

APPENDIX B

PRE-DESIGN INVESTIGATIONS

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APPENDIX B

LABORATORY AND FIELD TESTS: A limited number of laboratory tests using Quakake AMD and limestone were conducted in conjunction with this study. The tests were performed to provide empirical data on the reactivity of different limestones in acid mine drainage and other acidic solutions to provide a basis for the design of alternative prototype process units.

1. Beaker Tests: Known weights of crushed limestone were exposed to known volumes of AMD and the rate of the resulting reaction in terms of pH change versus time was recorded. (See Figures B5 - B12).
2. "Flow through" tests: The change in pH of a measured flow of AMD passing through containers filled with a weighed quantity of crushed limestone was measured.

From the results of these tests, the load factor required for a specified change in pH was computed for each unit. These empirical evaluations of process performance were compared with published predictive methods to confirm the order of magnitude of the proposed treatment process design criteria. In this investigation, the empirically observed load factor required to produce various pH changes was compared with predictions by Pearson and McDonnell. (1)

Beaker test results were translated in terms of load factor versus pH change by computing, for each point in time at which a pH reading was taken. The load factor is defined Eq. 4.18 on Page 18 of this report.

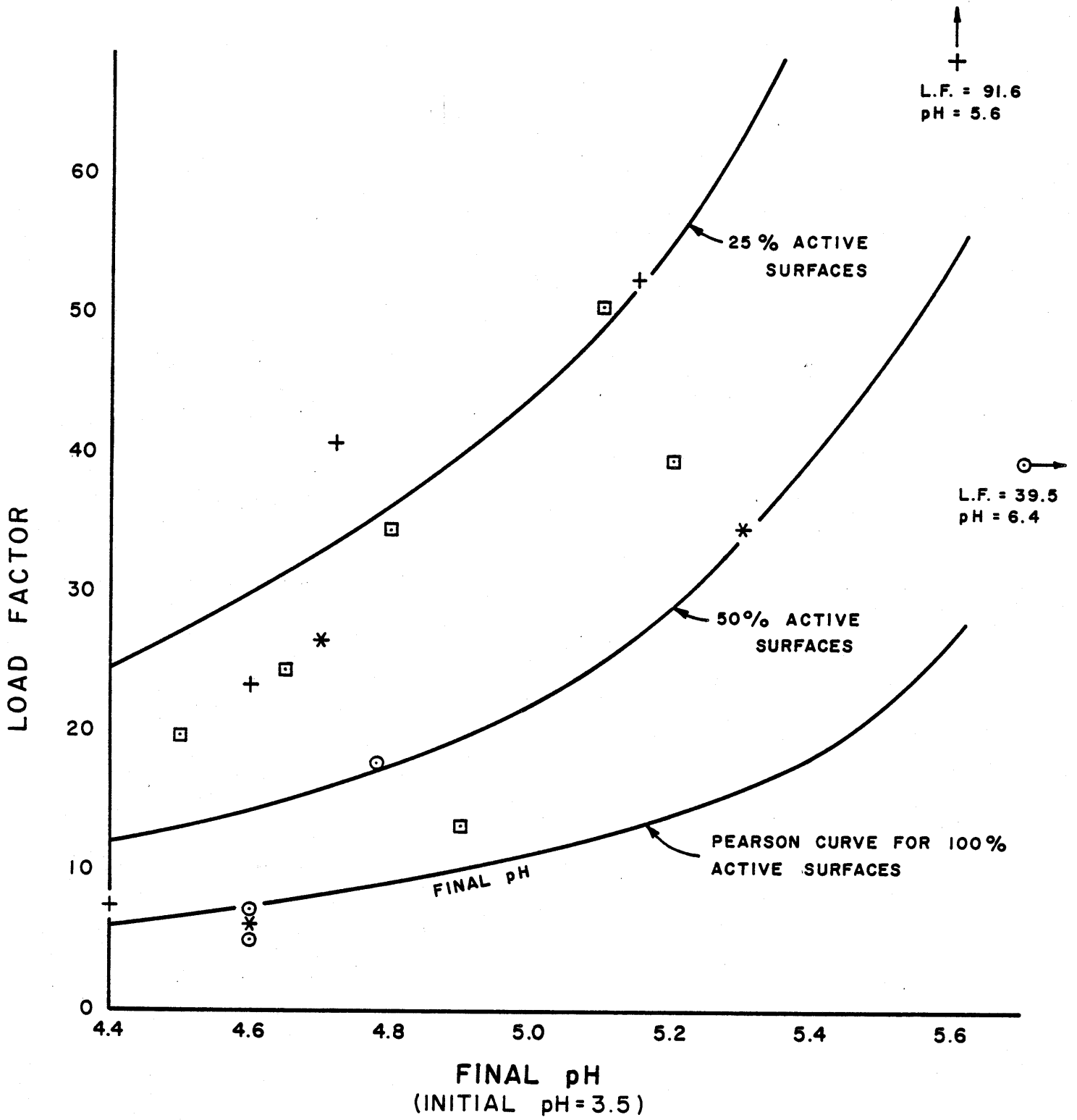
For comparative purposes, two types of limestone were used: a dolomitic limestone gravel from Hempt White Hill Quarry and marble chips from a chemical supply house. The chemical composition of each type is given in Table B1.

In general, the tests confirm:

1. The reaction rate increases with increasing surface area, that is, with decreasing particle size for a given weight of limestone.
2. The reaction rate increases with increasing amounts of CaCO_3 in the limestone.
3. The reaction rate decreases with use for both limestone types.

During the beaker tests, no coating of the limestone surfaces was observed, even though a decrease in surface activity was noted.

The plotted points in Figure B-1 show the relationship between final pH and load factor for both beaker tests and flow through tests, and for each of the two types of limestone. In each case, the initial pH was approximately 3.5. Also shown are lines representing the predicted relationship between load factor and final pH according to Pearson and McDonnell, assuming 100%, 50%, and 25% for the reactivity coefficient, which is defined as the reactivity of coated stone divided by the reactivity of clean stone.



LEGEND

- UNUSED MARBLE CHIPS
- USED MARBLE CHIPS
- * UNUSED HEMPT GRAVEL
- + USED HEMPT GRAVEL

Figure B1

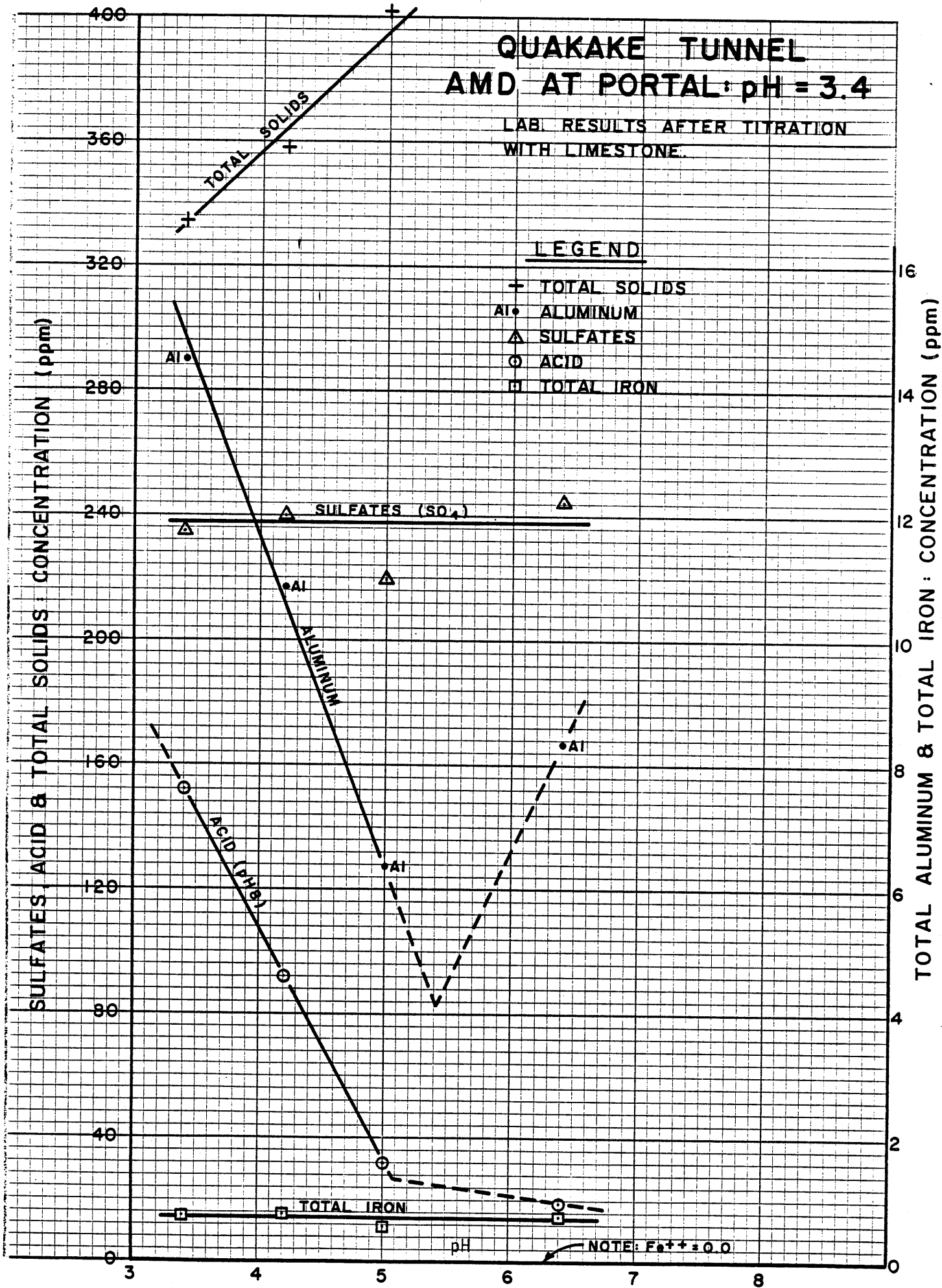
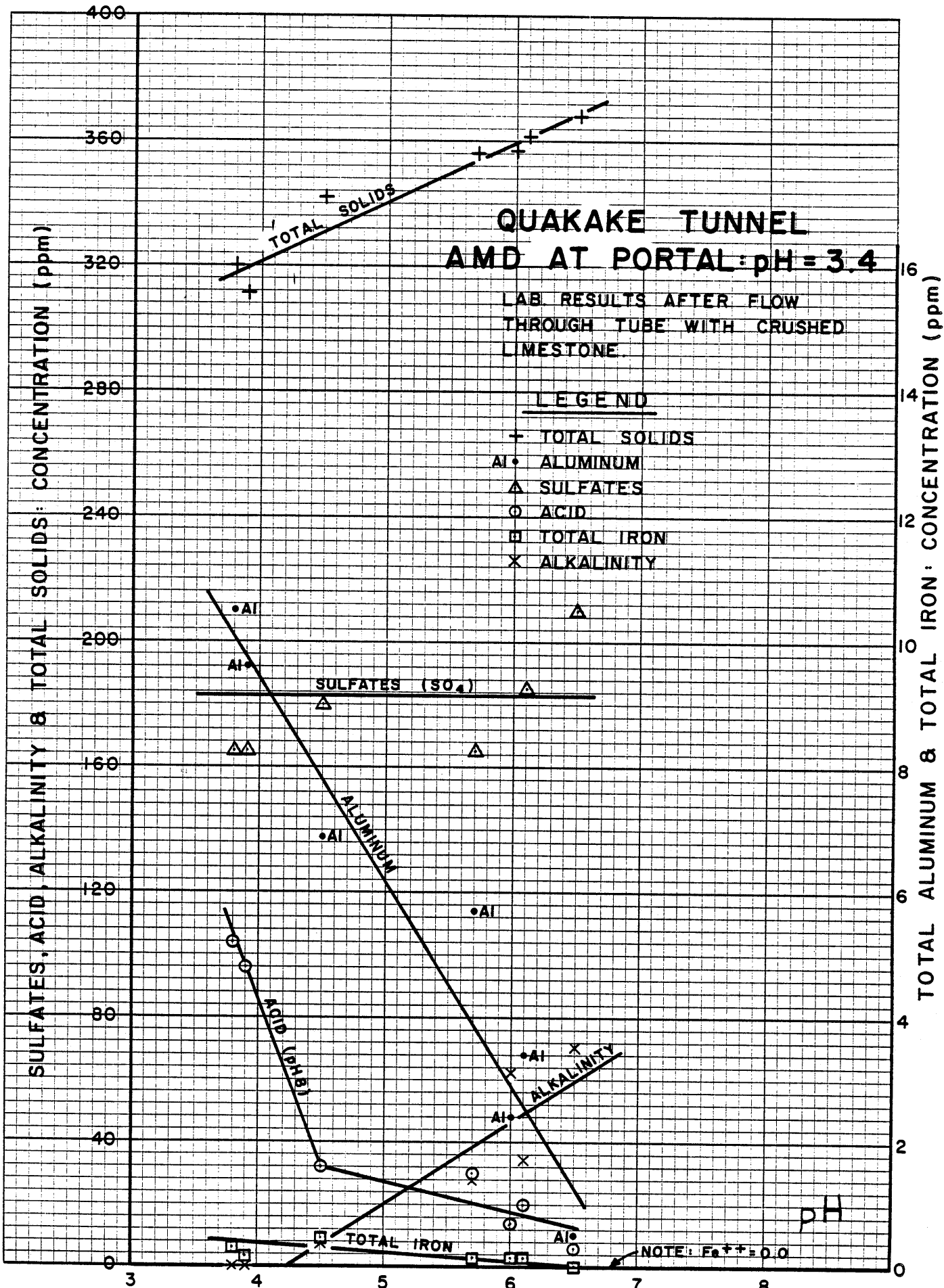


TABLE B1

CHEMICAL ANALYSIS OF LIMESTONE SAMPLES

	Hempt Limestone Percent	Marble Chips Percent
SiO ₂	6.9	2.3
Al ₂ O ₃	1.2	.83
Fe ₂ O ₃	.24	.11
FeO	.24	.16
MgO	6.8	.83
CaO	43.2	53.3
Na ₂ O	.03	.03
K ₂ O	.61	.22
H ₂ O ⁺	.15	.12
H ₂ O ⁻ (110°C)	.10	.04
TiO ₂	.00	.00
P ₂ O ₅	.02	.02
MnO	.00	.00
CO ₂	40.4	42.5
SO ₃	.25	.00
<hr/> Total	<hr/> 100.	<hr/> 100.

Analyzed by U.S.G.S. Laboratory, Arlington, VA.



During the laboratory tests, samples were withdrawn at various stages of neutralization by limestone and analyzed for acidity, alkalinity and metals concentrations. The results are shown in Figures B2 and B3.

Following the October 20th, 1975 review by the Department of the Interim Report, additional tests were conducted. Crushed limestone samples from Bethlehem Mines Corporation quarry of Anville, Pennsylvania were immersed in AMD at the Quakake Tunnel. Beaker tests were run on the exposed limestone and compared with the reaction between AMD and fresh limestone. Test results printed in Figure B3 indicate high reactivity of limestone after being subjected to reaction with AMD for a period of three months (85 days).

These experimental data generally confirm the order of magnitude of predictions of the load factor that is required to produce a final pH in the range of 4.4 to 5.6. They also generally lend some support to a suggested reactivity coefficient of the order of 0.2 or higher for coated stone.

COATINGS ON LIMESTONE IN QUAKAKE TUNNEL OUTFALL: To further investigate the occurrence of surface coating of limestone in prototype installations, containers of Hempt limestone were submerged at the Quakake Tunnel Outfall for a period of 3 months. During this period, a rust colored coating developed on the stone. The composition of the limestone before and after submergence (in the latter case which includes the coating material) is shown in Table B2. In addition, an attempt was made to identify the mineral constituents of the coating by carefully scraping the limestone and subjecting the scrapings to analysis by atomic absorption spectrophotometer. The results are presented in Table B3.

One of the submerged containers at the site was used as a "Flow Through" test reactor to determine the effect of coating on the reactivity rate of the limestone surface. A sketch of the apparatus is shown in Figure B4 with the pertinent laboratory and field tests. As evidenced by this data, the reaction rate decreased significantly with time.

Only minor discoloration of the AMD was observed during the routine samplings. A substantial amount of silty material was found within the interstices in the limestone. The results of a grain size analysis of this silty material are:

Sieve Size #40	100% passing
Sieve Size #200	72% passing

Limestone samples were also analyzed by the Pennsylvania State University Mineral Science Laboratory by the following methods:

<u>Facility</u>	<u>Method</u>	<u>Capabilities</u>
Scanning Electron Microscope with Energy Dispersive	X-Ray Analysis,	Surface Structure and Identification of Elements
	X-Ray Diffraction	Chemical Compounds
Electron Microprobe	Quantitative Analysis	

TABLE B2

CHEMICAL ANALYSIS OF UNCOATED AND COATED LIMESTONE

	<u>Uncoated Limestone Percent</u>	<u>Coated Limestone Percent</u>
SiO ₂	6.9	15.4
Al ₂ O ₃	1.2	2.0
Fe ₂ O ₃	.24	.20
FeO	.24	.40
MgO	6.8	12.1
CaO	43.2	31.5
Na ₂ O	.03	.05
K ₂ O	.61	.65
H ₂ O ⁺	.15	.45
H ₂ O ⁻ (110°C)	.10	.37
TiO ₂	.00	.00
P ₂ O ₅	.02	.02
MnO	.00	.00
CO ₂	40.4	36.8
SO ₃	.25	.47
<u>Total</u>	<u>100.</u>	<u>100.</u>

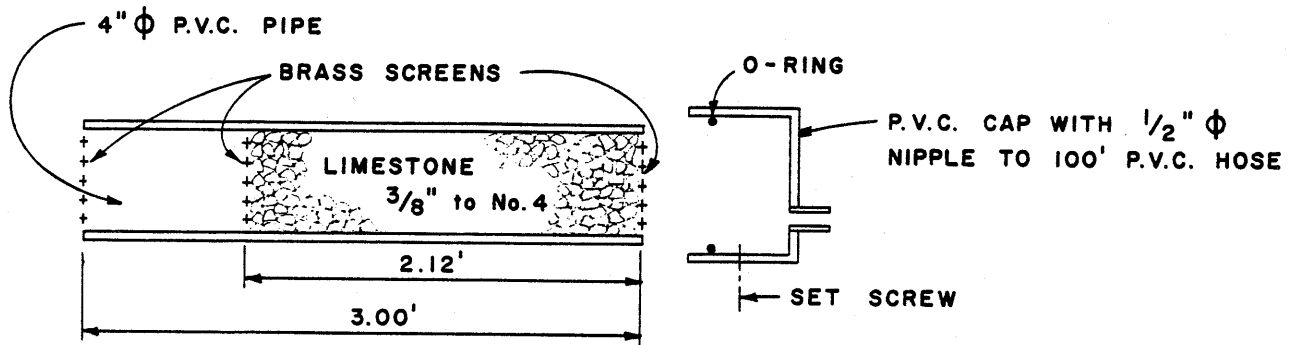
Analyzed by U.S.G.S. Laboratory, Arlington, VA.

TABLE B3

ANALYSIS OF LIMESTONE COATINGS

Calcium	66.37%
Magnesium	22.05%
Iron	1.21%
Aluminum	0.20%
Silicon	0.69%
Manganese	0.0006%
Potassium	0.01%
Sodium	0.00083%

Analyzed by B-H Laboratories, York, PA, by Atomic absorption.



DRY WT. OF LIMESTONE = 15.9 LBS.
 VOL. OF LIMESTONE = 0.094 C.F.
 VOL. OF VOIDS = 0.091 C.F.

FIELD TEST APPARATUS

FIELD MEASUREMENTS

DATE	LOC.	TIME	TEMP.	pH	FLOW	Δ pH	TR	Δ pH/TR
					gpm		min.	
12/11/73	Q1	13:10	9C	3.69	----	----	----	----
	TEST	13:40	9C	4.65	0.55	0.96	1.15	0.83
	TEST	14:38	9C	4.65	0.55	0.96	1.15	0.83
1/07/74	Q1	11:00	8C	3.48	----	----	----	----
	TEST	11:20	8C	3.65	0.75	0.17	0.84	0.20
2/04/74	Q1	11:00	6C	3.58	----	----	----	----
	TEST	11:15	6C	3.68	0.75	0.10	0.84	0.12
3/20/74	Q1	11:00	8C	3.55	----	----	----	----
	TEST	11:15	8C	3.62	0.55	0.07	1.15	0.06

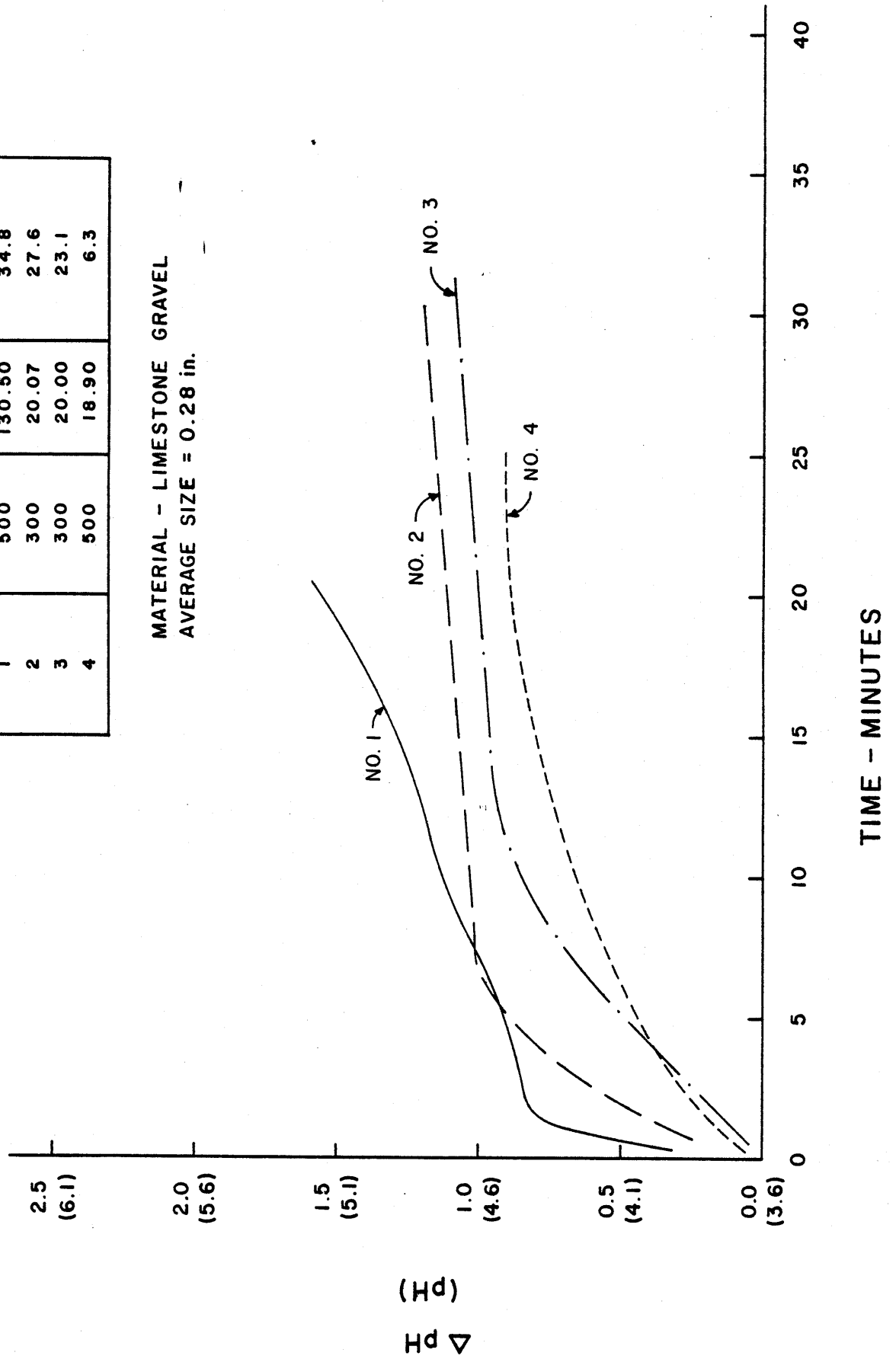
TR = RETENTION TIME

LAB. TESTS

DATE	LOC.	pH	pH ₄	pH ₈	SO ₄	Al	Fe	Mg	Mn	Ca	Si	TDS
			mg/l									
12/11/73	Q1	3.2	14	130	225	14.4	1.9	22.7	1.8	2.5	2.5	335
	TEST	3.9	0	108	210	11.0	1.4	29.4	1.7	7.4	1.3	398
	TEST	3.8	0	110	220	12.1	1.4	29.4	1.7	5.5	1.5	353
1/07/74	Q1	3.4	8	102	205	9.4	1.7	19.4	3.4	15.5	6.8	333
	TEST	3.8	0	94	215	11.1	4.0	19.2	3.4	14.3	6.4	413
2/04/74	Q1	3.0	16	102	100	5.7	1.8	21.1	3.8	1.1	4.5	313
	TEST	3.2	2	102	175	11.4	30.6	21.7	3.4	2.5	11.6	325
3/20/74	Q1	3.8	0	138	150	12.8	17.8	16.4	3.1	3.8	16.7	323
	TEST	3.8	0	98	150	16.0	33.1	15.7	6.3	6.3	11.1	318

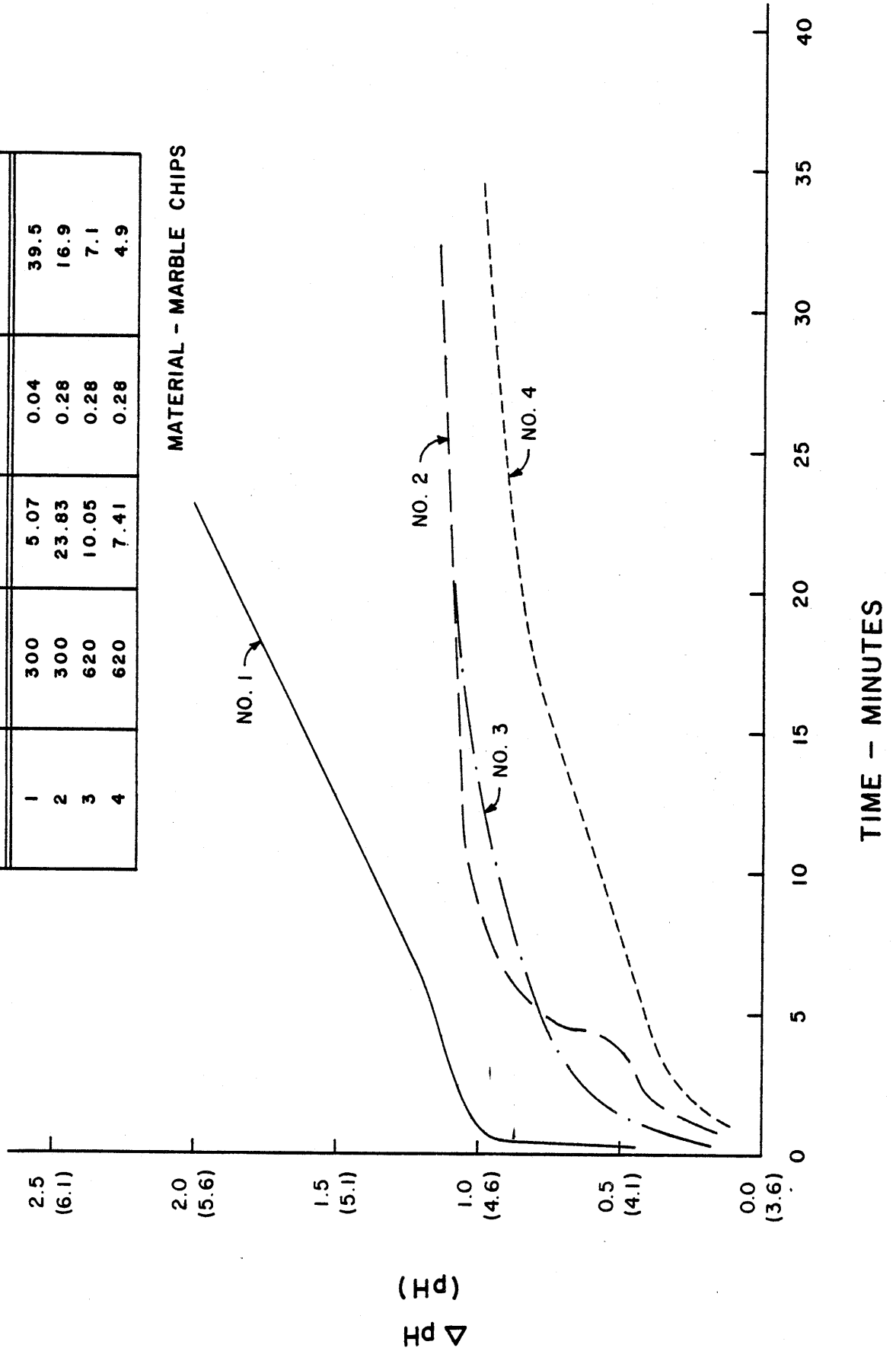
TEST NO.	VOL. AMD (ml.)	WEIGHT STONE (gm.)	LOAD FACTOR AT FINAL PH
1	500	130.50	34.8
2	300	20.07	27.6
3	300	20.00	23.1
4	500	18.90	6.3

MATERIAL - LIMESTONE GRAVEL
AVERAGE SIZE = 0.28 in.

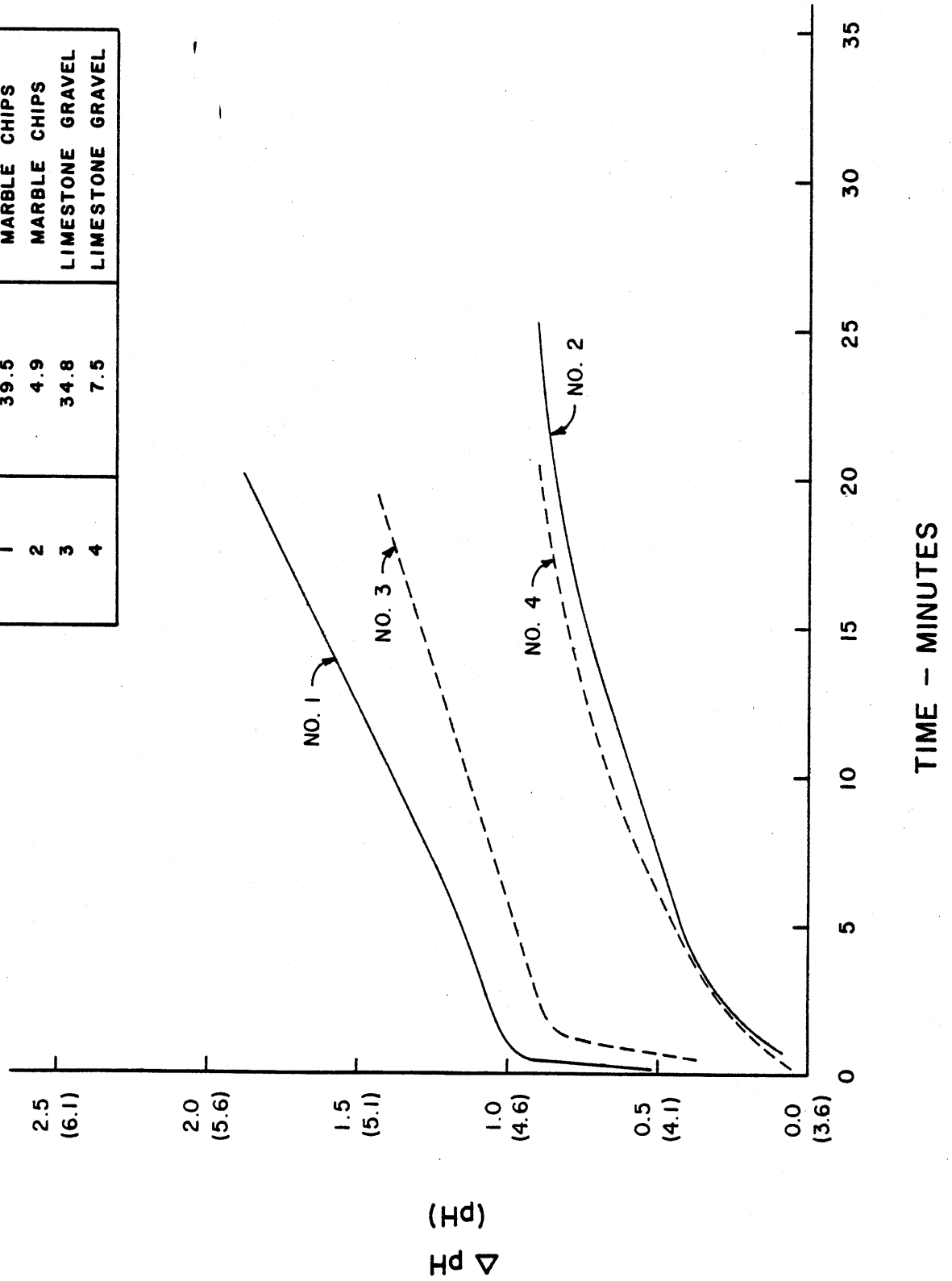


TEST NO.	VOL. AMD (ml.)	WEIGHT STONE (gm.)	MEAN PARTICLE SIZE (in.)	LOAD FACTOR AT FINAL pH
1	300	5.07	0.04	39.5
2	300	23.83	0.28	16.9
3	620	10.05	0.28	7.1
4	620	7.41	0.28	4.9

MATERIAL - MARBLE CHIPS

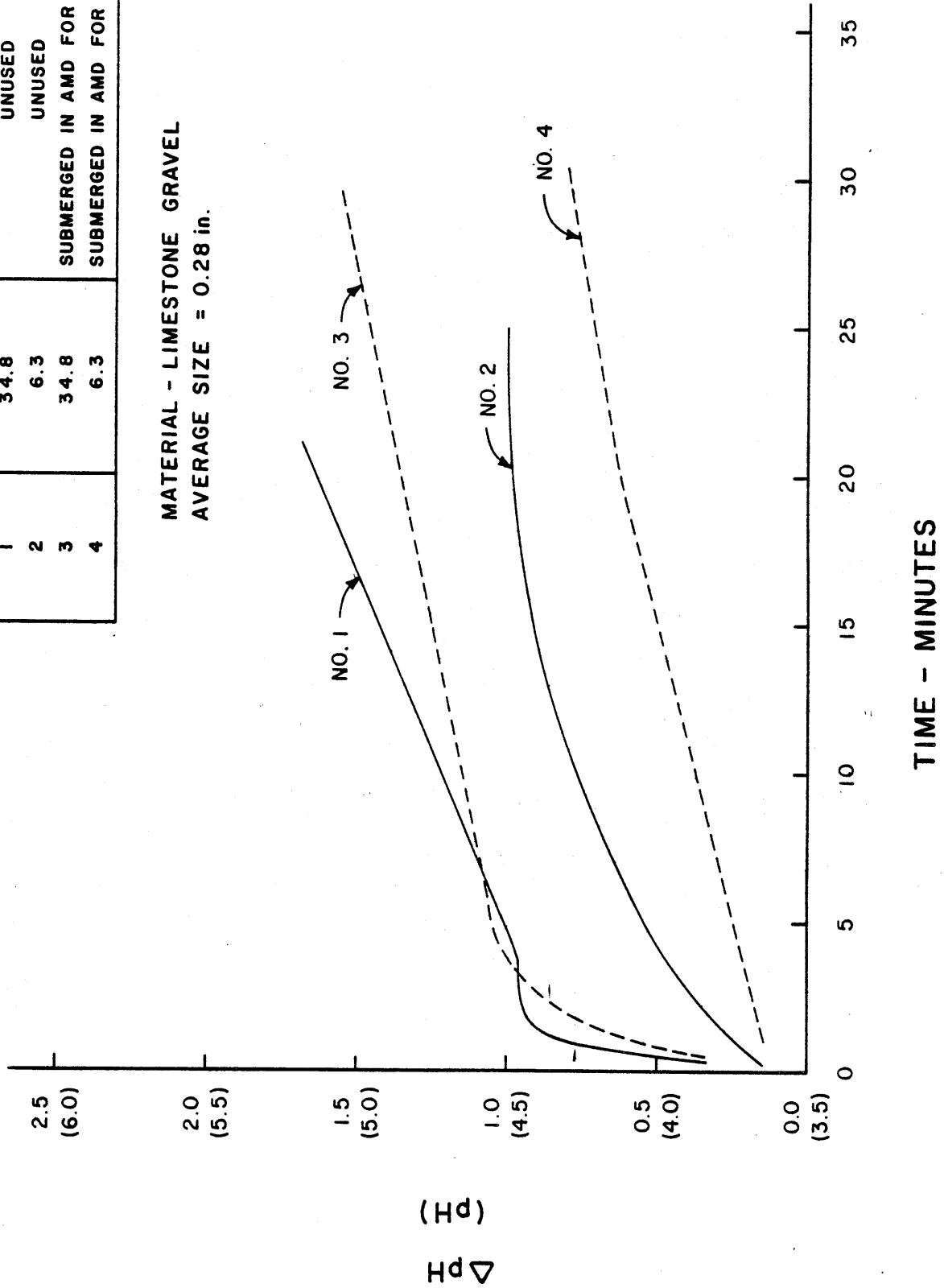


TEST NO.	LOAD FACTOR AT FINAL pH	MATERIAL
1	39.5	MARBLE CHIPS
2	4.9	MARBLE CHIPS
3	34.8	LIMESTONE GRAVEL
4	7.5	LIMESTONE GRAVEL



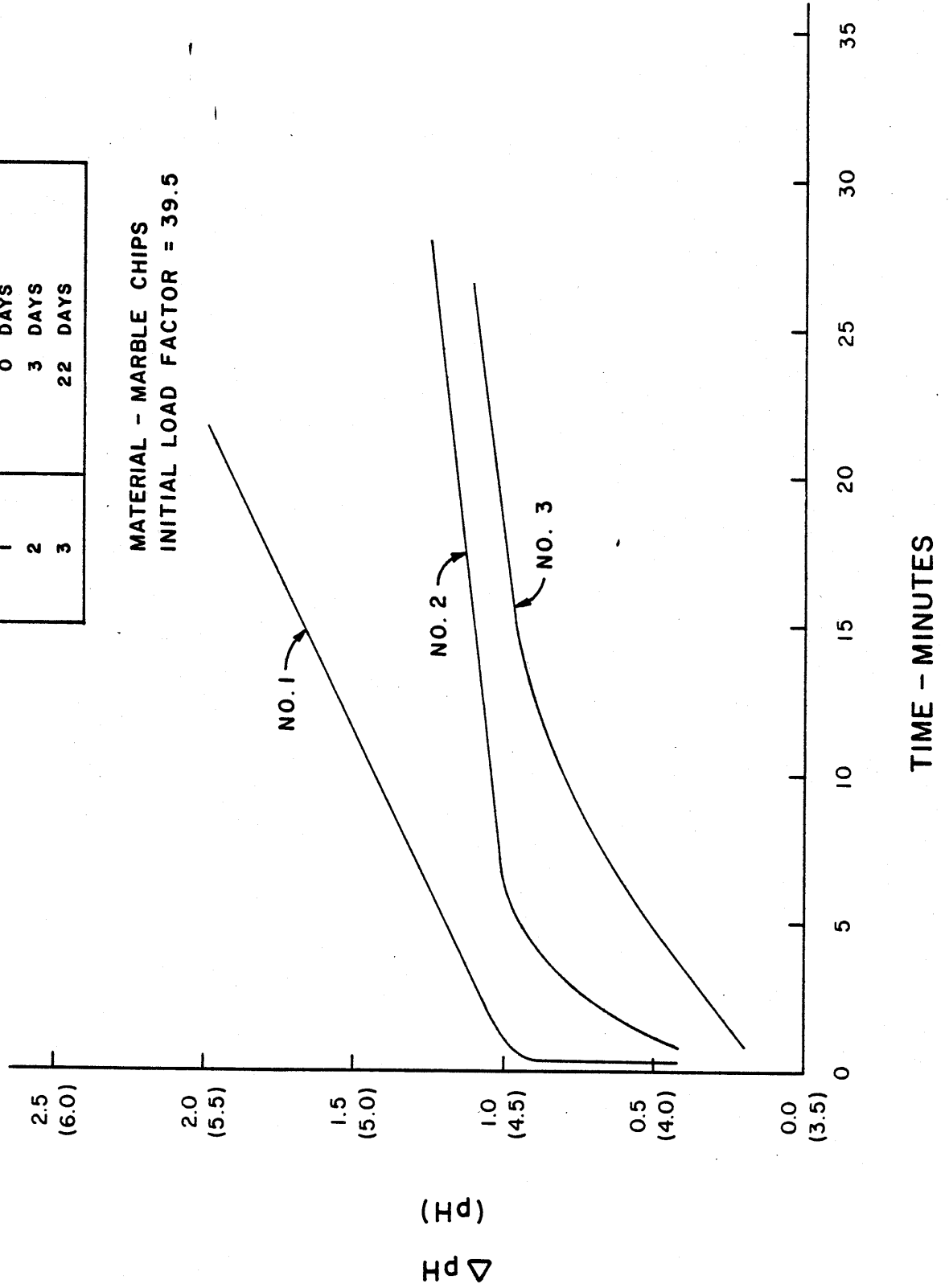
TEST NO.	LOAD FACTOR AT FINAL pH	MATERIAL CONDITION
1	34.8	UNUSED
2	6.3	UNUSED
3	34.8	SUBMERGED IN AMD FOR 30 DAYS
4	6.3	SUBMERGED IN AMD FOR 30 DAYS

MATERIAL - LIMESTONE GRAVEL
 AVERAGE SIZE = 0.28 in.

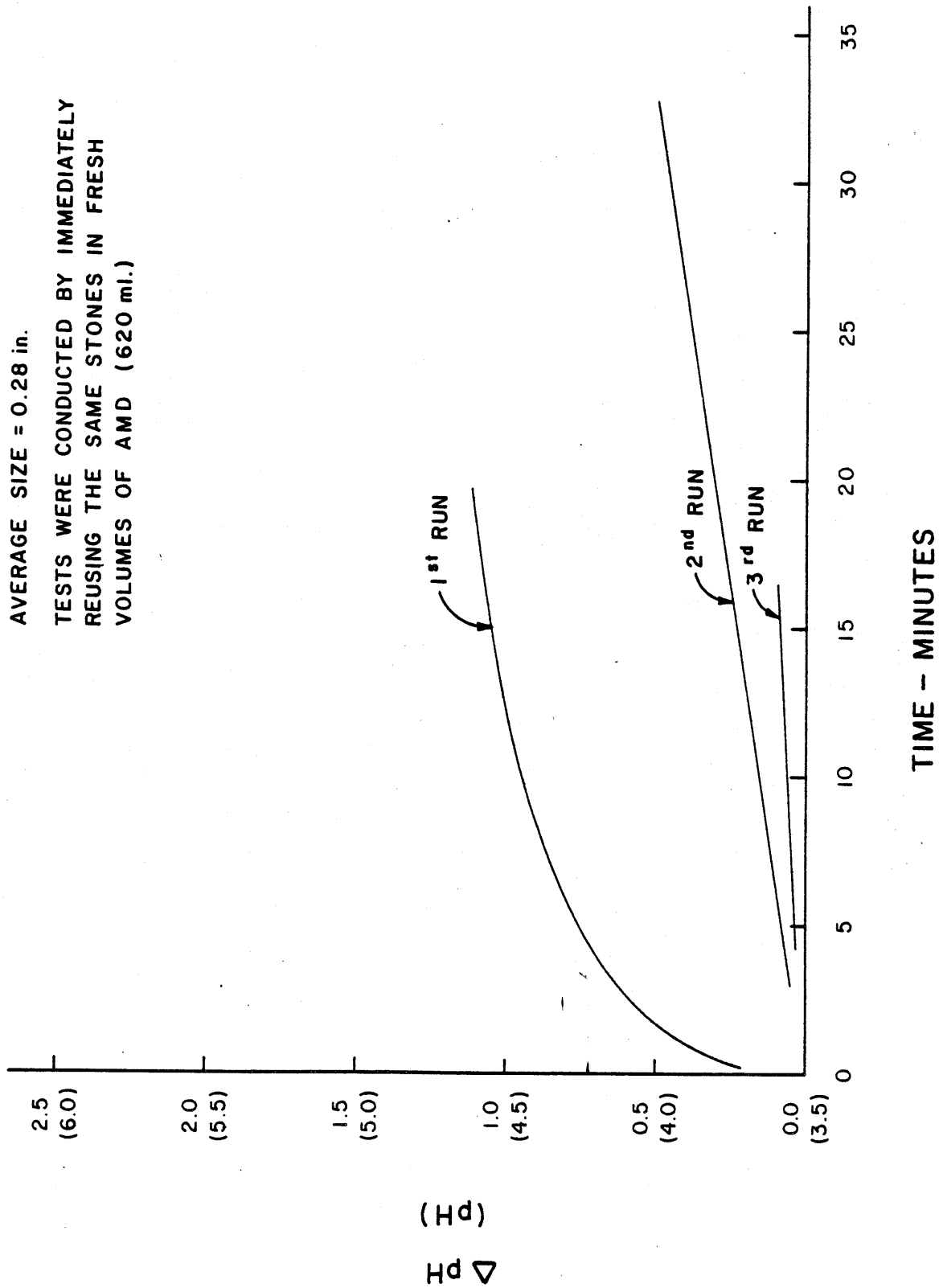


TEST NO.	TIME OF IMMERSION IN AMD BEFORE TEST
1	0 DAYS
2	3 DAYS
3	22 DAYS

MATERIAL - MARBLE CHIPS
 INITIAL LOAD FACTOR = 39.5

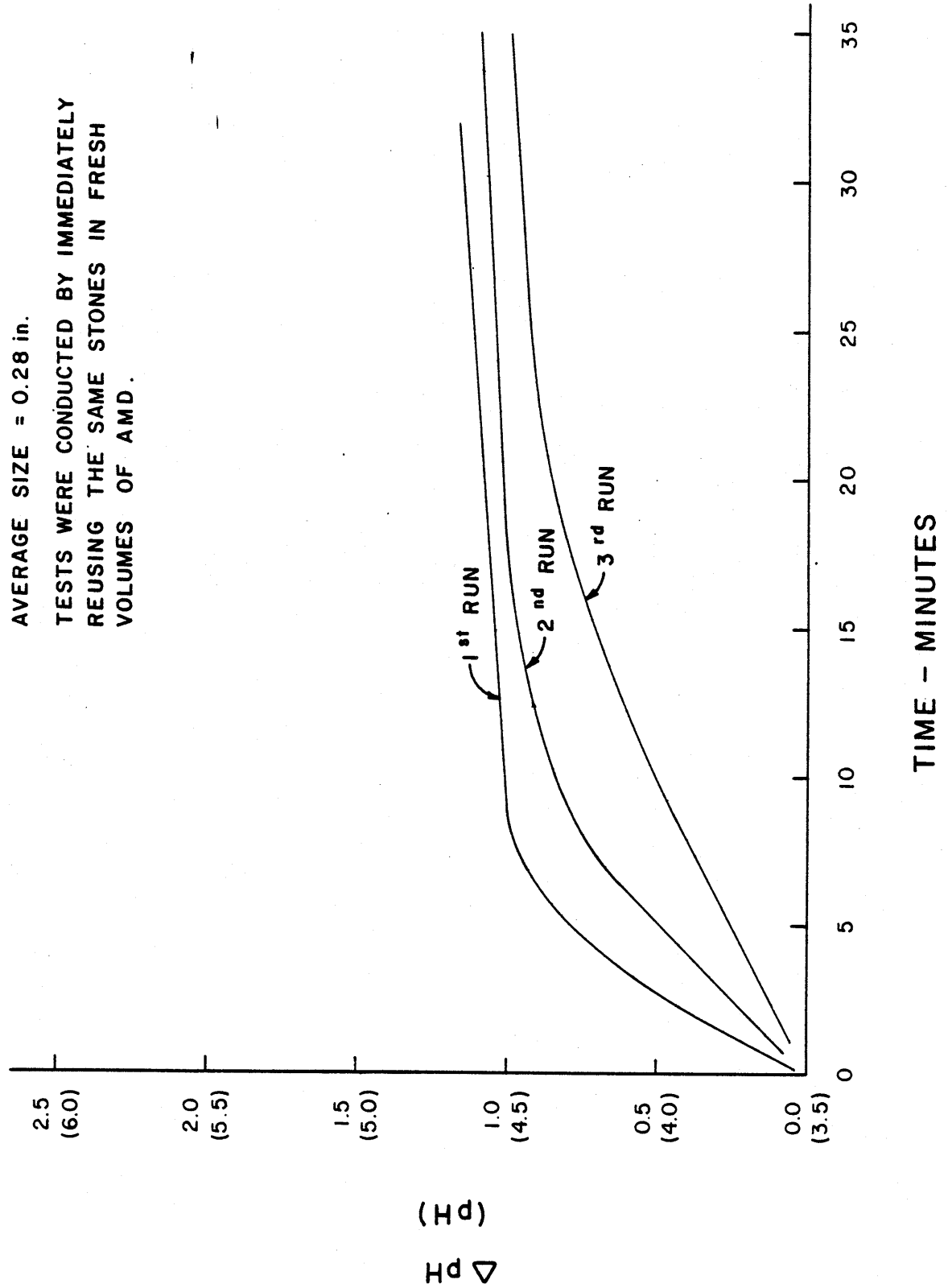


MATERIAL - MARBLE CHIPS
 INITIAL LOAD FACTOR = 7.1
 AVERAGE SIZE = 0.28 in.
 TESTS WERE CONDUCTED BY IMMEDIATELY
 REUSING THE SAME STONES IN FRESH
 VOLUMES OF AMD (620 ml.)



MATERIAL - MARBLE CHIPS
INITIAL LOAD FACTOR = 16.9
AVERAGE SIZE = 0.28 in.

TESTS WERE CONDUCTED BY IMMEDIATELY
REUSING THE SAME STONES IN FRESH
VOLUMES OF AMD.



Report from Pennsylvania State University

Analysis of Coatings on Calcite Chips

1. General Visual Observations

Careful examination of the chips shows that there are three types of coating:

- (a) an overall light grey coating of very fine texture;
- (b) a loosely adhering, flaky coating of a rusty brown color;
- (c) as (b) but off-white.

Regarding (b) and (c), it appears that the occurrence of these coatings is greatest on the very dark, almost black, calcite chips and tends to occur more frequently in slight surface depressions. The coatings flake off rather easily when thoroughly dry and may be collected with very little underlying material.

The finely textured light grey coating appears to cover most surfaces of the chips but coverage is not complete, as may readily be seen on the darker calcite.

2. Elemental Analysis

The coatings were examined using the KEVEX energy dispersive X-ray analyzer both in situ on the chips and when removed.

The overall light grey coating was removed by careful scraping with a scalpel taking great care only to remove the top surface and not disturb the underlying calcite.

The following elements were detected in each case:

- (a) Calcium - with very small amounts of Al, Si.
- (b) in situ - Fe S Al Ca Si K
85 5 3 2 1 1
removed - Al Si Fe Ca S K
30 20 15 15 10 4
- (c) in situ - Al S Si Ca Fe K
80 60 17 15 2 2
removed - Al Si S Ca Fe
10 30 7 5 1

Since (b) generally occurs in conjunction with (c), it would appear that, when removed, (b) contains some (c) but when examined on the chip the brown deposits show almost exclusively iron.

(Note that the above numbers give a semiquantitative indication of relative amounts but have no strict interpretation; also note that elements lighter than sodium are not detected.)

X-ray analysis and diffraction tests indicate that both permanent and flaky coatings were developed on the stone. The permanent coating is a crystalized calcite, whereas the flaky coatings consist of Iron and Aluminum compounds. Results of these tests are presented in the following pages.

The flaky nature of the Iron and Aluminum coating gives credence to the expectation that renovation of the limestone activity can be achieved by physical means. †

Abrasion of limestone such as in a fluidized bed flow conditions is considered as one possible method of limestone renovation.

The observed flaking of the coating upon drying of coated limestone samples also indicates possible renovation of a crushed limestone barrier after being given a "resting period." Construction of two parallel crushed limestone barriers and switching the flow of AMD from one barrier to the parallel bed would allow for the renovation process to be performed without interruption of AMD treatment. The renovation may require an application of clean water jetting through the barrier to aid in the removal of the dried flaky coatings.

It therefore appears that (b) is an iron compound, oxide or carbonate most likely, while (c) is an aluminum sulfate or silicate or mixture. Also (a) appears to be a calcium salt.

3. X-Ray Diffraction

(a) Not many peaks except those due to calcite. d-spacings and intensities of extra peaks are

d	3.82	3.34	2.50
I	100	70	70

(b) Pattern gave the following d-spacing and intensity data

d	3.02	3.31	3.06	1.99	4.25	3.77	2.28	2.49
I	100	50	40	30	30	20	20	10

(c) Pattern gave the following data

d	3.02	2.88	3.32	2.28	2.45
I	100	100	60	30	?

of the latter two patterns the 3.02 and 2.28 peaks are due to calcite. 3.32 seems a common peak almost certainly due to SiO₂ (quartz) as would be 4.25 and 2.46. This leaves

(a) 3.82

(b) 3.06 1.99 3.77 (Fe, O, CO₃, ?)

(c) 2.88 2.78 2.45 (Al, SO₄, SiO₂, ?)

The only near fit found in the index for any of these, bearing in mind the elements involved, is for (c) and is CaO, MgO, Al₂O₃·SiO₂ or calcium aluminum magnesium silicate. But where is the magnesium? The identity of the compounds deposited on the calcite remains a mystery.

4. Scanning Electron Microscope Studies

Earlier work on the surface coating by X-ray diffraction revealed only CaCO₃ which can only be interpreted by saying

- (i) the coating is CaCO₃, or
- (ii) the coating is amorphous and the CaCO₃ comes from the substrate.

Of these alternatives (b) was selected because of the apparent amorphous nature of the coating as revealed by optical microscopy. In these studies X-ray diffraction of the surface coating (a) showed mainly CaCO₃ (calcite) however superficial the layer removed for the purpose. The conclusion is that the material is in fact calcite.

5. Conclusions

The calcite chips have three coatings

- (a) an overall coating of recrystallized calcite which is relatively porous;

- (b) a brown coating, rich in iron, which is not so porous and which flakes off when dry;
- (c) an off-white coating similar to (b) which is rich in aluminum and sulfur.

The exact nature of the compounds in (b) and (c) has not been determined.