RATES of PENETRATION of SOLVENTS
into
BITUMINOUS SAND

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Introduction

At present, the worlds largest undeveloped reserve of petroleum hydrocarbons is the bituminous sand of northern Alberta. These sands underly an area of thousands of square miles in an apparently continuous bed of around 100 feet in thickness.(1) Except where it outcrops on river banks, this deposit is covered by up to 600 feet of overburden. All attempts at commercial extraction of the bitumen to date have involved excavating the sand and processing it either by flotation or solvent extraction. This method can only be used where there is little or no overburden and a suitable disposal ground for waste sand. The bituminous sand is extremely difficult to excavate and to handle. It has been suggested (Dr. Seyer) that it may be possible to extract the bitumen with solvents without disturbing the sand by methods similar to those used to recover salt from underground salt deposits as a brine solution. This thesis is a record of some preliminary work done towards determining the feasibility of this method of extraction.

Experimental

Various solvents were allowed to flow radially into uniformly compacted cylinders of bituminous sand. The rate of penetration of the solvent was measured under constant head.

Apparatus

The principal piece of equipment used was a 13 inch piece of standard 4 inch steel pipe with a loosely fitted piston mounted on a slightly longer piece of 3 inch pipe. Two sheet metal disks of the inside diameter of the pipe were placed one at each end to prevent the sand from sticking to the piston or base when under pressure. The top disk and piston had holes at their centres to accommodate a length of steel rod 0.325 cm. in diameter used to keep a central channel in the sand open during compression. A lead fitting as shown in Fig. 1 was pressed solidly into the sand during the compression. The coarse threads on this fitting (not shown in Fig. 1) ensured a rigid connection between the glass feed tube and the sand. The feed tube (No. 6 pyrex) was sealed into this fitting by a porcelain cement setting over night. This type of connection was found necessary to prevent slight jarring of the feed tube from starting a leak between the bitumen and the glass tube. The solvent was maintained in this tube at a mark 30 cm. above the top of the sand. A large bulb blown in the tube just below this mark permitted a considerable volume of solvent to flow into the sand between additions without too great a loss of head. A 35 ohm heating coil wound on the inside of a 6 inch diameter sheet metal tube 12 inches long was used to heat the sand while under compression. To extrude the sand, the 4 inch pipe holding the sand was supported on a longer piece of 5 inch pipe by a bushing fitting the two sizes of pipe while the piston forced the sand out.

The press used to compress the sand and extrude it from the pipe was a 200,000 pound Olsen Testing Machine in the Forest Products

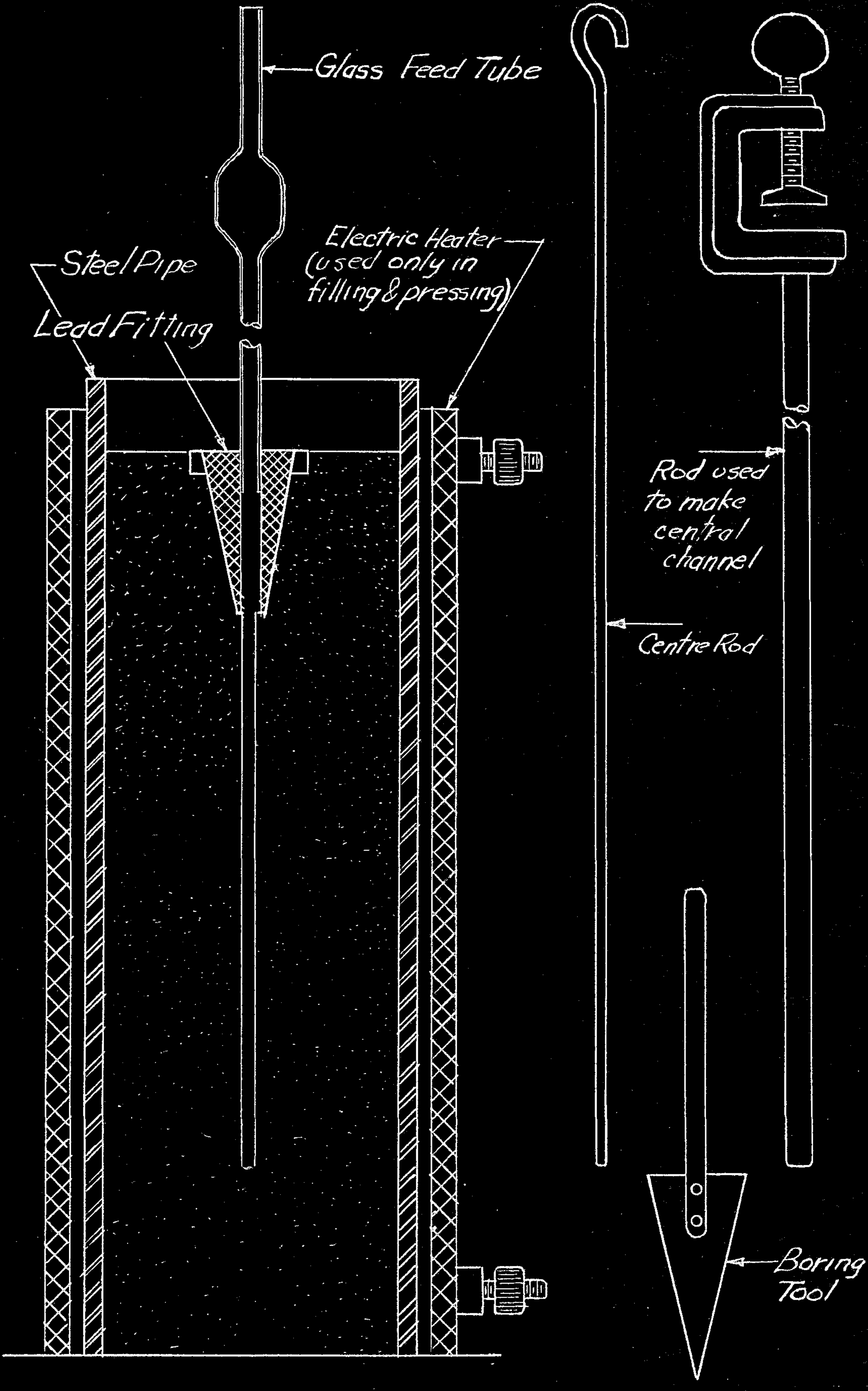


Fig. 1. Apparatus

Laboratory at the University. This machine was also used to make the central channel in the sand.

Proceedure

The sand to be loaded into the test pipe was heated on a water bath until completely softened. It was carefully broken up with a large spoon and small lumps of non bituminous material present were removed as completely as possible. The sand was put into the pipe a few spoonfuls at a time then tamped down with a short length of 1 1/2 inch wooden dowel to remove as much entrapped air as possible. One ampere flowing through the heater kept the pipe warm while being loaded. When the pipe was filled, the heater was disconnected and the sand allowed to cool overnight.

The following day the pipe was put in a lathe and a cone shaped hole bored in the top of the sand to accommodate the lead fitting. This hole was bored with a triangular tool having the same shape as the longtitudinal section of the lead fitting. The central channel was formed next by forcing a 3/8 inch rod (Fig. 1) into the sand to a distance from the bottom of the pipe approximately equal to the pipe radius. The rod was easily centred on the sand with the aid of the tapered hole already bored. The lead fitting, after being coated with tar sand applied hot, was placed in its hole. A steel rod was put into the central channel to keep it open during compression. The top metal disk was put on and the piston put in place. A pressure of 25,100 pounds (2,000 psi) was applied and the sand allowed to stand for 9 days. A pressure drop of 2 - 3,000 pounds occurred overnight for the first few days, decreasing to a few hundred pounds towards the end of the 9 day period. The pressure on the sand was raised to 25,100 pounds once every 24 hours.

One ampere flowing through the heater maintained the sand at the centre of the pipe at about 60°C. After standing 9 days, the heater was disconnected and the sand allowed to cool overnight under pressure, then removed from the press. This treatment was found to be sufficient to bring the sand close to its equilibrium condition.

The top disk was easily removed without disturbing the sand after warming it with a bunsen burner. The central rod was removed after loosening it by twisting. The glass tube was then cemented to the lead fitting. The pipe full of sand was placed in a large glass jar in a water bath (22° C.) to minimize the effects of fluctuations in room temperature. Solvent was added up to the 30 cm. mark on the feed tube (measured from the top of the lead plug) from a 50 ml. burette. Additional volumes necessary to return the level to this mark were measured from a 5 ml. burette at approximately logarithmic time intervals. The solvent level would drop as much as a centimeter in the intervals between additions and hence the head was not absolutely constant.

A 2 1/2 inch cap on the feed tube made from number 10 pyrex glass tubing, reduced evaporation losses. An evaporation correction was determined by measuring with a cathetometer the drop in level in a capped piece of tubing similar to the feed tube.

At the conclusion of the experiment, the sand was extruded from the pipe. A force of 7,000 pounds was found necessary to start the sand moving. About one quarter of the length of the extruded sand was cut off each end with a hack saw blade that had been ground to a knife edge. The blade was heated during cutting by a gas flame to soften the bitumen in the sand. The part of the sand into which the solvent had penetrated was found to be very soft and easily scooped out with a spoon without disturbing the remainder of the sand. The volume of the cavities so formed was measured as carefully as possible with a centimeter scale.

Properties of the Sand.

The bituminous sand used was taken from the Abasand workings early in 1944. It had a bitumen content of 18.36% and a density in its natural state of 1.989 grams per c.c. The density of the compressed sample was 1.925 grams per c.c. The extracted sand particles were found to have a density of 2.659 grams per c.c. Taking the density of the bitumen as 1.022 (Seyer and Krieble)(2) The fraction of unfilled voids may be calculated as shown:

In 1,000 grams bituminous sand there will be:

183.6 grams of bitumen of volume	179.6 c.c.
816.4 grams of sand " "	307.0 c.c.
Total	486.6 c.c.

Volume of 1,000 grams of bituminous sand

	Natural	Compressed
	502.8	519.5 c.c.
Volume of sand plus bitumen	486.6	486.6
Volume of unfilled voids:	16.2	32.9
Fraction voids of total volumes	3.2%	6.3%

Mesh	Retained
50	0
60	0.1
70	0.5
100	42.9
140	45.4
200	5.4
Passing 200	5.7

Table I - Screen Analysis

Table I gives the analysis of the sand as percents retained on U.S. standard screen sizes. Measuring the deflections caused by various loads on the compressed sand for both increasing and decreasing loads gives the results shown in Table II and Figure II. The sample tested was 11.9 inches long and 12.6 square inches in cross section. For an increasing load the Modulus of elasticity, remained constant at 272,000 psi. after the load reached 6,000 pounds (500 psi)

$$E. = \frac{(19,000)\ (11.9)}{(o.066)\ (12.6)}$$

$$= 272,000 \text{ psi.}$$

LOAD	DEFLECTION	(INCHES)
(Pounds)	Increasing	Decreasing
0	0	0.003
1000	0.016	0.067
2000	o.030	0.081
3000	0.043	0.090
4000	0.053	0.097
5000	0.061	0.104
6000	0.067	0.108
7	0.072	0.112
8	0.077	0.115
9	0.080	0.118
10	0.084	0.1195
11	0.087	0.121
12	0.090	0.1225
13	0.094	0.124
14	0.097	0.125
15	0.100	0.126
16	0.103	0.127
17	0.106	0.128
18	0.109	0.128
19	0.112	0.129
20	0.115	0.130
21	0.119	0.131
22	0.122	0.132
23	0.126	0.132
24	0.129	0.133
25	0.133	0.133

Table II. Load vs Deflection

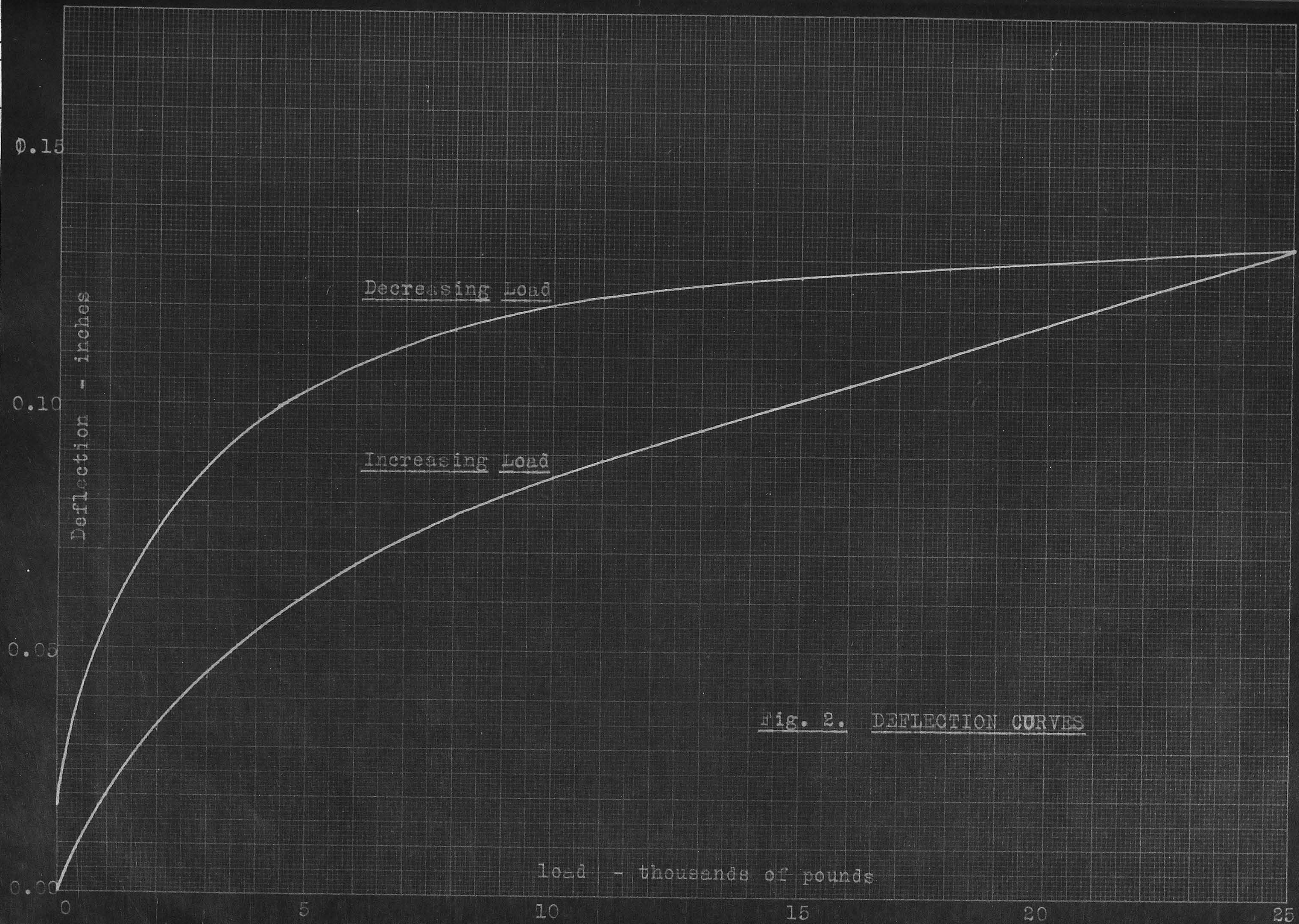


Fig. 2. DEFLECTION CURVES

Results.

The results were obtained as a series of volumes of solvent added at definite times after the start of the experiment. These volumes were corrected for evaporation loss from the feed tube by subtracting the solvent loss from a similar tube in the same interval of time. Over long intervals of time when the glass cap was not removed, the evaporation losses were 0.0029, 0.0019, and 0.0031 c.c. per hour for carbon tetrachloride, benzene and carbon disulphide respectively. When the cap was removed frequently to add solvent at the beginning of a run, the evaporation losses were slightly higher but of less consequence due to the much shorter intervals between solvent additions. The results are shown in Table 3 to 25 hours corrected for evaporation losses. Readings were actually taken up to 300 hours as shown in Fig. 3.

CARBON TETRACHLORIDE		BENZENE		CARBON DISULPHIDE	
Time	Volume	Time	Volume	Time	Volume
0.0722	0.45	0.0681	0.32	0.302	0.27
0.117	0.15	0.0945	0.15	0.373	0.35
0.190	0.10	0.138	0.12	0.454	0.29
0.281	0.08	0.167	0.06	0.536	0.30
0.330	0.06	0.236	0.10	0.636	0.27
0.471	0.09	0.282	0.03	0.732	0.21
0.563	0.03	0.350	0.02	0.807	0.18
0.680	0.09	0.442	0.05	0.889	0.20
0.850	0.10	0.592	0.05	0.983	0.31
0.985	0.06	0.825	0.07	1.17	0.28
1.14	0.11	0.985	0.12	1.38	0.23
1.53	0.12	1.34	0.11	1.65	0.43
2.08	0.20	1.83	0.10	2.08	0.37
2.39	0.10	2.50	0.10	2.51	0.36
2.71	0.10	2.78	0.05	2.99	0.36
3.10	0.12	3.30	0.07	3.55	0.36
3.55	0.17	2.83	0.06	4.41	0.50
3.98	0.10	4.32	0.05	5.20	0.43
4.87	0.27	5.10	0.07	5.58	0.20
5.88	0.23	5.99	0.08	6.16	0.31
7.05	0.33	6.83	0.06	7.04	0.40
8.17	0.41	7.83	0.08	8.19	0.51
9.13	0.28	8.83	0.06	8.87	0.30
11.82	0.58	11.38	0.13	16.20	3.01
14.80	0.60	12.78	0.07	16.53	0.16
19.10	0.79	14.60	0.08	20.64	1.50
24.08	0.85	23.07	0.33	23.62	1.08

Table III, Volumes of Solvent Added.

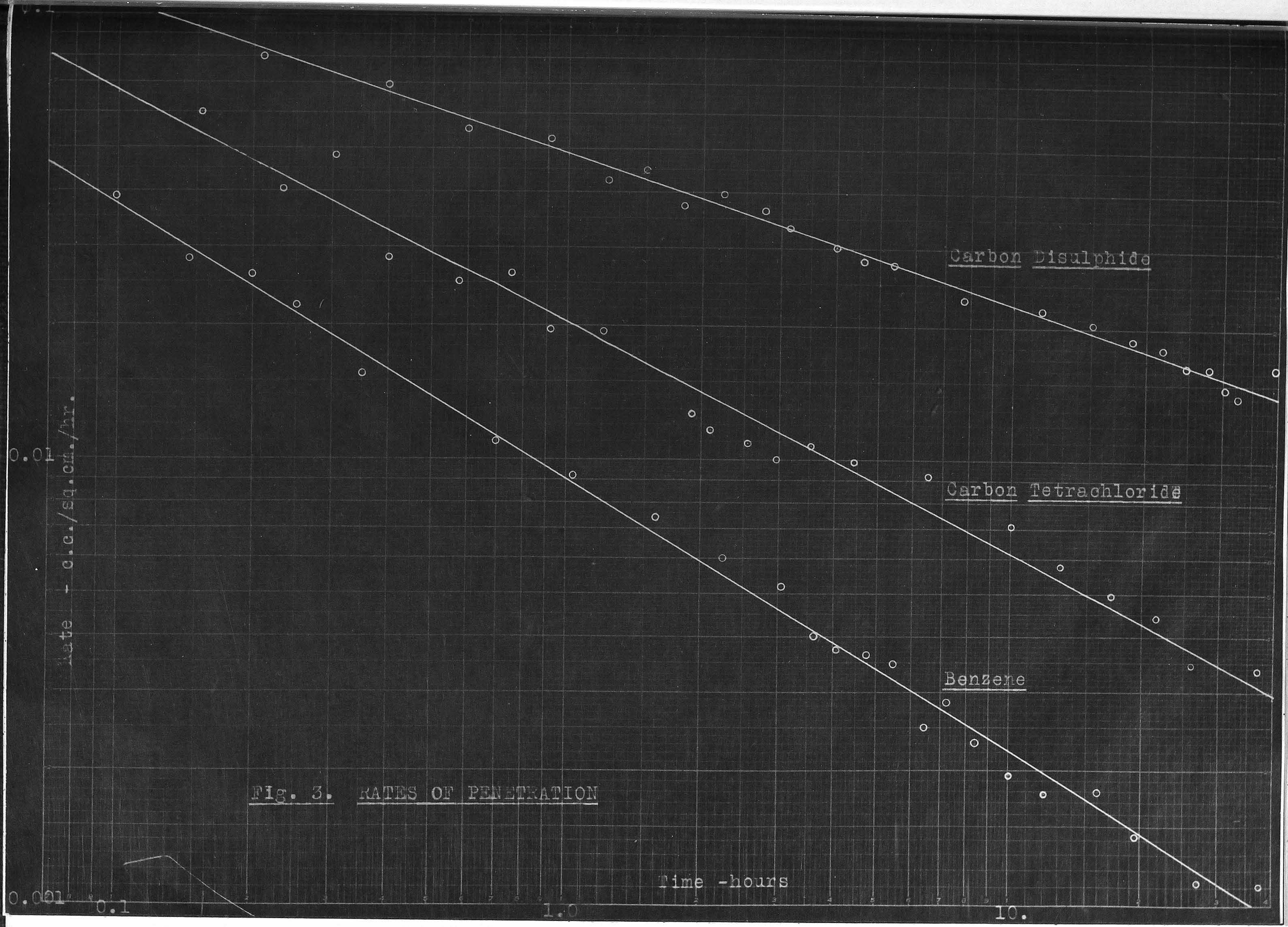


Fig. 3. RATES OF PENETRATION

CARBON TETRACHLORIDE		BENZENE		CARBON DISULPHIDE	
Time	$\Delta v/\Delta t$	Time	$\Delta v/\Delta t$	Time	$\Delta v/\Delta t$
0.0426	0.332	0.0601	0.188	0.276	0.264
0.0925	0.142	0.0813	0.089	0.338	0.244
0.154	0.0596	0.116	0.103	0.414	0.211
0.236	0.0382	0.152	0.075	0.495	0.183
0.307	0.0502	0.202	0.536	0.586	0.153
0.402	0.0283	0.259	0.241	0.686	0.143
0.517	0.0142	0.316	0.109	0.771	0.142
0.623	0.0326	0.391	0.201	0.848	0.114
0.766	0.0259	0.517	0.0123	0.936	0.108
0.918	0.0193	0.709	0.0111	1.076	0.0869
1.06	0.0280	0.905	0.0074	1.272	0.0702
1.33	0.0102	1.164	0.0113	1.515	0.0613
1.80	0.0126	1.598	0.0074	1.86	0.0526
2.08	0.0112	2.17	0.00566	2.29	0.0442
2.55	0.0107	2.64	0.00706	2.75	0.0385
2.91	0.0100	3.04	0.00522	3.27	0.0328
3.33	0.0135	3.57	0.00403	3.98	0.0306
3.77	0.00709	4.08	0.00377	4.81	0.0278
4.43	0.00978	4.71	0.0036	5.39	0.0272
5.38	0.00687	5.55	0.00342	5.87	0.0272
6.47	0.00891	6.42	0.00252	6.60	0.0239
7.61	0.0128	7.33	0.00284	7.61	0.0227
8.65	0.00952	8.33	0.00229	8.53	0.0239
10.48	0.00487	10.11	0.00185	12.54	0.0213
13.31	0.00570	12.08	0.00174	16.37	0.0254
16.95	0.00496	13.69	0.00153	18.58	0.0189
21.59	0.00443	19.15	0.00143	22.13	0.0187

Table IV, Rates of Penetration.

By dividing the volume of solvent added at any time by the time elapsed to the preceeding addition, an average rate of penetration is obtained over this period. By dividing this figure by the surface area of the central channel, the rate is found per square centimeter (table 4). These were plotted as the instantaneous rates at the mean of the two times.

The graphs of these points on log-log paper were found to be straight lines. By applying the method of least squares, the relations between the rates and time were found. Integrating these expressions gives the volumes of solvent that will penetrate the sand per square cm. in a given time. These equations are given in Table 5 and the corresponding graphs are shown in Figures 4 and 5.

Carbon Tetrachloride	Benzene	Carbon Disulphide
$\frac{dv}{dt} = 0.0199t^{-0.522}$	$\frac{dv}{dt} = 0.00903t^{-0.615}$	$\frac{dv}{dt} = 0.0484t^{-0.339}$
$v = 0.0416t^{0.478}$	$v = 0.0235t^{0.385}$	$v = 0.0732t^{0.661}$

Table 5, Equations

At the conclusion of the experiments longtitudinal sections of the volumes of sand permeated by the solvents were found to be as in Fig. 6.

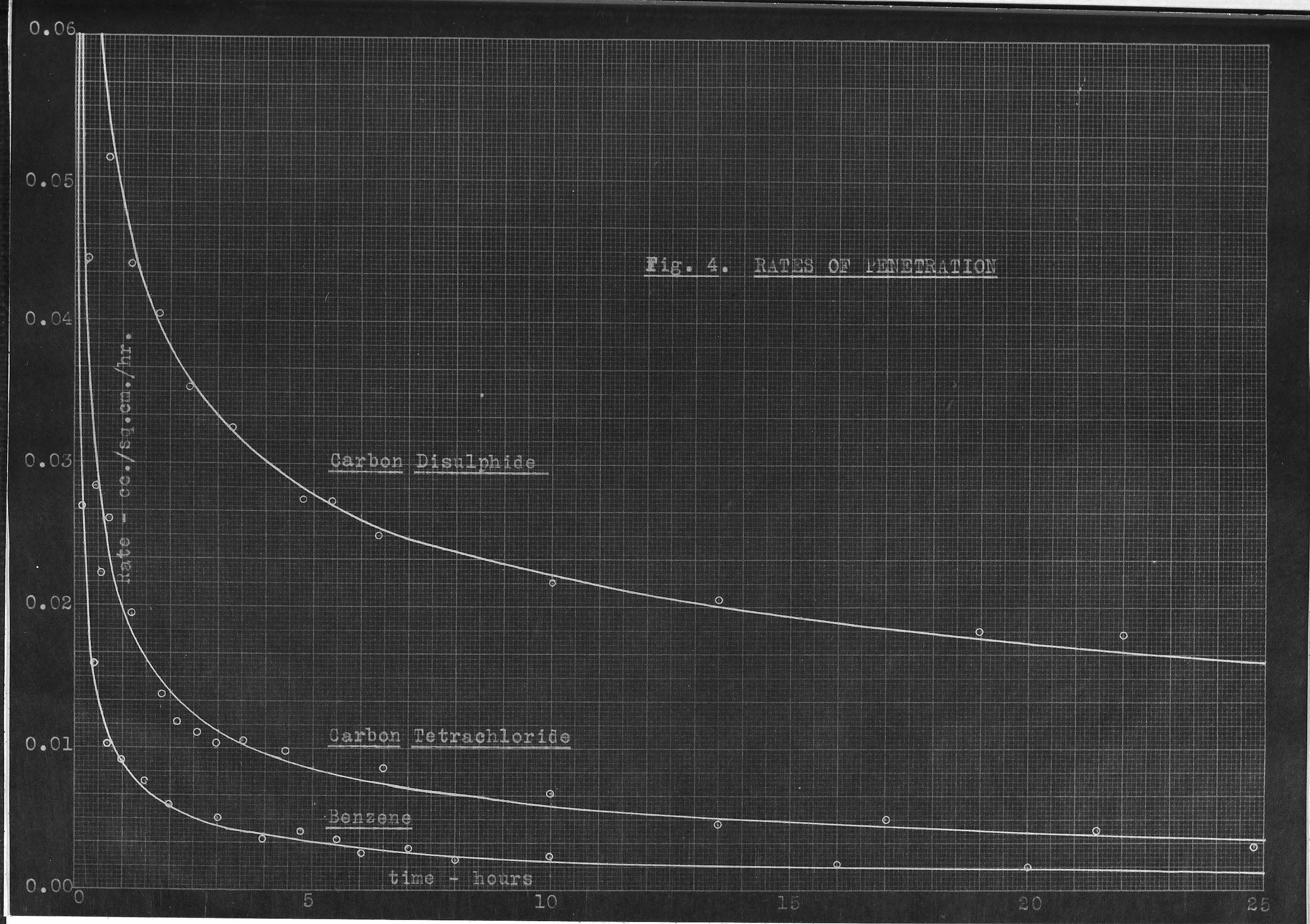


Fig. 4. RATES OF PENETRATION
Carbon Disulphide
Carbon Tetrachloride
Benzene
Rate - cc./sq.cm./hr.
time - hours
0.06
0.05
0.04
0.03
0.02
0.01
0.00
0
5
10
15
20
25

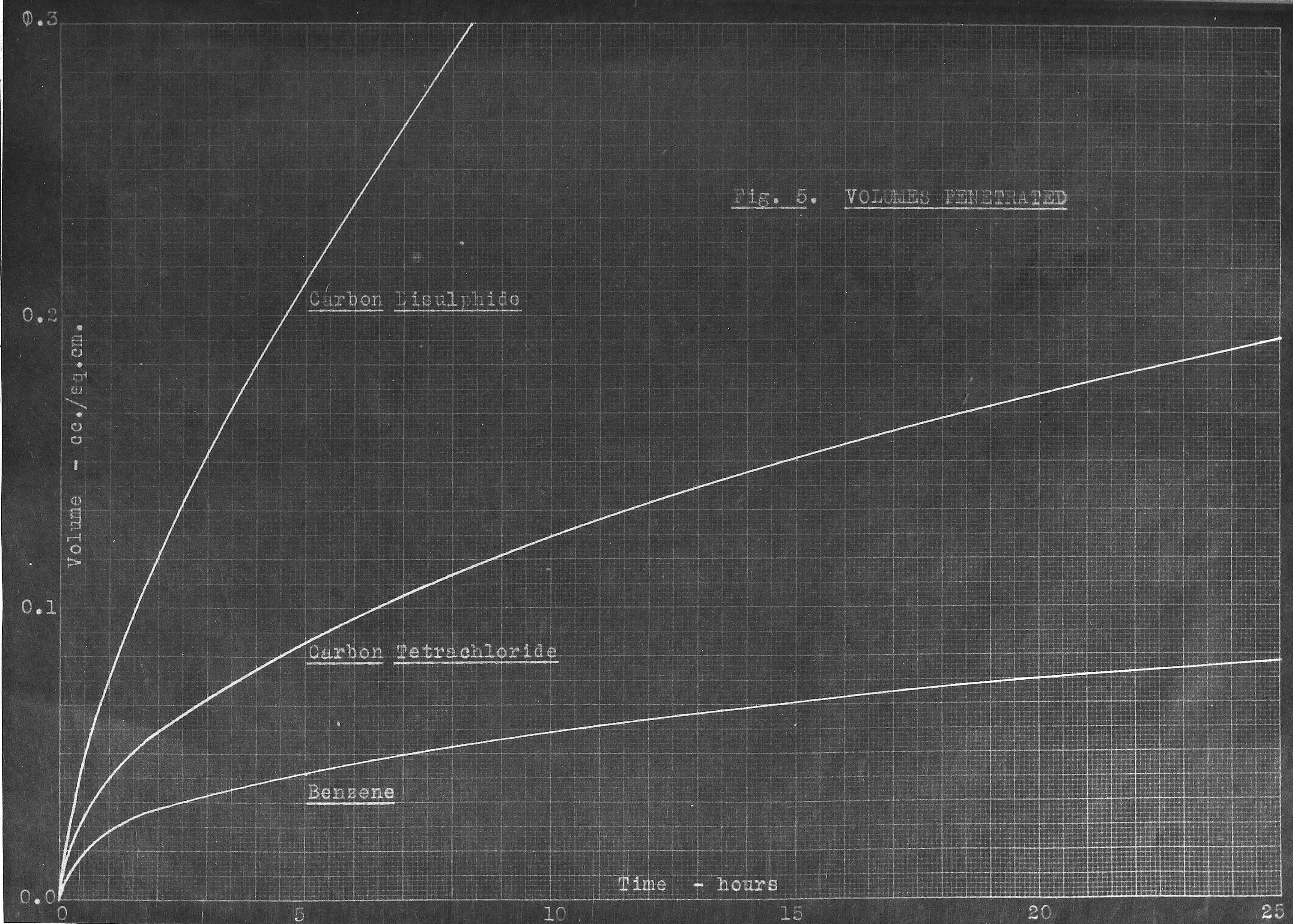
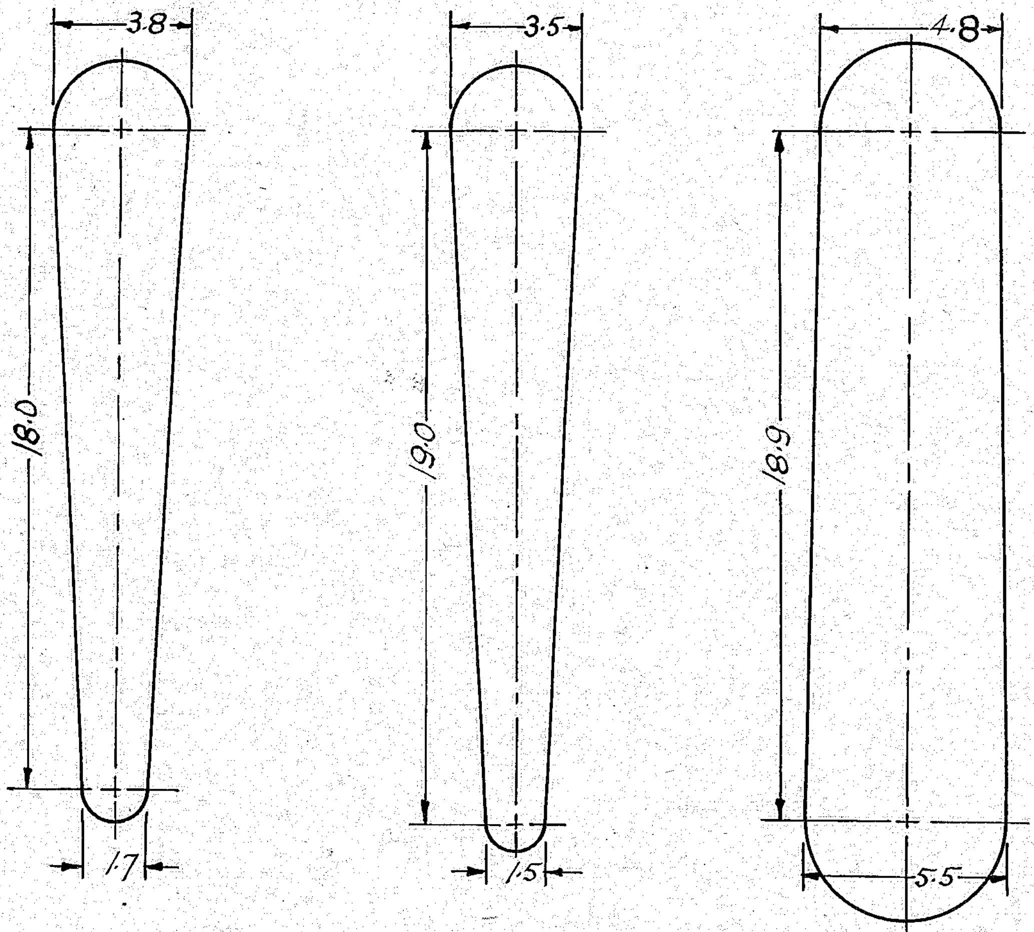


Fig. 5. VOLUMES PENETRATED
Carbon Disulphide
Carbon Tetrachloride
Benzene
Volume - cc./sq.cm.
Time - hours
0.3
0.2
0.1
0.0
0
5
10
15
20
25



Carbon Tetrachloride | Benzene | Carbon Disulphide

Fig. 6 Longtitudinal Sections of Sand Permeated by Solvents.

These volumes, calculated from the above dimensions allowing 2 cc. for the central channels were found to be:

132 c.c.	108 c.c.	465 c.c.

The solvents penetrated into these volumes in

385 hours	292 hours	101 hours

Applying the equations in Table 5, the volumes of solvent which penetrated the sand per sq. cm. in these times was,

0.715 c.c.	0.209 c.c.	1.57 c.c.

The surface areas of the central channels were:

23.08 cm^2	27.07 cm^2	19.28 cm^2

and hence the total volumes of solvents penetrated were:

16.5 c.c.	5.7 c.c.	30.3 c.c.

Expressed as fractions of the volumes of sand into which the solvents had penetrated, these volumes were:

12.5%	5.2%	6.6%

The last two figures (for benzene and carbon disulphide) are close to the fraction of unfilled voids in the sand (6.3%), the first (for carbon tetrachloride) is roughly twice this figure.

Conclusions

The rates of penetration of carbon tetrachloride, benzene, and carbon disulphide radially into bituminous sand were measured under constant head. The rates were found to be initially high, falling off rapidly with time. After a few hours, they became substantially constant at very low figures.

The volumes of solvent which penetrated the sand were found to be roughly equal to the volumes of unfilled voids in the sand with the exception of carbon tetrachloride. In this case the solvent volume was twice that of the unfilled voids. There was no evidence of swelling with any of the three solvents used.

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2. Krieble and Seyer, A chemical Investigation of the Asphalt in the tar Sands of Northern Alberta, Journal of American Chemical Society, Vol. 53, page 1337 (1921).