C	hard, some shrinkage and bubbly
2% BP	1% DMA	5% BDMA	58 min	64.4°C	w/sand, hard
2% BP	1% DMA	5% TMPTMA	54 min	85.6°C	hard, shrinkage w/cracks and ridges
2% BP	1% DMA	5% TMPTMA	45 min	69.6°C	w/sand, w/evap., hard
2% BP	1% DMPT		22 min	51.75°C	
2% BP	1% DMPT		27 min	62°C	like thick honey
2% BP	1%DMPT	5% BDMA	22 min	97.25°C	hard-cured
2% BP	1% DMPT	5% BDMA	30 min	70.5°C	w/sand
2% BP	1% DMPT	5% TMPTMA	19 min	93.8°C	hard
2% BP	1% DMPT	5% TMPTMA	30 min	71.2°C	w/sand
2% BP	1.14% DMPT		25 min	59.6°C	thick syrup-like
2% BP	2% DMA		1 hr 12 min	59.5°C	soft jelly-like
2% BP	2% DMPT		14 min	50.8°C	
2% BP	2% DMPT		20 min	38.4°C	
2% BP	1% DMPT	5% TMPTMA	20 min	66.4°C	flexible to breakable, small amount of shrink.
2% BP	1% DMPT	5% TMPTMA	21 min	75.6°C	flexible to breakable, small amount of shrink.
2% BP	0.5% DMA 0.55% DMPT		3 min	57.25°C	thick honey-like
2% BP	0.5% DMA 0.55% DMPT	5% BDMA	24 min	94.2°C	hard, small % shrinkage
2% BP	0.5% DMA 0.55% DMPT	5% BDMA	35 min	77.4°C	w/sand, hard
3% BP	1% DMPT		22 min	69.2°C	part hard, part soft
3% BP	1% DMPT		28 min	66.4°C	will not flow, soft to touch
3% BP	1% DPMT		38 min	65.75°C	w/sand, hard
3% BP	1% DMPT	5% TMPTMA	15 min	95°C	
3% BP	1% DMPT	5% TMPTMA	25 min	78.5°C	w/sand, hard
3% BP	1.5% DMA		48 min	94.25°C	hard, w/bubbles
3% BP	1.5% DMA		54 min	62.75°C	w/sand, hard
3% BP	1.7% DMPT		11 min	60.75°C	thin liquid
3% BP	2% DMPT		11 min	59.2°C	thin syrup
3% BP	0.86% DMPT 0.75% DMA		16 min	65.5°C	thick honey-like
3% BP	0.86% DMPT 0.75% DMA	5% TMPTMA	16 min	86°C	hard
3% BP	0.86% DMPT 0.75% DMA	5% TMPTMA	31 min	69.6°C	w/sand, hard
3% BP	1% DMPT	5% TMPTMA	16 min	65.75°C	lots of shrink., curlin at adges, very flexible
3% BP	1% DMPT		14 min	57°C	very thick, gooey, not cured
2% LP	0.62% DMA				
2% LP	0.62% DMA	5% TMPTMA			
2% LP	0.7% DMPT				
2% LP	0.7% DMPT	5% TMPTMA			
2% LP	0.7% DMPT	5% BDMA			
2% LP	1.5% DMA				
2% LP	1.5% DMA				
2.7% LP	2% DMPT		1 hr 43 min	83.2°C	flexible, soft, air bubble holes, no shrinkage
3% LP	.93% DMA				
3% LP	.93% DMA	5% TMPTMA			
3% LP	1% DMA				
3% LP	1.05% DMPT				
3% LP	1.05% DMPT	5% TMPTMA	54 min	67°C	hard, lot of shrinkage
3% LP	1.05% DMPT	5% BDMA	2 hr 12 min	78.5°C	hard, shrinkage
3% LP	1.05% DMPT	5% BDMA	2 hr 33 min	61.5°C	w/sand
3% LP	1.5% DMA	5% TMPTMA			
3% LP	2% DMA				
4% LP	1.6% DMPT		1 hr 4 min	74.5°C	bubbly hard mass
4% LP	3% DMPT		1 hr 48 min	66°C	bubbly hard mass
4% LP	1.6% DMPT	5% TMPTMA	1 hr 10 min	66.8°C	bubbly, shrinkage

Polyester-Styrene

1% MEKP	0.25% CoN		53 min	58.25°C	hard, no shrinkage
1.5% MEKP	0.75% CoN		43 min	74.25°C	hard, no shrinkage
1.5% MEKP	0.75% CoN		1 hr 25 min	38.25°C	w/sand
2% MEKP	1% CoN		1 hr 23 min	43.5°C	w/sand, hard, no shrink

data:

1. It is possible to polymerize MMA at room temperature by using a promoter/accelerator.
2. Benzoyl peroxide will initiate polymerization at 1-3% level.
3. Lauroyl peroxide is less reactive than the benzoyl peroxide. In addition, it was observed there was a definite lag time before the polymerization began with the lauroyl peroxide. The polymerization apparently began immediately with the benzoyl peroxide.
4. In most formulations, a solid product was not found when no cross-linker was present. In all formulations containing the cross-linking agents were solid. In addition the cure time was lowered in most cases when the cross linkers were included. There seems to be only small differences in BDMA and TMPTMA in relationship to cure times.
5. DMPT seems to be more reactive than DMA in producing a short cure time. The most effective concentrations are those when the accelerators and initiators are in the 1:1 stoichiometric ratio.
6. The mixtures of DMA and DMPT seem to behave like DMPT alone.
7. Sand tends to lower the cure temperature and increase cure time. This is an expected result since the sand will act as a heat sink.
8. Butylacrylate does not affect the curing time. The finished product is much more flexible with BA included.

Polyester-Styrene

The polyester-styrene was obtained as a premixed material from the supplier, W. R. Grace. The styrene is polymerized with methyl ethyl ketone peroxide (MEKP) and cobalt naphthanate (CoN) as an accelerator. The styrene cross links the polyester chains together, thus producing a solid crosslinked material. The results indicate there is little difference in cure time (with sand) for MEKP concentrations of 1.5-3%. The ratio of CoN to MEKP was maintained at 1:2 for all batches.

Hyper- and Sub-Ambient Studies

A constant temperature bath has been assembled and calibrated for use over the 40 to 110°F temperature range. A few preliminary experiments have been conducted to develop an alterantive containment and measurement system to those used for the room temperature studies.

The monomer mix is allowed to equilibrate at the reaction temperature in two separate batches. The initiator is in half the monomer and the accelerator in the remainder. These two portions are mixed and poured into a test tube containing sand. A thermocouple is immersed in the sand-monomer mixture. The curing time and temperature are monitered just as the "pie pan" experiments were.

A differential thermocouple has been found to be necessary due to artifacts seen when the cooler or heater is activated to maintain the temperature. One bead is in the monomer-sand mix and the other bead is in the bath. The differential thermocouple is made by forming a bead on each end of a negative thermocouple wire with

two separate positive wires. The signal from the thermocouple is obtained from these two positive leads. The signal is a measure of the difference between the two beads and is independent of the ambient temperatures.

Data have been taken at 40°F for MMA using 3% BP, 2% DMPT, and 5% TMPTMA. The mixture had a curing time of 67 minutes.

Therefore, it is possible to cure these polymers at low ambient temperatures. Additional work will be done to further characterize the curing properties.

Polymer Impregnated Concrete

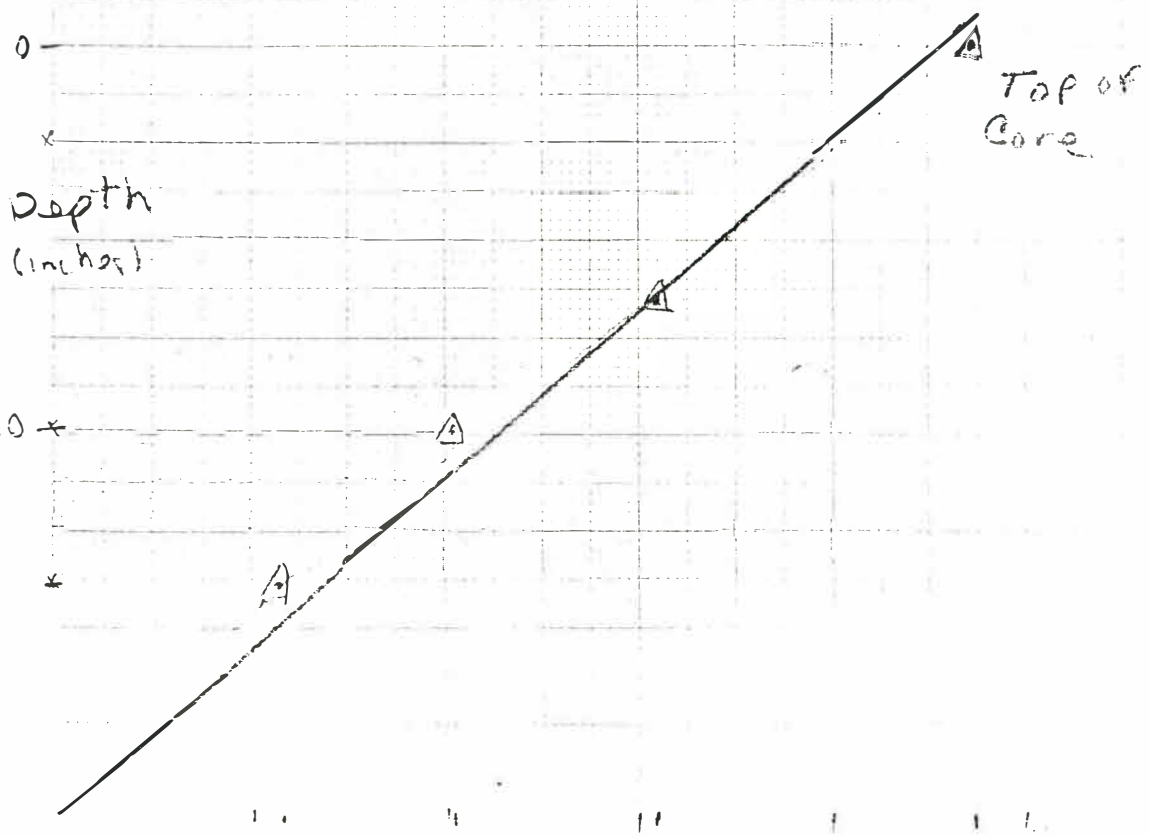
Penetration of the monomer into cured concrete has been studied along with the curing of the monomer in the concrete.

Penetration Studies

Concrete core samples from the Oklahoma Department of Transportation were sliced into 7" diameter by 3" high chunks. MMA monomer was pooled atop the slices and allowed to penetrate into the concrete. The concrete was broken and the penetration depth of the monomer was measured with a ruler. The literature states that the penetration depth of the monomer is highly dependent upon the moisture content of the concrete. Therefore, several drying schemes were used prior to the penetration studies.

Figures 1 and 2 are plots of the penetration depth in inches as a function of the square root of time. According to capillary rise theory, this plot should yield a straight line as shown on these two plots. These data were taken with two different core samples. Both of these had been dried for 24 hours at 110°C after they were

Figure 1

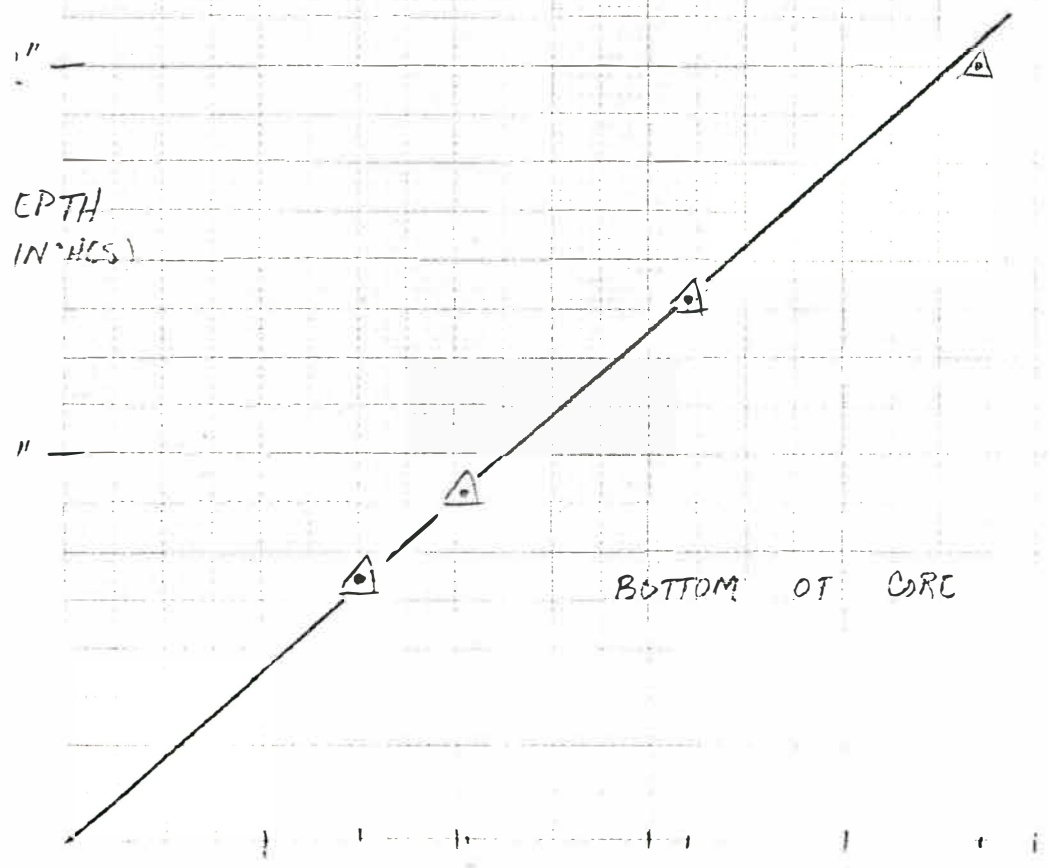


OKLAHOMA CORE B-1
PENETRATION EXPERIMENT
PENETRATION DEPTH (INCHES)
VERSUS $\sqrt{\text{TIME}}$ $(\text{HRS})^{1/2}$

DEPTH	TIME	$\sqrt{\text{TIME}}$
.6	1.33	1.1547
1.0	9.166	2.04
1.4	7.5833	3.096
2.1	22.4166	4.7346

VACUUM DRIED
FOR 24 HRS AT 110°C

Figure 2



OKLAHOMA HIGHWAY CORE NO. B-19
PENETRATION TEST
DEPTH OF PENETRATION (INCHES)
VS. √TIME FOR SOAKING (HRS ½)

DEPTH	TIME	TIME ½
.70"	2.25	1.5
.90"	4.25	2.062
1.4"	10.25	3.2
2.0"	22.25	4.72

VACUUM DRIED FOR 24 HRS
AT 110°C

sliced. Each point was taken with a different level within the core. The surface of all but the top of the core was different than might be expected on the surface of a deck.

Figures 3 and 4 are plots of the same variables shown in Figures 1 and 2. The cores used for these data were dried in an oven with no vacuum for 24 hours at 110°C. The penetration depth is limited to 1 1/4 inches in this case.

Figure 5 illustrates the penetration depth as a function of $(\text{time})^{1/2}$ for a core dried in a vacuum oven for varying time periods. Notice there seems to be a large dependence on drying temperature and also possibly the surface condition of the concrete. The deepest penetration was found with the top of the core dried at 112°C.

Curing Studies

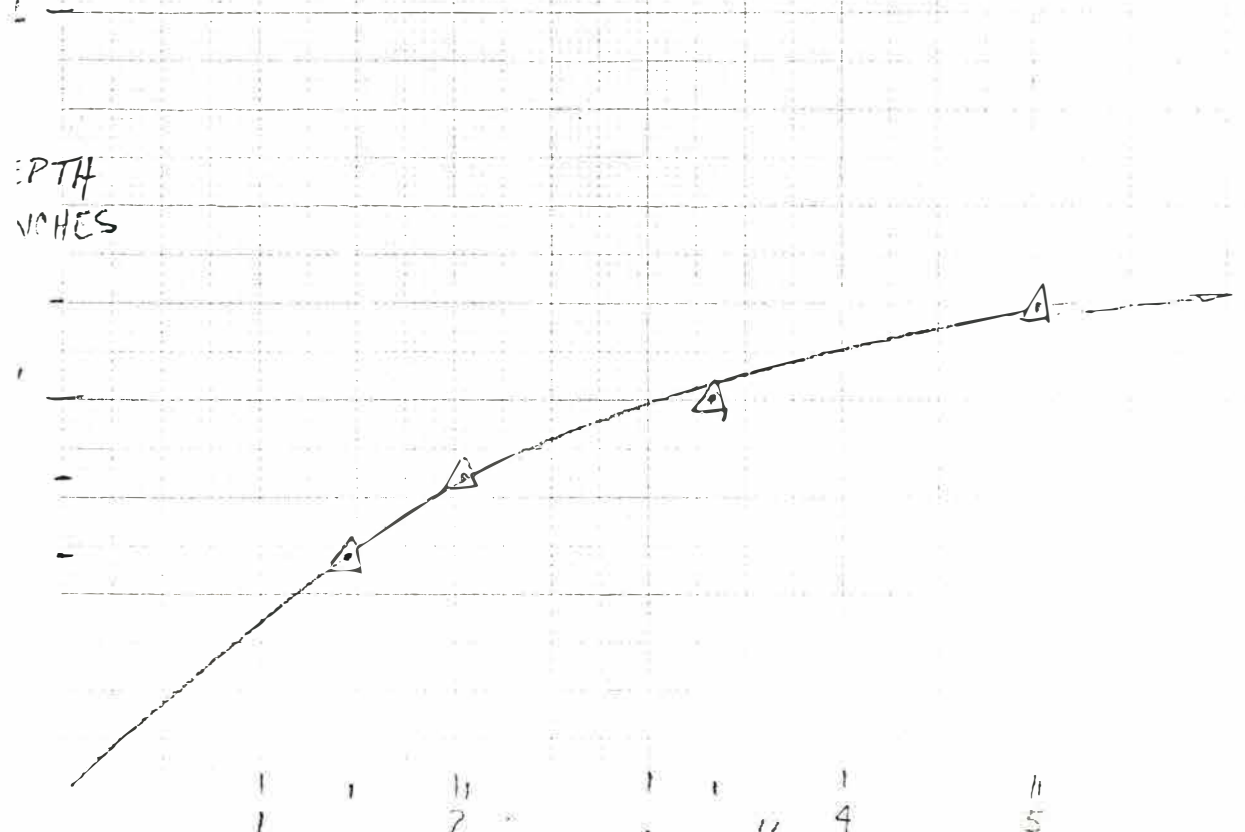
A few core slices have been impregnated followed by polymerization of the monomer mix by heating to 150-170°F. These experiments have been of exploratory nature. All have used a mix consisting of MMA with 1.5% BP and 10% TMPTMA. It is necessary to use a sand cover over the concrete to prevent evaporation of the monomer mix before the polymerization occurs. Soak times of 12 to 16 hours have been used followed by 7 to 12 hours polymerization. All concrete was dried under vacuum for 24 hours. Penetration depths of about 1 1/8 inches were obtained.

This work will continue using slabs cast specifically for the experiments.

Literature Survey

The literature found by library and computer searches is being read and data concerning properties of the materials is being tabu-

Figure 3

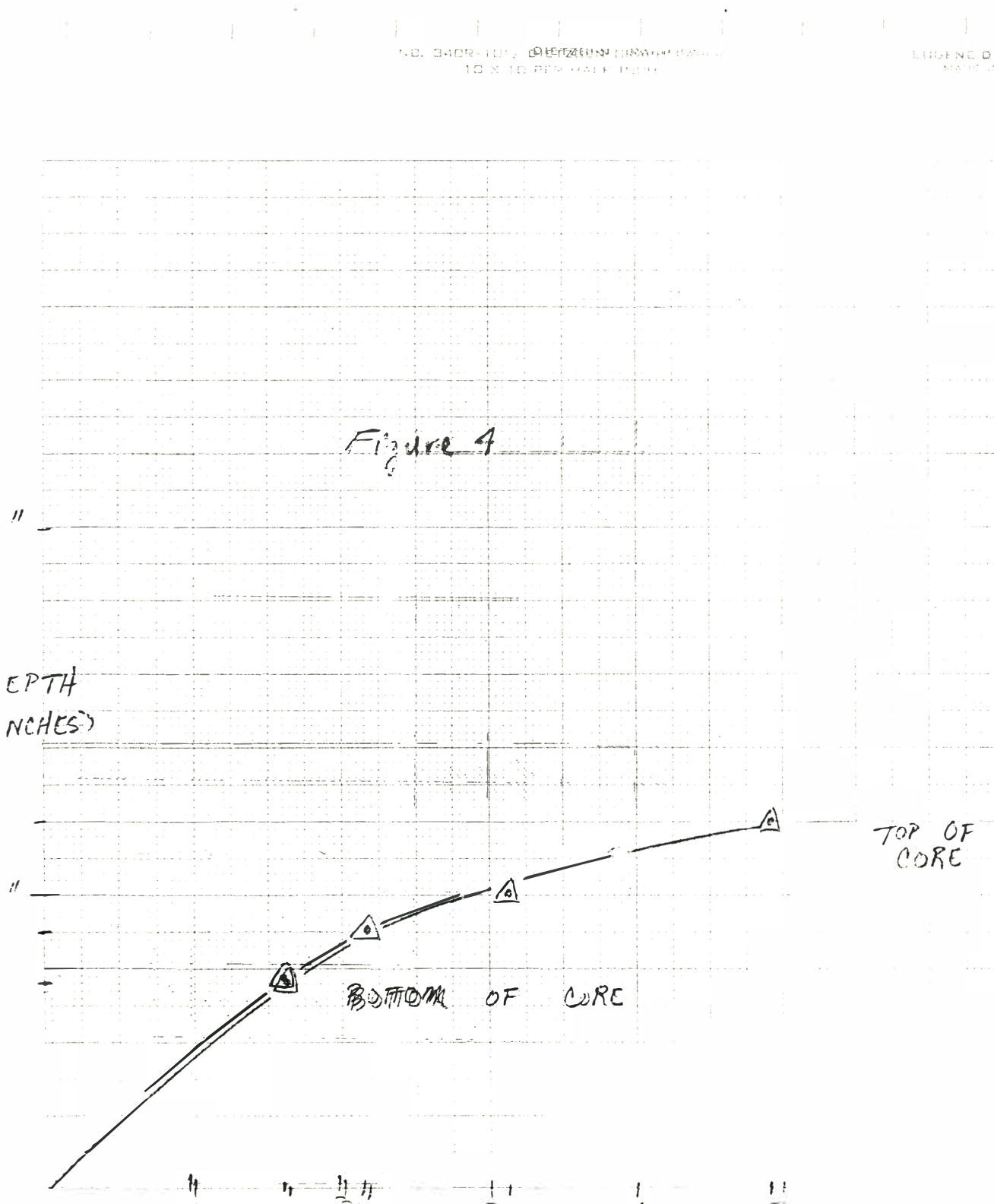


OKLAHOMA HIGHWAY 30RC
B-2B
PENETRATION EXPERIMENT
DEPTH OF PENETRATION - (INCHES) VS √TIME - (HRS) ½

DEPTH	TIME	√TIME
.6	2.166	1.4719
.8	4.25	2.06
1.0	11.166	3.34
1.25	25.166	5.02

NORMAL DRYING
FOR 24 HRS AT 110°C
No Vacuum

Figure 4



OKLAHOMA HIGHWAY CORE ~~B-22~~
PENETRATION EXPERIMENT
DEPTH OF PENETRATION (INCHES)
VS. ~~√TIME~~ FOR SOAKING (HRS)$^{1/2}$

DEPTH	TIME	(TIME)$^{1/2}$
.7	2.66	1.633
7/8	4.75	2.179
1.0	10.4166	3.227
1.25	24.166	~~4.916~~

NORMAL ~~DRYING~~ (NO VACUUM)
FOR ~~24~~ HRS AT 110°C

lated. An additional TRIS search was made during the past two months. Additional titles were found and copies will be requested.

Additional Materials

Investigation into using an additional matrix polymer for the polymer concrete has been made. The Russians have reported successful use of furans as a matrix polymer. The Quaker Oats Corporation, who is the primary producer of furans in the U.S., stated they could not cure furans at room temperature. Curing temperatures as high as 400-500°F (200-260°C) have been reported.

Plans for Future Work

Polymer Concrete

Two main goals have been set for the next quarter. The curing time over the 40-110°F temperature range will be determined for a range of formulations involving both MMA and polyester-styrene. These studies will be pointed towards development of standard mixes to be specified dependent upon temperature.

The second goal is to cast a number of test specimens for use in mechanical testing. Mixes using the various cross-linkers, initiators, flexblizers, and accelerators will be used to determine the best combination from a mechanical criteria.

Polymer Impregnated Concrete

Concrete test slabs for impregnation will be cast and cured. These will be impregnated with MMA, TMPTMA mixes, and polymerized. The resulting realed slabs will be subjected to freeze-thaw, water absorption and permeability testing.