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THE PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION OF ANTRIM OIL SHALE

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ABSTRACT

By conservative estimates, Michigan's Antrim shale contains about 2.5 trillion barrels of oil in place - roughly 60 times the nation's current oil reserves. Efforts to extract value from this shale were initiated by Dow in the mid-fifties. A variety of physical measurements and chemical analysis have been made during this period to support the laboratory and field retorting experiments. The purpose of this report is to summarize what we know about this resource today.

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A. SUMMARY OF PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION

PHYSICAL PROPERTIES (SECTION B)

Subsection	Property	Mean	Range	Page
1	Densities (#/ft^3 of shale)	Mean	Range	7
	apparent, including pore volume	145	143 - 147	
	grain, excluding pore volume, 5000 psi Hg	152	-	
	skeletal (true), exluding pore volume, He	154	150 - 158	
	mineral (grain), retorted shale	170	-	
2	Effective porosity (% voids), Dow Chem #3 core	Mean		9
	raw shale	1.58		
	oxidized, dry conditions	19.6		
	retorted under hydrogen	18.9		
	water-steam retorted	18.9		
3	Permeability (md), Dow Chem #3 core	Mean	Range	18
	raw shale, normal to bedding planes	<0.001	-	
	raw shale, along bedding planes	0.73 (a)	0 - 5.55	
	retorted shale, along bedding planes	3.41 (a)	0 -42.40	

Note (a) probably high, relative change correct (see text)

PHYSICAL PROPERTIES (SECTION B) - Cont.

Subsection	Property	Mean	Range	Page
4	Diffusivity of oxygen	Mean	Range	25
	Diffusivity of oxygen through retorted shale at one atmosphere and 600°C (ft^2/hr)$^{(b)}$	0.11	0.09 - 0.13	

note (b) estimated values at other temperatures & pressures in text.

Subsection	Property	Mean	Range	Page
5	Mechanical properties at room temperature, forces normal to the bedding planes	Mean	Range	29
	compressive strength (psi)	5790	2530 - 9030	
	tensile strength (psi)	60	-	
	Young's modulus x 10^{-6} (psi)	0.62	0.35 - 1.00	
	linear compressibility x 10^6 (psi^{-1})	1.6	1.0 - 2.9	
	volumetric compressibility (est.) x 10^6 (psi^{-1})	4.3	3.0 - 8.6	
	linear expansion coeffiecient, various minerals, x 10^6 (°C^{-1})	8	4 - 12	
	Poisson's ratio, shales	0.20	0.11 - 0.36	

CHEMICAL COMPOSITION (SECTION C)

Subsection	Component	Mean	Range	Page
1	Primarily volitile species (wt 5 element in raw shale	Mean	Range	
	a) total carbon, Rhoburn #1, 1300 - 1400 ft	4.6	1.7 - 7.9	37
	b) inorganic carbon	0.17	0.10 - 0.37	42
	c) total hydrogen, Rhoburn #1, 1300 - 1400 ft	0.84	0.36 - 1.20	48
	d) total sulfur	2.6	1.5 - 4.5	50

CHEMICAL COMPOSITION (SECTION C) - Cont.

Subsection	Component	Page
2	Complete elemental analysis of "average" shale	54

Major Elements	Concentration (wt%)
H	0.95
Na	0.25
K	1.97
Mg	0.95
Ca	1.39
Ti	0.20
Fe	3.53
Al	6.97
C	6.35
Si	24.84
N	1.6
O	(47.2) (c)
S	3.17
Cl	0.22
Subtotal (see note)	(99.6) (c)

Minor Elements	Concentration (wt%)
Li	0.006
Rb	0.021
Cs	0.0005
Sr	0.006
Ba	0.037
La	0.0003
Y	0.005
Zr	0.07
V	0.037
Cr	0.006
Mo	0.011
W	0.0023
Mn	0.03
Co	0.001
Ni	0.014
Cu	0.018
Ag	0.001
Zn	0.003
Ga	0.01
Pb	0.004
As	0.0036
F	0.09
Th	0.0049
U	0.0015
Subtotal	0.38

Total, major plus minor elements 100.0 (c)

Note (c) calculated oxygen by difference, one determination on oxygen gave 43 wt%.

CHEMICAL COMPOSITION (SECTION C) - Cont.

Subsection	Component	Mean	Range	Page
3	Fischer assay (gallons per ton of raw shale)			58
	oil	9.6	3.79 - 12.54	
	water	5.5	4.6 - 7.7	

THERMAL PROPERTIES (SECTION D)

Subsection	Property	Mean	Range	Page
1	Heat of combustion			63
	heating value (BTU/# of raw shale)	1,500	265 - 3,704	
	heating value (Btu/# of total carbon)	20,000	18,500 -21,400	
2	Specific heat at constant pressure, c_p (Btu/#-°F)			65

Temperature (°C)	Raw shale	Spent shale
25	0.19	0.19
50	0.20	0.20
100	0.22	0.21
150	0.36 (extrapolated)	0.22
200	-	0.24
300	-	0.26
400	-	0.27
500	-	0.28

THERMAL PROPERTIES (SECTION D) - Cont.

Subsection	Property	Page
3	Thermal diffusivity, estimated (ft^2/hr.)	65

Temperature (°C)	Raw Shale	Spent Shale
100	0.039	0.021
200	0.032	0.019
300	0.025	0.017
400	0.020	0.016
500	0.016	0.016

EFFECTS ON HEATING (SECTION E)

Subsection	Property	Page
1	Thermogravemetric analysis, weight loss data	71

Temperature (°C)	Atmosphere	Weight loss (%)
150	nitrogen	1 - 2
300	nitrogen	2 - 3
above 500	nitrogen	8 - 9
600 - 900	air	12 - 13

EFFECTS ON HEATING (SECTION E) - Cont.

Subsection	Property	Page
2	Differential thermal analysis	76

Atmosphere	Summary
helium	broad endotherm with product evolution over temperature range from 400 to 700°C
	no evidence for release of water of hydration at low temperatures (eg: no sharp spikes in this range)
	only one sharp feature, β to α quartz transition occuring at about 540°C
air	strong exotherm beginning at about 200°C
	local maxima at 380 and 620°C
	combustion apparently complete by 660°C

Subsection	Auto-ignition temperature (°C)	Range	Page
3			76
	raw shale blocks heated in air	500 - 550	
	retorted shale blocks heated in air	550 - 600	
	partially retorted shale beds	300 - 310	

Subsection	Ash fusion temperatures	in °C	in °F	Page
4				80
	initial deformation	1120	2046	
	softening point	1175	2147	
	Fluid point, above	1433	2611	

B. PHYSICAL PROPERTIES

1) Density

Several types of densities can be defined. The true or skeletal density is measured by helium displacement over an evacuated and pre-weighed ground sample. The pore volume is excluded in this determination. The grain density is closely related to the skeletal density except that the volume is measured by mercury displacement at 5000 psig. Pore volume accessible to the helium molecule but not mercury (at 5000 psig) is included so that the grain density should be lower than the skeletal density in general. Finally, an apparent density can be measured by zero pressure mercury displacement. Mercury will not enter the pores at low pressures and this density includes the pore volume. (Comparison of the skeletal and apparent densities allows computation of the total effective porosity as described in the next section.)

Values of the skeletal and apparent densities are shown in Table 1 for four core samples from the current field activities. The average values of the skeletal density (154 #/ft^3) agree very well with the value of 150 #/ft^3 recommended by Katz(1). Densities measured by water displacement should be close to the skeletal density since most of the pore volume is probably water filled for samples equilibrated at ambient humidity. One recent determination gave 2.439 gm/cc (152 #/ft^3). Finally, grain densities measured on 98 samples from Dow Chem #1 averaged 2.44 gm/cc (152 #/ft^3) in agreement with the skeletal density values shown above.

Table 1 -- Shale densities measured in current studies

Well, Sanilac County Location (See Section G)	Depth (ft.)	Skeletal Density (#/ft^3)	Apparent Density (#/ft^3)
Rhoburn #1	1320	158	145
	1340	150	143
	1380	154	147
Rhoburn #3 (chips, top of cavity)	1322-1331	154	147
Mean (#/ft^3)		154	145
Mean (gm/cc)		2.471	2.332

Samples from the Dow Chem #1 well were retorted under hydrogen or water, or under a dry oxidizing atmosphere. In all cases, the density increased from the initial value (2.44 gm/cc or 152 #/ft^3) to 2.73 gm/cc (170 #/ft^3) as the organic and water were removed. This gives a measure of the ultimate density of the mineral.

2) Porosity and pore size distributions

The fraction of pores with diameters greater than a given size is found by first measuring the skeletal and true densities to give the total effective porosity. Then the incremental volume of mercury forced into the pores is measured as the pressure is increased in stages. The pore size invaded at each pressure level is known. Plots of the pore size distributions obtained for the raw shale samples summarized in Table 1 are given in Figures 1-4 and summarized in Table 2. The total porosities are fairly high (4.5 to 8.8%). However, 70 to 90% of the pores are smaller than 0.01 microns (100 A). The results agree fairly well with earlier data on the Smith #1 core (4.75% average porosity over 65 samples). Shallow or weathered shales showed increased porosity. Helium displacement was not used for measuring the skeletal density in the studies. This would tend to make the values somewhat low. However, samples were dried at 400 to 500°F. Dehydration and mild retorting might be expected under these conditions, increasing the porosity.

One preliminary series of experiments was done to test the effect of retorting on the porosity and permeability of the shale. Eight shale samples from the Midland Fee #1 well with an initial porosity of 5.4% (1 determination) were baked to a red, oxidized appearance under a dry atmosphere. Porosities averaged 24.8% with a range from 19 to 32%. A second series, with samples averaging 4.46% initial porosity (20 determinations) showed porosities of 28.89% (20 determinations) after retorting under water at only 325 to 340°C.

FIGURE 1 - PORE SIZE DISTRIBUTION FOR SAMPLE AT 1320 ft., RHOBURN NO. 1

(See Section G For Well Location)

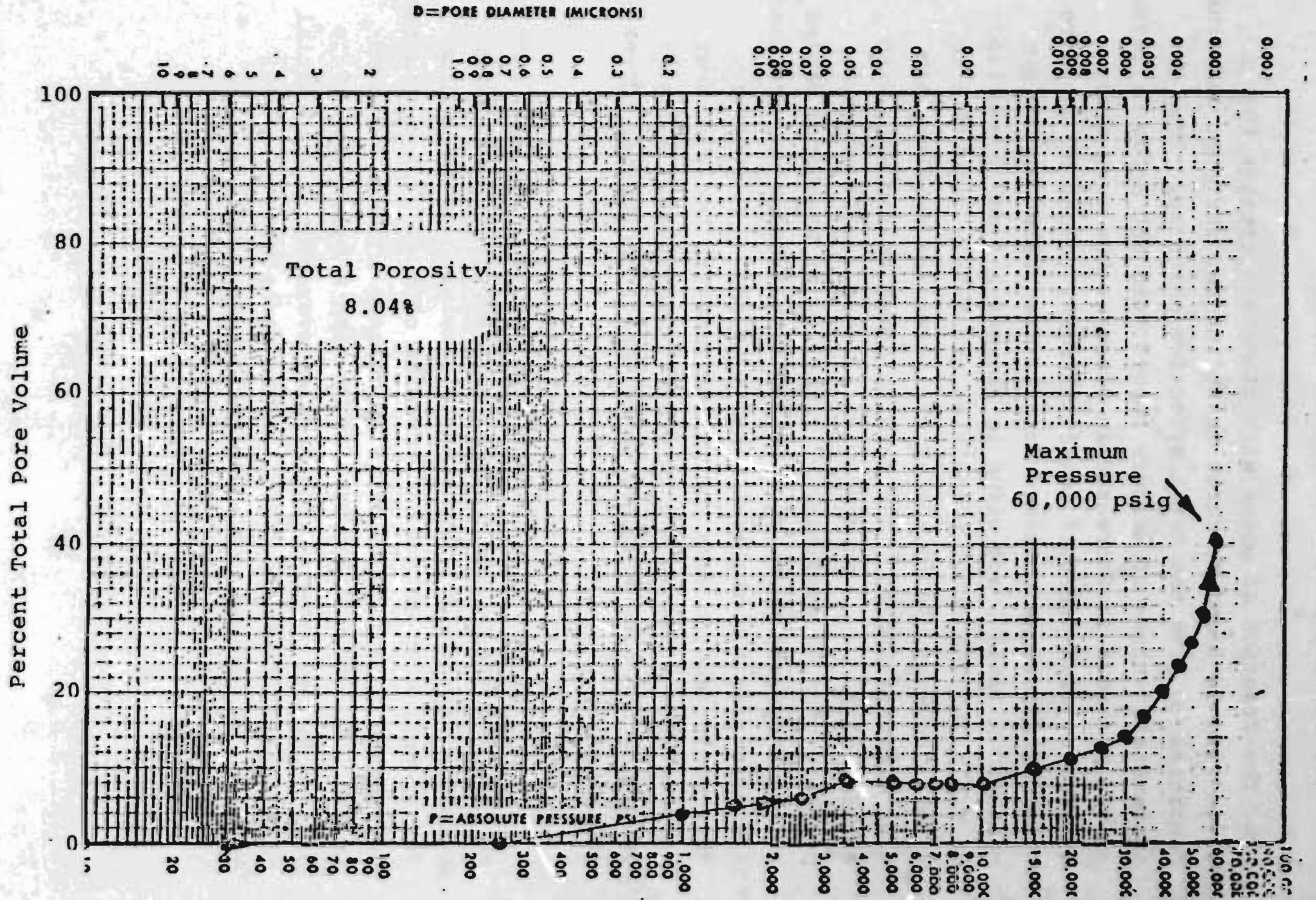


FIGURE 2 - PORE SIZE DISTRIBUTION FOR SAMPLE AT 1340 ft., RHOBURN NO. 1

(See Section G For Well Location)

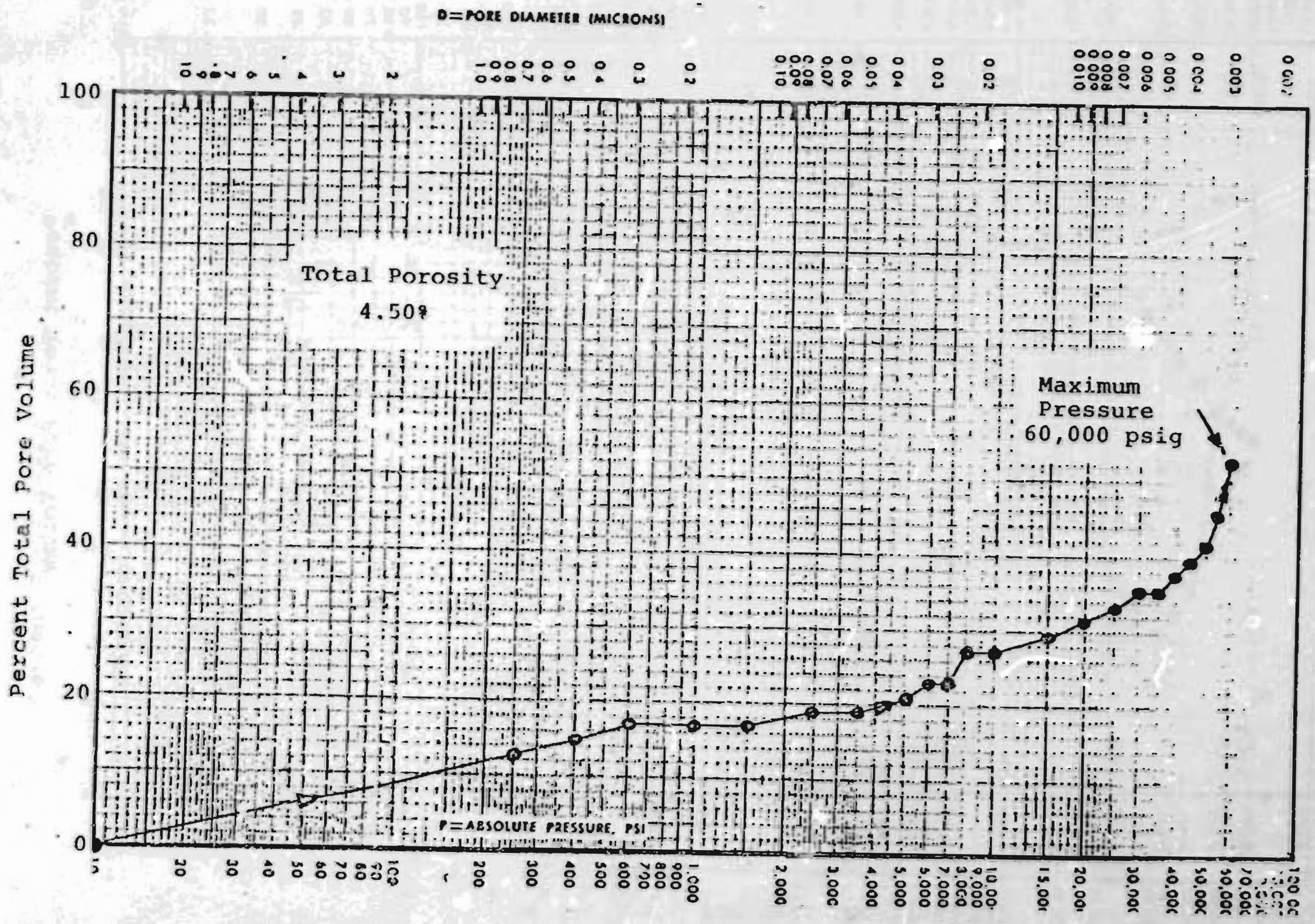


FIGURE 3 - PORE SIZE DISTRIBUTION FOR SAMPLE AT 1380 ft., RHOBURN NO. 1

(See Section G For Well Location)

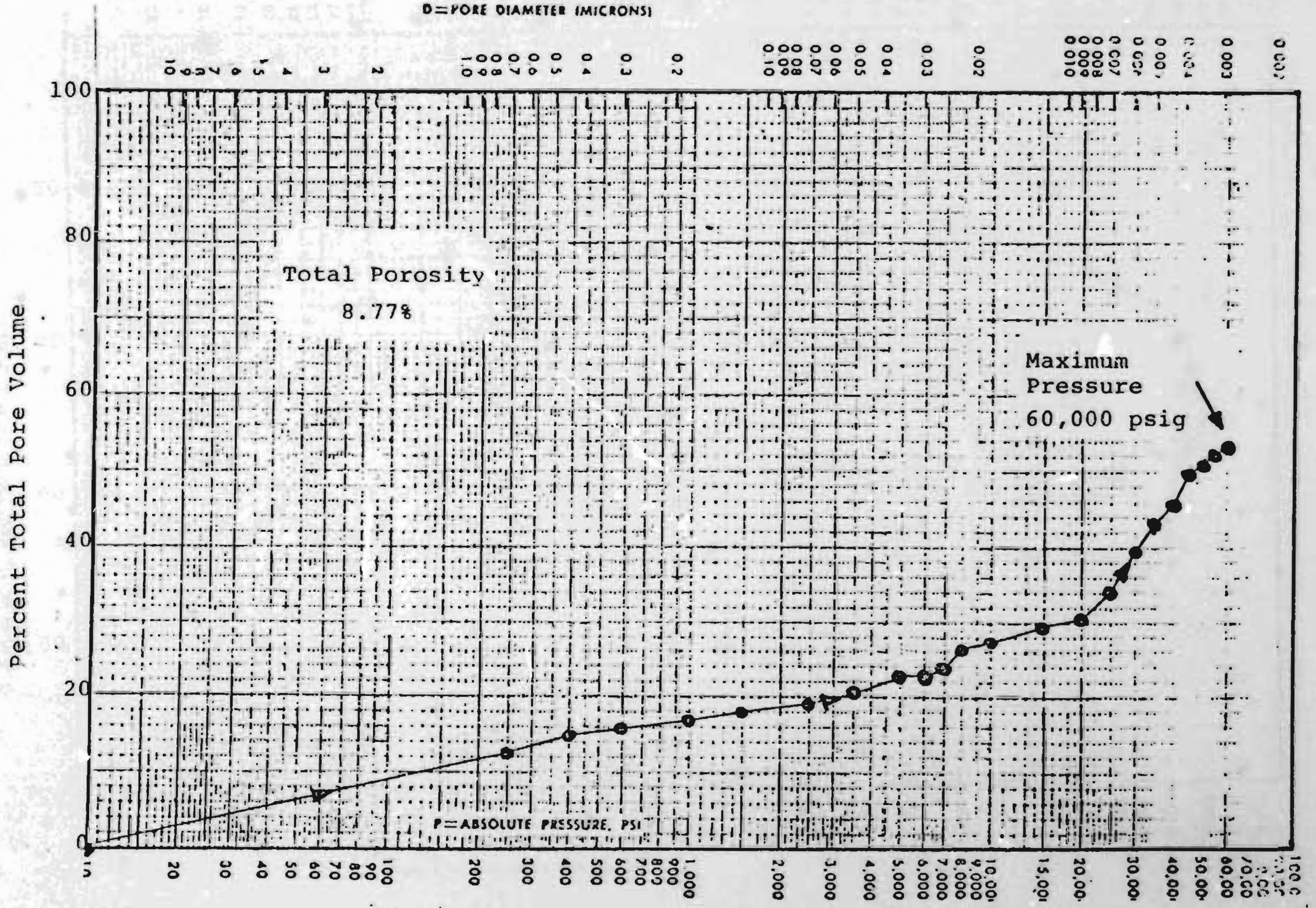


FIGURE 4 - PORE SIZE DISTRIBUTION FOR SAMPLE FROM SAND PUMP, RHOBURN NO. 3

(See Section G For Well Location)

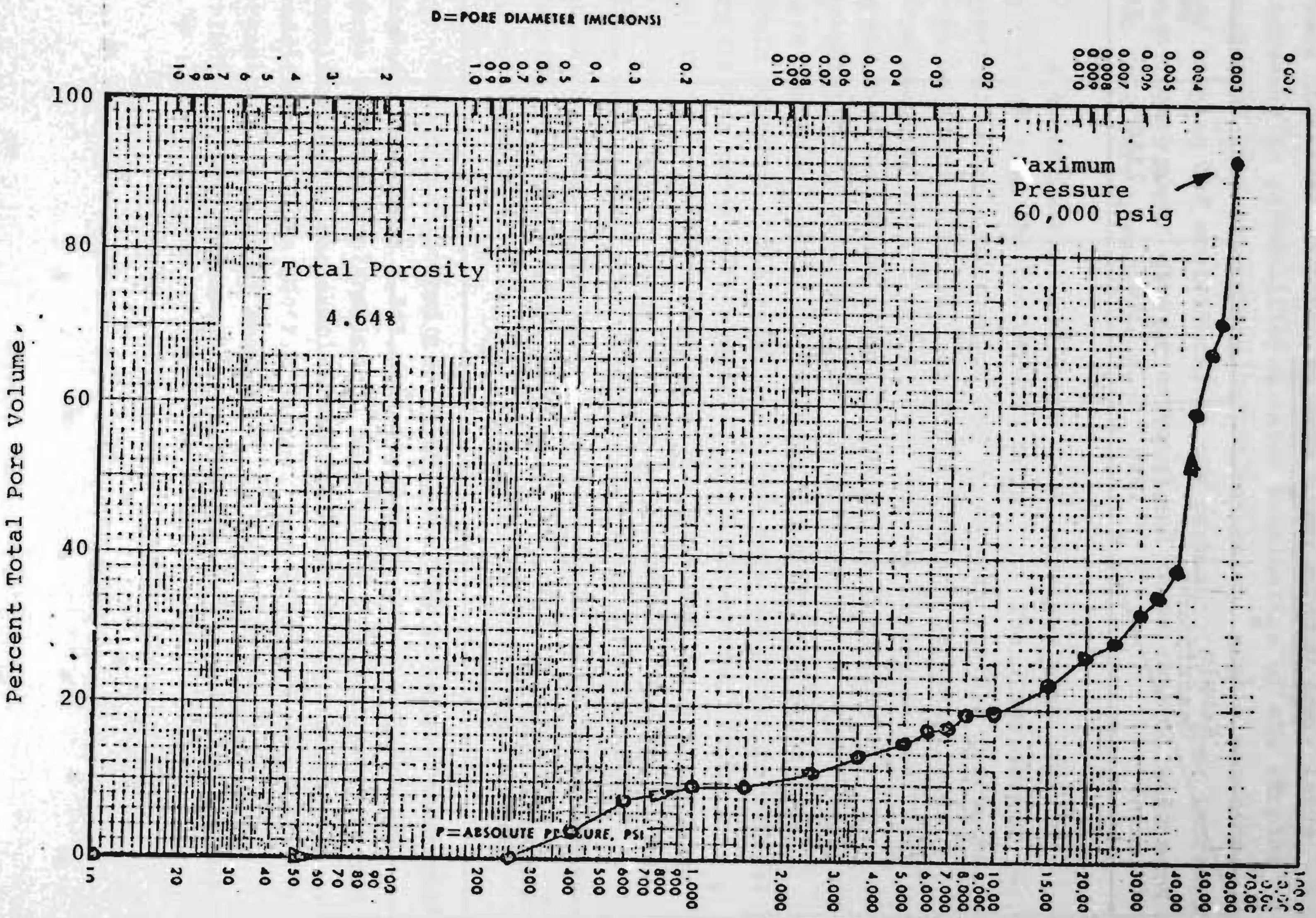


TABLE 2 - PERCENT OF PORES LARGER THAN INDICATED PORE SIZE FOR VARIOUS SHALE SAMPLES

Sample Description / Pore Size (Micron)	Well #1 1320'	Well #1 1340'	Well #1 1380'	Well #3 Sand Pump Sample
100	0	0	0	0
30	0	0	0	0
10	0	2	3	0
3	0	7	7	0
1	0	11	11	0
0.3	3	17	16	7
0.1	5	18	18	10
0.03	8	23	23	17
0.01	11	30	30	25
0.003	40	52	53	93
Skeletal Density (He) (g/cc)	2.527	2.398	2.486	2.474
Apparent Density (g/cc)	2.320	2.289	2.267	2.359
Porosity (%)	8.04	4.50	8.77	4.64

These increases in porosity were accompanied by very large increases in permeability. Later examination of the samples suggested that fracturing during retorting, sample mounting, and testing had contributed to the permeability. Some increase in porosity might also be expected and these considerations led to a more careful study.

A second series was done starting with over 100 plugs from the Dow Chem #3 well. The plugs were examined under a microscope and those with visible fractures were rejected. The initial porosities and permeabilities were measured on all plugs after careful drying at 110°C for seven days to remove adsorbed water. No retorting or dehydration is expected under these conditions. The plugs were rechecked under a microscope and defective plugs were again rejected. The remaining plugs were subjected to careful retortings under air, hydrogen, and water-steam. After retorting, the plugs were carefully examined for a third time and the defective plugs were again discarded. The remaining plugs were again dried carefully at 110°C before testing. It is hard to imagine how such a test could be performed more carefully. These results are the best which can reasonably be achieved testing unconfined samples at room temperature.

The initial porosities were lower than observed in other studies, averaging 1.58% over 98 determinations. There are three possible explanations. Some of the previous work envolved drying the samples rapidly under fairly severe conditions (400 to 500°F). Removal and oxidation of some organic and a loss of some water of hydration may have contributed to an increased porosity. Secondly, this was a fresh core. Gradual oxidation of old core samples may contribute to the porosity. Finally, although the well was physically close to some of the other wells tested (Midland Fee #1, Brazos Smith #1) the cores tested may have come from a relatively non-porous strata.

The porosities measured for the retorted samples were also lower than those measured in the first crude screening experiments. The three retorting methods were comparable and the results averaged 19.1% over 76 determinations. The more severe drying conditions used in the first series should not have an important effect on the porosities of the retorted samples since these samples had already been exposed to much more severe conditions. There is a second possibility. Comparison of the permeability increases between the two series suggests that the samples tested in the first runs were highly fractured. This may explain some of the increased porosity.

3) Permeability

A great number of permeability experiments were run on raw and retorted shale samples in earlier work. The unit of permeability is the Darcy. A solid sample 1 cm thick with a permeability of 1 darcy will allow a flow of 1 cc/sec of fluid having a viscosity of 1 cp through each square centimeter under the action of 1 atm of driving pressure. Values are reported as millidarcies (1000 md = 1 darcy). Values were measured at 23°C using nitrogen or air at a differential pressure of 0.5 atm.

The earliest studies shown in Table 3 were performed using standard oil field practices. Samples were dried under severe conditions (400 to 500°F) and values were reported

Table 3 - Horizontal Permeabilities and Porosities for Antrim Oil Shale Samples From Deep Wells

Source Well	Dow White Fee #1	Brazos Smith #1	Dow Midland Fee #1
Hor. Perm (md)			
mean	2.14	0.76	--
range	0.0 - 25.00	0.0 - 12.0	0.0 - 0.13
no. dets.	39	65	2
Porosity (%)			
mean	5.19	4.2	4.51
range	3.1 - 8.4	2.8 - 5.0	--
no. dets.	40	65	22

Average effective permeability (106 determinations)	1.25 md
Average effective porosity (127 dets.)	4.57%

to the nearest 0.1 or 0.0 md. These values are regarded as zero in oil production. Vertical permeabilities were not detected down to 0.01 md. This is not surprising for a clay mineral since the clay platelets are oriented parallel to the bedding planes. Horizontal permeabilities varied wildly between locations and between samples measured at any one location (Table 3). Very high values may be found if the sample contains one or more natural or induced fractures. Thus, the average value is higher than what is expected in deep shale confined at high overburden pressures.

Some preliminary permeability experiments were also run on retorted samples with porosities increased up to 25 to 30% by oxidation or mild water-steam retorting (see last section). The vertical permeability was increased to perhaps 0.1 md while the horizontal permeability was much improved, averaging 107.5 md in 10 determinations. It is felt that the very high results were associated with fracturing during the retorting, sampling, or drying procedures. A second, much more careful study was performed to eliminate this fracturing effect as much as possible.

The details of the experimental procedure followed in this second study on core samples from the Dow Chem #3 well are described in a previous section. The permeability data was reported down to the limits of the equipment (0.001 md). Earlier work was only reported down to 0.1 to 0.01 md following oil field practice.

No vertical permeability was noted in raw shale samples down to 0.001 md. No vertical permeability tests were made on retorted samples.

The horizontal permeability results are summarized in Table 4 for all those samples surviving the entire examination and testing procedure through final retorting. It is assumed that the samples which failed may have had initial hairline fractures which may have caused the sample to break after repeated handling and thermal cycling. The initial average horizontal permeability was 0.73 md for these 38 determinations. This is in fair agreement with the value of 1.25 md obtained in 106 determinations from plugs cut from other deep wells (Table 3). The results for the retorted samples were independent of the method employed within experimental scatter and these have all been lumped. The average permeability was only 3.41 md over the 38 tested samples compared with an average permeability of 107.5 md measured on retorted samples in the first crude screening experiments. The increased care used in this study in rejecting fractured samples appears to have been most important.

Although the observed factor of five increase in permeability may be correct, a closer examination of the data suggests that the mean values shown in Table 4 are high. The permeabilities of a few samples tend to be large (1 - 10 md) while the bulk of the others are zero or near zero. The mean values are of little use in describing any property in this case. It makes more sense to follow certain sub-groups within the population. Also, the large values may simply be incorrect, the result of fine fractures too small to be seen or affect the mechanical strength of the sample in normal handling.

In 8 of the 38 cases, the permeability decreased significantly on retorting, dropping from an average of

Table 4 - Horizontal Permeability of Samples from Dow Chem #3 Before and After Retorting

Sample Number	Permeability of Raw Shale (md)	Permeability of Retorted Shale (md)		
		oxidized	hydrogen	water-steam
2H	1.390	0.813		
6H	0.140	0.833		
8H	0.750		0.070	
9H	2.520			0.014
11H	0.450	0.681		
12H	8.160		0.071	
13H	5.550		0.070	
15H	0.001			0.008
16H	0.767	0.904		
17H	0.703		0.001	
18H	0.649			2.540
19H	0.117			0.048
21H	0.807	1.075		
23H	0.403	0.689		
25H	0.106		4.140	
26H	2.530	35.80		
27H	0.080	12.32		
29H	1.610		0.001	
32H	0.042		42.400	
33H	0.038			0.312
36H	0.001	0.233		
38H	0.177			0.522
39H	0.252	0.448		
40H	0.001		1.510	
41H	0.080	0.618		
43H	0.094			1.030
44H	0.001			0.105

Table 4 Cont'd.

		Permeability of Retorted Shale (md)		
Sample Number	Permeability of Raw Shale (md)	oxidized	hydrogen	water-steam
45H	0.008	0.283		
46H	0.004	0.043		
47H	0.001		0.008	
48H	0.001			0.048
49H	0.001		0.011	
50H	0.001			0.016
51H	0.009	0.448		
52H	0.075		13.700	
53H	0.005		6.950	
54H	0.005			0.388
55H	0.196	0.303		
Mean Values	0.729	3.407	(all retorting methods)	

2.60 md (range 0.12 - 8.16 md) to only 0.14 md (range 0.0 - 0.81 md). Many of these samples had very large initial permeabilities which dropped to well under 0.1 md after retorting. This behavior seems completely inconsistent with the idea that removal of the organic allows increased permeability through the zones with increased porosity.

It is tempting to recompute the averages throwing out successively lower permeability values as "bad". A logical cutoff for this procedure cannot be established. However, it is reasonable to look at the change in permeability between subgroups where successively higher permeability results have been eliminated. If removal of the organic fraction is helpful, then the impermeable samples should show relative improvement as well as the permeable ones. The ratios of the retorted to raw shale values are generally in the range observed for the mean of all data (Table 5). Factor of four or five improvements may be possible. However, the actual permeabilities expected in confined shales may be less than 1 md even after retorting.

Table 5 - Comparison of Permeability Results for Raw and Retorted Shale Samples Eliminating Successively Lower Ranges of Permeability

Data Set Description (Number of Samples Remaining)	Permeability (md)		Ratio Retorted-to-raw Shale
	Raw Shale	Retorted Shale	
mean all data (38)	0.73	3.41	4.7
eliminate samples over 10 md (34)	0.74	0.74	1.0
eliminate samples over 1 md (23)	0.18	0.31	1.7
eliminate samples over 0.5 md (15)	0.04	0.19	4.8

4) Oxygen Diffusivity Through Retorted Shale

Chromatography provides one method for measuring the diffusivity of a gas through the pores of a solid. Various mechanisms act to "smear out" a pulse of the test gas flowing in a carrier stream through a fixed bed of the solid including diffusion into and out of the pores. The effective diffusivity might be estimated from the residence time distribution using a model presented by Schneider and Smith(8). Unfortunately, calculations for this system suggests that pore diffusion would make only a small contribution to the effection axial diffusivity compared to other effects.

A second approach is to use measured combustion rates to infer the diffusivity assuming that the diffusion of oxygen into the shale is the rate limiting step. Combustion rates measured on 1-3/8" cubes of shale ranged from 14 to 22 hours for 90% conversion of the fixed carbon at 600°C. The reaction is not controlled by the combustion kinetics. Coke burnoff rates on finely divided catalyst particles suggest reaction times on the order of minutes.(3) Therefore, mass transfer must be the dominant resistance. The outside film resistance should be unimportant for these large cubes employed so the primary contribution must come from the diffusion of reactants and products through the shale mass. But, the oxidation equilibrium is far toward the combustion products(9) so it seems unlikely that the concentration of the products in the pores would represent a significant limitation on the combustion rates.

Briefly, the time required for 90% conversion of the fixed carbon is related to the effective diffusivity, D_E, by

$$t_{90\%} = \frac{0.093\ \rho_B R^2}{bD_E C_A} \quad \ldots\ldots \quad (1)$$

where ρ_B is the molar density of solid reactant B, b is a stoichiometric coefficient, D_E, is the diffusivity, C_A is the concentration of gas phase reactant A.(11) Equation 1 applies to spherical particles of radius R. Diffusion normal to the fracture planes is expected to be very low (see next section). Therefore an infinite cylinder is probably a more appropriate geometry. Equation 1 still applies but the constant is increased to 0.167.

The carbon burnoff data is shown in Figure 5. The results are fit nicely using equation 1 with a mean radius of $S/(\pi)^{1/2}$ where S is the length of a cube side ($\pi R^2 = S^2$) and an effective diffusivity of 0.029 ± .006 cm^2/sec.(13) The range corresponds to the extremes in 90% burnoff times (14 - 22 hours). These results can readily be scaled to other cylinder diameters (Figure 6). Mass transfer resistance on the surface and chemical kinetic limitations would become important for very small particles.

Katz predicted a diffusivity of 0.020 cm^2/sec. at 400°C from visual observations on burned out cores.(1) The molecular diffusivity of non-polar gases is proportional to $T^{1.823}$ (50) so the corresponding diffusivity at 600°C is 0.032 cm^2/sec., in excellent agreement with the present value. Estimated values of the diffusivity at other temperatures and pressures are shown in Table 6 assuming that the diffusivity is proportional to $T^{1.823}/P$.(50)

Figure 5 -- Carbon Burnoff For 1-3/8" Cubes Under Air at 600°C

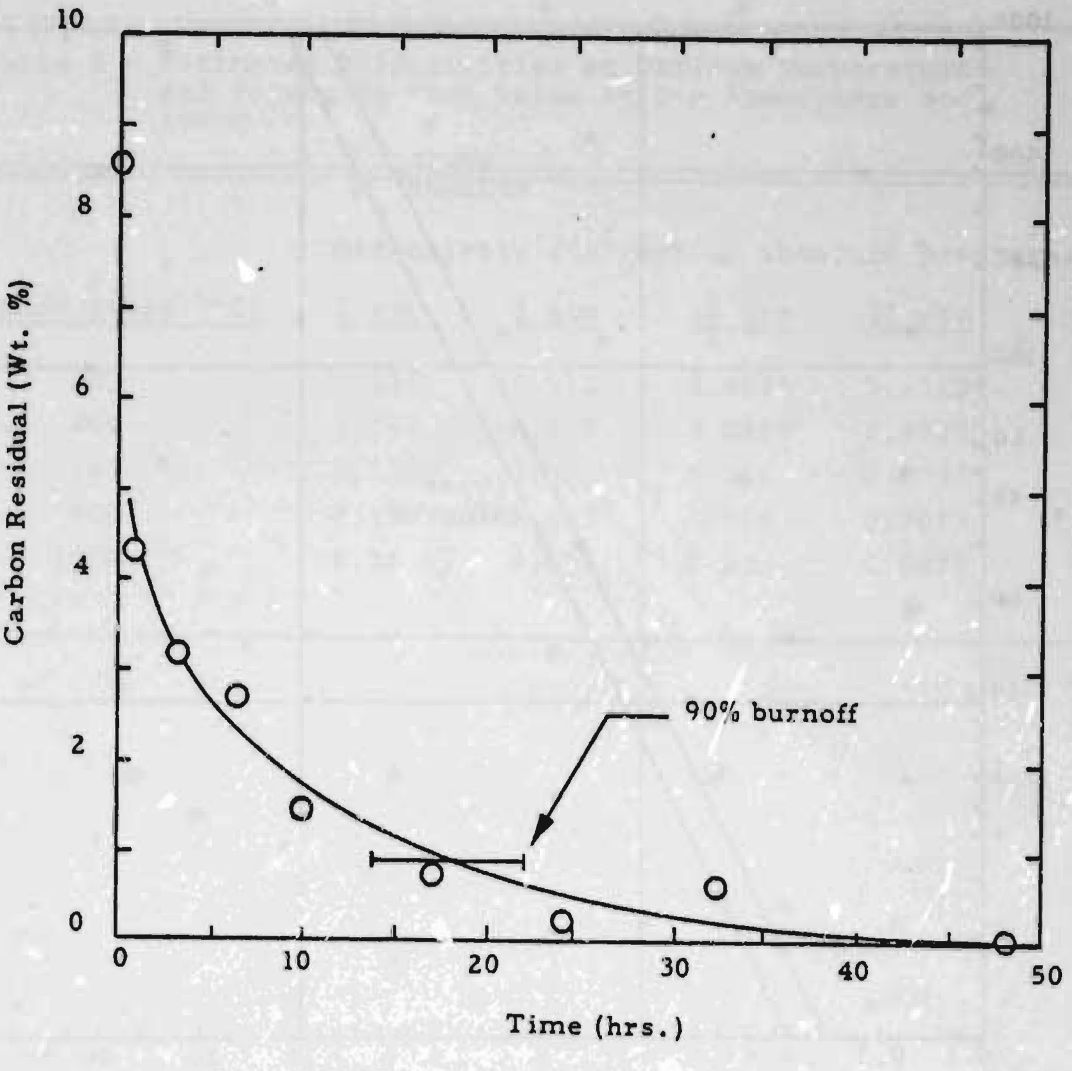
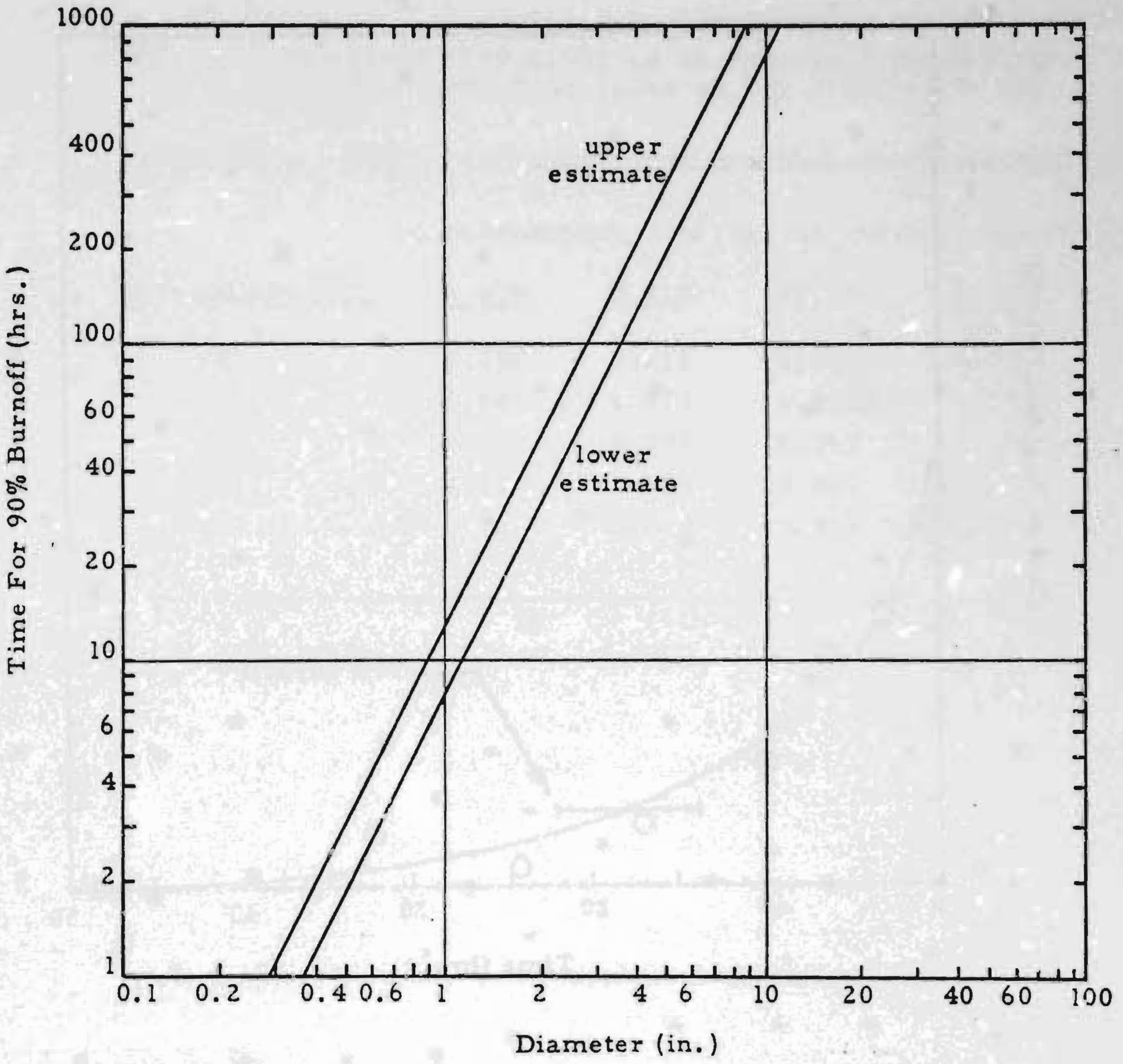


Figure 6 -- Estimated Times for 90% Burnoff for Various "Cylinder" Diameters at Atmospheric Pressure and 600°C



This will be most correct at low pressures and high temperatures where ideal gas assumptions are most accurate.

Table 6 - Estimated Diffusivities at Various Temperatures and Pressures from Value at One Atmosphere and 600°C

	Diffusivity (ft^2/hr) at absolute pressures			
Temperature (°C)	1 atm	3 atm	10 atm	30 atm
200	0.036	0.012	0.0036	0.0012
400	0.068	0.023	0.0068	0.0023
600	0.11	0.037	0.011	0.0037
800	0.16	0.053	0.016	0.0053
1000	0.22	0.073	0.022	0.0073

5) Mechanical properties

Some mechanical property measurements have been collected from earlier work by the Nuclear and Basic Research Laboratory. All experiments were run on core samples with the forces normal to the bedding planes. However, the shale is highly anisotropic. For example, the tensile strength is expected to be much higher for a sample pulled along the bedding planes. Additional experiments would be useful. In the absence of more data, the application of this data to samples stressed along other axis must be regarded as highly speculative.

In one series, Dow's Highway and Construction Materials section found compressive and tensile strengths of 5430 psi (5 determinations) and 64 psi (1 determination) respectively. In a later study, a number of samples from the Dow Chem #3 well (see section G) were tested at the University of Michigan Highway Laboratory (Table 7).(1) The average compressive strength measured over the nine reliable samples (5985 psi) compares well with the value shown above. Young's modulus was measured in compression. The data was non-linear and the intermediate slope values recommended by Katz(1) and reported here are somewhat higher than the load-secant or initial slope values.

Katz considered the problem of estimating the compressibility of the shale at elevated temperature and pressure.(1) The linear compressibility, β_L, is the ratio of the fractional change in length to the applied pressure, or

$$\beta_L = \left(\frac{\text{length change, } \Delta L}{\text{length, } L}\right) \times \left(\frac{\text{area}}{\text{force}}\right)$$

Table 7 - Compressive Strength and Young's Modulus (in Compression) for Antrim Shale (Reference 1)

Sample Depth (feet)	Young's Modulus, E (psi)	Compressive Strength (psi)
2644	840,000	9030
2773	610,000	7960
2881	1,000,000	5950
2903	400,000	4950
2903	510,000	6430
2957	350,000	3690
2668	840,000	4280
2668	420,000	5590
Average values (psi)	620,000	5985

with units of psi^{-1}. It is simply the reciprocal of Young's modulus measured along that axis, or $\beta_L = 1/E$. The volumetric compressibility, β_r, is the fractional change in volume divided by the applied pressure. For any material, $\beta_V = \beta_{Lx} + \beta_{Ly} + \beta_{Lz}$ where the terms of the right are the linear compressibilities along the x,y, and z axis. We only know Young's modulus along the one axis normal to the bedding planes so the volumetric compressibility cannot be determined with any degree of confidence. For the purposes of calculation we might assume that the shale behaves isotropically with regards to this property. Then, $\beta_{Lx} = \beta_{Ly} = \beta_{Lz}$ and $\beta_V = 3/E$. From the data in Table 7

$$\beta_L = 1.6 \times 10^{-6} \text{ psi}^{-1}, \text{ and}$$

$$\beta_V \quad (= 3\beta_L) = 4.8 \times 10^{-6} \text{ psi}^{-1}$$

at room temperature and in the absence of confining pressure.

Data on the compressibility of other minerals from reference 1 is summarized in Table 8.(1) The intermediate load secant values shown should be comparable to the values shown in Table 7. Notice that the linear compressibility of kerogenaceous Marlstone (Western oil shale) is comparable to the linear compressibility of the Antrim calculated from the values in Table 7 (1.6×10^{-6} psi^{-1}). These compressibilities are high compared to other minerals.

Poisson's ratio is the unit contraction in width divided by the unit elongation for an element in tension. Values for shales average 0.20 with a range from 0.15 to 0.27. These may be reasonable values for the Antrim. Actual data would be desirable.

Table 8 - Data on the Compressibility of Other Minerals (References 54, 55)

Mineral Description	Density (gm/ml)	Linear Compressibility,(a) $(=1/E) \times 10^{6}$ (psi^{-1})	Poisson's(a) Ratio
Sandstone			
Pa.	2.16	0.493	0.17
Pa., dolomite	2.20	0.360	0.18
Mich., calcareous	2.60	0.137	0.16
Limestone			
Ohio, fossiliferous	2.69	0.0982	0.25
Marlstone			
Colorado	2.22	0.552	0.29
Colo., Kerogenaceous	1.95	1.12	0.39
Colo., dolomitic	2.10	0.800	0.42
Shale			
Carbonaceous	2.30	0.438	0.27
Dolomitic	2.30	0.578	0.22
Tenn., silty	2.53	0.555	0.14
Mich., siltstone,	2.73	0.132	0.22
siliceous	2.78	0.140	0.17
W. Va., carbonaceous	2.74	0.331	0.15
Antrim Shale			
This Study	2.32	1.6	--

Note (a) - intermediate load-secant values

As shown in Table 9 for various rocks (calculated from values, reference 51), increasing the confining pressure generally decreases the compressibility (Table 9). The difference between the enclosed and unenclosed values results from whether fluids are contained in the pores under pressure. This effect should not be important in raw shale samples due to the relatively low porosity (5% typically). Data on the speed of sound through solids suggests that the effect of temperature on the compressibility of solids confined at high pressure should be small (Table 10).(1) These observations may be useful for estimating the compressibility at high temperatures and pressures.

Values of the thermal expansion coefficient are shown in Table 11 for various unconfined samples at low temperatures. Limited data at elevated temperatures suggests a factor of two increase in the expansion coefficient as the temperature increases from room temperature to 400-500°C (Table 12). The effect of confining pressure may be small (Table 12 for Vinal Haven diabase).

Table 9 - Compressibility of Rocks at Room Temperature and Various Pressures (Reference 51)

Mineral	Pressure	Compressibility x 10^6 (psi^{-1})	
	(psig)	Enclosed	Unenclosed
Granite, Quincy, 100 ft	0	0.522	0.132
	1700	0.277	0.128
	8500	0.175	0.115
Granite, Quincy, 275 ft	0	0.620	0.146
	1700	0.351	
	8500	0.173	
Granite, Rockport	0	0.633	0.135
	1700	0.348	0.129
	8500	0.184	
Norite, Sudbury	0	0.217	0.114
	1700	0.155	0.112
	8500	0.114	0.108
Norite (gabbro) Pa.	0	0.407	0.097
	1700	0.284	0.092
	8500	0.115	0.087
Diabase, Vinal Eaven	0	0.118	0.101
	1700	0.110	
	10200	0.087	
Dunite, Balsam Gap	0		0.077
	1700		0.075
	8500		0.066
Dolomite	0	0.256	0.082
	1700	0.175	0.082
	8500	0.102	0.082
Quartzitic sandstone	0	0.405	0.184
	1700	0.295	0.183
	8500	0.213	0.179
Marble, Vermont	0	0.242	0.096
	1700	0.228	0.095
	8500	0.104	0.087
Limestone, Pa., carbonaceous	0	0.210	0.170
	1700	0.190	0.169
	8500	0.162	0.166

Table 10 - Effect of Temperature on Velocity of Shear Waves at High Pressures
Reference 52

Rock	(a) P Kg/cm	(b) Vo Km/sec	Ratio of Velocity at P & T to velocity at P and 0°C at Indicated Temperatures					
			100°C	200°C	300°C	400°C	500°C	600°C
Quartzite	3000	4.031	.9975	.9948	.9917	.9872	.9806	.....
	4000	4.045	.9980	.9956	.9925	.9883	.9325	.9734
Albitite	3000	3.406	.9922	.9847	.9766	.9661	.9467	.....
Anorthosite	7500	3.712	.9955	.9905	.9850	.9808	.9756	.....
Bronzitite	8000	4.58	.9923	.9846	.9764	.9677	.9584	.....
Amphibolite	5000	4.224	.9942	.9884	.9826	.....	.....	.....
Dunite, N.Z.	8500	4.406	.9833	.9676	.9510	.9358	.....	.....
Dunite, N.C.	6000	4.306	.9872	.9745	.9625	.9500	.9356	.....
Marble	3000	3.483	.9871	.9724	.9572	.....	.....	.....
Granite, Barre	3500	3.59	.9957	.9912	.9870	.9820	.9764	.9625
Granite, Chelmsford	5000	3.596	.9946	.9870	.9755	.....	.....	.....
Granite, Rockport	4000	3.48	.9936	.9858	.9766	.9605	.9371	.9047
Quartz diorite	3000	3.59	.9936	.9874	.....	.....	.....	.....
Diabase, Maryland	3000	3.85	.9895	.....	.....	.....	.....	.....
Gabbro, Mellen	5000	3.758	.9892	.9770	.9623	.9452	.9252	.....
Hornblende - garnet granulite	5000	4.32	.9949	.9878	.....	.....	.....	.....
	6000	4.348	.9950	.9814	.9623	.9429	.9238	.....
Eclogite	5000	4.585	.9942	.9884	.9826	.9768	.9710	.9652

Note a) 1 kg/cm^2 = 14.23 psi

b) Vo = Velocity of shear waves at pressure P and 0°C in Km/sec.

Table 11 - Linear Expansion Coefficients of Various Rocks Over Temperature Interval from 20 to 100°C (Reference 51)

Rock Type	Number of determinations	Average linear Expansion Coefficient $\frac{1 \Delta L}{L \Delta T}$ $({}^{\circ}C^{-1})$ (a)
Granites and rhyolites	21	$8 \pm 3 \times 10^{-6}$
Andesites and diorites	4	7 ± 2
Basalts, gabbros, and diabases	10	5.4 ± 1
Sandstones	10	10 ± 2
Quartzites	2	11
Limestones	20	8 ± 4
Marbles	9	7 ± 2
Slates	3	9 ± 1

Note a) Assumed antrigrade scale

Table 12 - Effect of Temperature and Pressure on Thermal Expansion Coefficient (Reference 53)

T(°C)	Solenhofen Limestone at 1 kg/cm^2 (a)	Vinal Haven diabase (a) at 1 kg/cm^2	Vinal Haven diabase (a) at 10,000 kg/cm^2
0-100	3.2×10^{-6}	6.2×10^{-6}	7.6×10^{-6}
100-200	1.5	9.0	7.2
200-300	5.3	9.8	8.5
300-400	12.5	10.7	10.3
400-500		11.2	11.0

Note a) 1 kb/cm^2 = 14.23 psi

C. CHEMICAL COMPOSITION

A total of 38 elements have been detected in the shale. It is convenient to divide these into largely volatile and largely fixed elements. Volatile elements (C, H, and S) are those species primarily recovered during the retorting process. Fixed elements are thought to remain bound to the spent shale matrix. Organic oxygen and nitrogen, oxygen in bound and adsorbed water, and inorganic nitrates would probably be recovered as well. However, these materials have not been accounted for during the experimental retorting program and the available data is included under the section on fixed elements.

1) Volatile Elements

The data has been organized into four sub-sections covering data on total carbon, inorganic (carbonate) carbon, total hydrogen, and total sulfur.

a) total carbon analysis

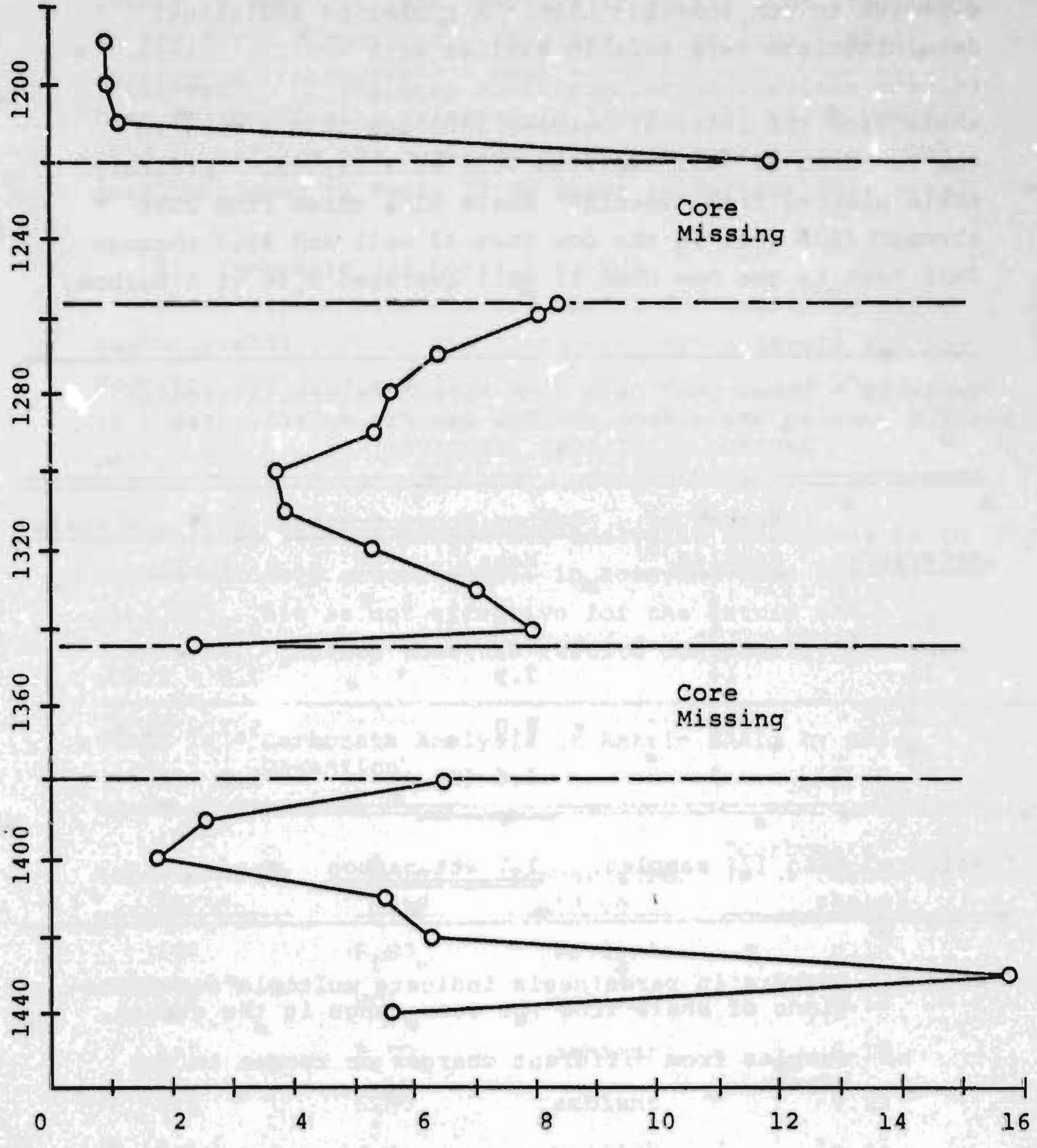
Total carbon analyses have played a key role in analyzing the retorting process. As discussed in the next section, carbonate levels are low so that the total carbon analysis provides a good measure of the product yields (gas, oil and coke) and the residual energy available on the retorted shale. Hydrogen analysis would have a similar utility except for the difficulty is distinguishing between organic hydrogen and the hydrogen associated with adsorbed or bound water.

Total carbon is measured by a combustion method. Samples are burned under oxygen and the carbon dioxide (and water) are trapped and weighed. The method should be good to 0.01 wt % carbon but the actual uncertainty is more like 0.1 wt % carbon due to variations within a given sample. Larger uncertainties are introduced in obtaining representative samples from a given shale mass.

The variation of shale quality through the strata is apparent from Figure 7. Total carbon analysis at 10-foot intervals through the Antrim were measured on a core from Rhoburn #1 in Sanilac County (see Section G). The trends shown appear to be real, although data taken on a finer scale might show more erratic behavior. The shale from 1400 to 1440 feet is interfingered with the Traverse limestone and some of the higher carbon results in this region may be associated with high carbonate concentrations. Similarly, the shale from 1200 to 1220 feet is quite lean and has been dubbed "false Antrim" at this location.

An average of all the data in Figure 7 yields 5.57 wt % C (22 samples). As suggested above, the shale in the upper and lower regions may not be representative. Data over the interval from 1300 to 1400 feet averages 4.55 wt % C (9 samples). Five samples from the top of the shot zone in Rhoburn #3 averaged 5.6 wt % C with a range from 5.2 to 6.3 wt % C. The corresponding depth range in Rhoburn #1 is 1335 to 1343 feet.

Figure 7 - Total Carbon Analysis of Rhoburn #1 Core Samples



How do these results compare with data from other locations? Shale from Dow Bay Fee #2 averaged 7.7 wt % C in 27 samples (Table 13). This shale was selected visually to have a rich, black, homogeneous appearance and might be expected to run somewhat high. A number of additional determinations were made in earlier work

"Special" shale from the interval between 2800 and 2830.5 feet in the Dow Chem #2 well averaged 7.33 wt % carbon. "Ordinary" shale blended from "special" shale plus cores from 2596 through 2800 feet in the Dow Chem #2 well and 2830 through 2965 feet in the Dow Chem #1 well averaged 6.46 wt % carbon.

Table 13 - Summary of Data from Recent Retorting Studies on Shale from the Dow Bay Fee #2 Well (See Section G for well locations)

Reference	Number of Samples[(b)]	Carbon Concentration (wt % raw shale) Mean[(a)]	Carbon Concentration (wt % raw shale) Range
24	1	6.0 (3)	5.9 - 6.2
25	14	7.9	7.0 - 8.4
7	9	8.0	5.1 - 11.8
12	3	6.6 (9)	5.2 - 8.7
Weighted mean (27 samples)		7.7 wt% carbon	

Note a) numbers in parenthesis indicate multiple determinations of shale from the same range in the strata.

b) samples from different charges or ranges in the strata

In summary, it appears that values from 4 to 6 wt % carbon are typical of the entire formation. Discrete bands of much richer and much leaner shales are found. It is possible that shale at our field location in Sanilac County is somewhat lean, especially in the zone fractured in the first experiment. This may not be true. Shale selected for experimental work in past studies may have been systematically selected to "look rich" which would tend to inflate the measured carbon concentrations. The data tabulated in Table 13 is known to reflect this bias.

b) Inorganic (carbonate) carbon

Total carbon balances are useful for measuring hydrocarbon yields only if the inorganic carbon levels are low. However, the determination of carbonates in raw shale is a difficult analytical problem. Even the present infared method may not be entirely satisfactory.

The traditional method for analyzing carbonates is to digest a finely ground sample in acid and trap the CO_2 evolved. This is not effective for the Antrim shale (Table 14). Notice that the results continually increase

Table 14 - Carbonate Analysis on Antrim Shale by Acid Digestion.

Acid-to-Water Ratio	Acid Used	Temperature Range	"Carbonate" Analysis (wt % carbon in raw shale)
1:8	H_2SO_4	ambient	0.14
1:4	HCl	ambient	0.12
1:2	H_2SO_4	ambient	0.19
1:1	H_2SO_4	ambient	0.22
Conc.	H_2SO_4	boiling	7.00

as the acid strength increases. The very high value reported for boiling concentrated sulfuric acid is thought to be due to oxidation of organic carbon under these severe conditions.

A second approach was to pyrolyze ground shale samples under a nitrogen purge and collect the offgases for CO_2 analysis.

Samples were charged into a cold tube furnace. Then the furnace was turned on and the sample heated to final temperature in about 15 to 30 minutes. Peak carbon dioxide evolution occured at about this time and decomposition was generally complete after 90 minutes. This was chosen as the cutoff to minimize CO_2 dilution by the carrier. The results were found to be independent of mesh size for 12 by 20 mesh and 20 by 40 mesh particles. The smaller mesh size was chosen to minimize tailing. The results seem to continually increase with temperature (Figure 8). There may be some evidence for flattening above 1000°C (one point) but the choice of 1000°C as the high temperature limit seems somewhat arbitrary. Shale fusion was a problem at higher temperatures.

A third method was tested which seems to be much more reliable. Infared analysis were run on a mull of the shale using PbSCN as an internal standard.
Data on a variety of Antrim shale samples analyzed with both methods are compared in Table 15. One determination on a sample of Western shale showed 17.9 wt % total carbon and 3.71 wt % carbon as carbonate by the IR method. This agrees nicely with literature data. Two samples of Western shale with 21.1 and 21.9 wt % carbon gave 4.2 and 4.6 wt % carbon as carbonate.(34) The IR results on Antrim ran

Figure 8 - Variation of Carbon Evolved as CO_2 Under N_2 Versus Pyrolysis Temperature

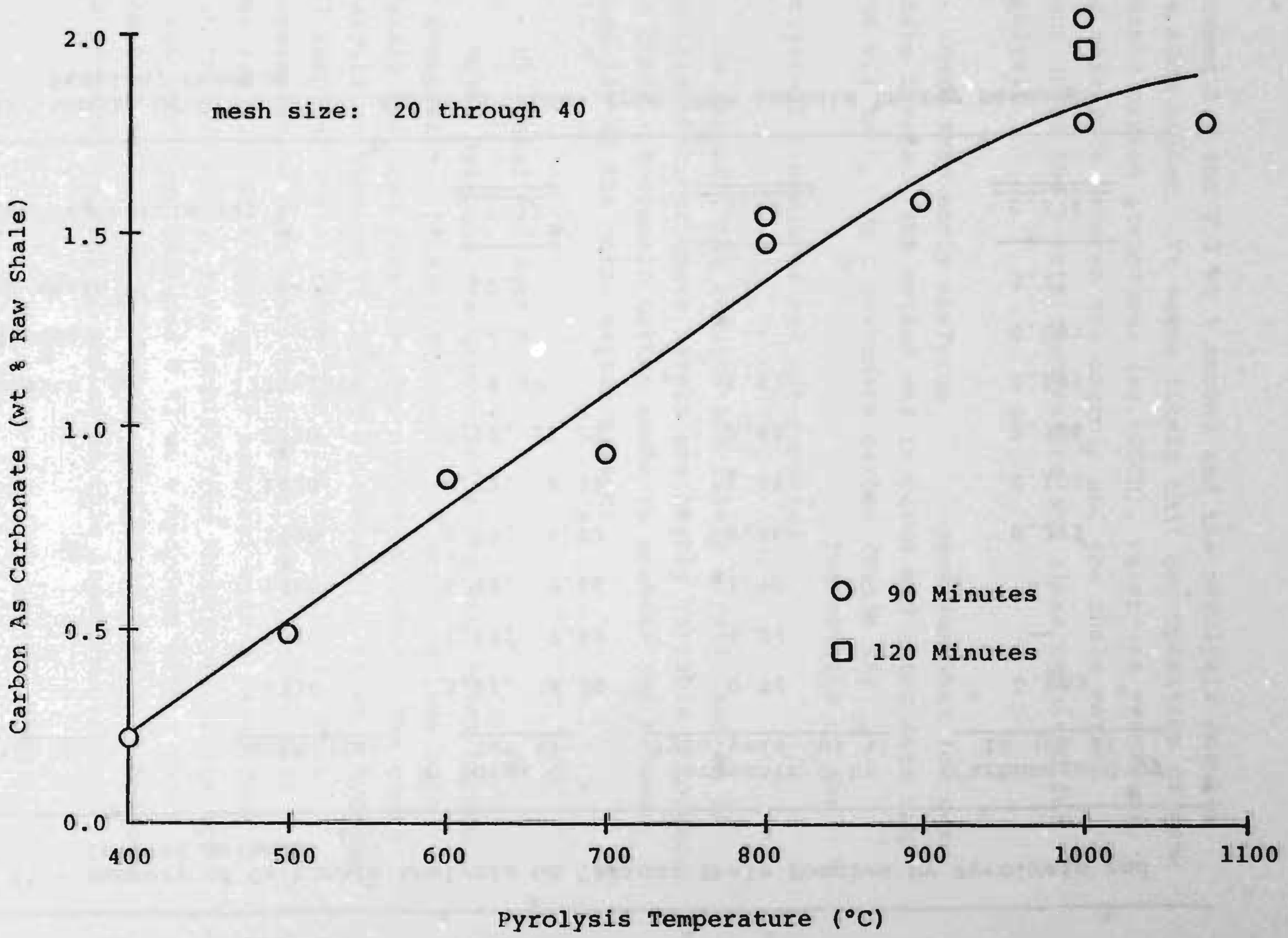


Table 15 - Summary of Carbonate Analysis on Various Shale Samples by Pyrolysis and Infared Methods

Well No.	Depth (ft)	Total C (wt %)	Carbonate C by Pyrolysis (wt %)	Carbonate C by IR (wt %)
1	1310	3.91, 4.36	0.98	0.103
	1340	7.93, 7.98	1.84	--
	1380	6.48, 7.66	1.90	--
	1400	0.65, 0.77	0.96	0.272
	1420	9.72, 8.38	1.69	0.102
	1430	20.92, 11.05	2.43	0.366
4 (composite)	1320-1329	4.90	1.83	0.105
4 (sand pump)	--	6.4	--	0.097
Western shale[a]	--	17.9	--	3.71
Mean Values, Antrim (wt %)		7.22	1.66	0.174

Note a) sample of Green River shale obtained from USBM Laramie Energy Research Station, Wyoming between 0.1 and 0.3 wt % carbon and the pyrolysis results are much higher. It seems likely that decomposition of some organic oxygen structures (eg.•COOH), water-gas reactions, and reactions between the organic and the shale matrix occur under the severe temperature and times required for pyrolysis.

Some very early analyses gave somewhat low carbonate levels. The method was improved and later data ran from 0.1 to 0.7 wt % carbonate carbon (Table 16). The details of the analytical procedures are not reported.

In summary, the results are fairly erratic and it is possible that carbonate levels are highly variable throughout the shale. Inorganic carbon seems to account for between 2 and 10% of the total carbon present.

c) Total hydrogen

Total hydrogen was determined along with total carbon by combustion. Determinations on raw shale include both organic hydrogen plus adsorbed and bound water. The core analysis on Rhoburn #1 (Figure 8) averaged 0.94 wt % hydrogen (22 samples) with a range from 0.36 to 1.7 wt %. More representative data over the interval from 1300 to 1400 feet ran 0.84 wt % hydrogen (9 samples) with a range from 0.36 to 1.20 wt %. Five samples from Rhoburn #3 at the top of the shot zone averaged 0.81 wt % hydrogen with a range from 0.68 to 0.91 wt %. Values of 0.80 to 0.85 wt % hydrogen are probably typcial of shales at this location.

Table 16 - Summary of Carbonate Determinations Obtained

Shale Description	Total C (wt %)	Inorganic C (wt %)	References
"Special" Antrim[(a)]	7.275	0.31	21
	7.37	0.11	
	7.35	0.63	
"Standard Blend" Shale[(a)]	6.42	0.67	21
	6.40	0.70	
	6.55	0.70	
SUR-1	8.095	0.215	
SUR-2	8.525	0.24	

Note a) See Section D1 for complete description.

Additional values were determined on samples from the Dow Bay Fee #2 core (Table 17). The total carbon analysis were high compared to the Rhoburn #1 data and the hydrogen values show a corresponding increase.

Table 17 - Summary of Data from Retorting Studies on Dow Bay Fee #2 Core

Reference	No. Samples	Total Carbon conc. (wt %)[(a)]	Hydrogen Concentration (wt % raw shale) Mean[(b)]	Range
24	1	6.0	0.9 (3)	--
25	12	7.9	1.1	0.9 - 1.2
7	9	8.0	1.0	0.8 - 1.4
12	3	6.6	1.0 (9)	0.9 - 1.3

Note a) See Table 13 for range

b) Numbers in parenthesis show multiple determinations on same samples.

Hydrogen analyses were made in earlier studies. Two determinations on "special" shale (7.33% total carbon) averaged 0.89 wt % hydrogen. Three determinations on opposite "standard blend" shale (6.46 wt % carbon) averaged 0.98 wt % hydrogen. Samples identified as SUR-1 and SUR-2 ran 1.095 and 1.10 wt % hydrogen with 8.095 and 8.525 wt % total carbon. Rich shales are somewhat richer in hydrogen.

d) Total Sulfur

Samples of shale from the Dow Bay Fee #2 well ran 1.5 and 1.9 wt % total sulfur with total carbon analysis of 5.2 and 6.2 wt % respectively.(12) One additional determination gave 3.17 wt % sulfur with 6.35 wt % total carbon (see Table 20). A summary of earlier data from several sources shows 2.68 wt % total sulfur in eight determinations (Table 18). Additional data averaged 2.64 wt % total sulfur over nine analyses with fairly rich shales (Table 19). There seems to be a rough proportionality between the concentration of sulfur and carbon in these samples (Figure 9). This is somewhat odd since pyrites are thought to be the principal source of sulfur. (see Section F).

The average over all 20 determinations is 2.6 wt % sulfur with a range from 1.5 to 4.5 wt %.

2) Fixed Elements

The primary emphasis in this section is on those elements other than carbon, hydrogen, and sulfur which are thought to be largely retained on the shale after retorting. The results for major constituents (greater than 0.1 wt %) are shown in Table 20. Minor constituents are shown in Table 21. The data is organized by groups moving from left to right across the periodic table. A simplified periodic table is attached for convenience. (Figure 10).

The data was taken from two general sources. Sources 1 through 10 taken from earlier work are described in Table 22. These analyses were performed in four series (1-2, 3-6, 7-9 and 10). The elements sought and the methods

Table 18 - Summary of Sulfur Analysis on Antrim Oil Shale From a Variety of Sources

Sample	Source of Data	Total S % wt.
Paxton shale, dried dust free	Battelle	2.9%
#A1 234 Paxton shale, dried	Fowler Huron	2.5%
Battelle's Bulk Paxton (raw shale) sample	Battelle	2.73
Two duplicates Battelles Bulk	Dow	2.92 2.78
Paxton shale, raw Lyon's large chunk	Dow	
Paxton shale, raw same as above duplicate sample	Dow	2.43
Paxton shale, raw		2.21
shale - three	Huron	2.04
locations		2.50
Antrim 2300' Well #83	Dow	4.1
Mean value (10 determinations)		2.7

Table 19 - Total Sulfur Analysis from Retorting Experiments

Shale Description	Total C (wt %)	Total S (wt %)	Reference
Raw Alpena Shale	8.75	4.45	
"Special" shale	7.275	3.425	
	7.37	3.63	
	7.35	--	
"Standard Blend"	6.42	1.93	21
	6.40	2.14	
	6.55	2.06	
SUR-1	8.095	3.00	
SUR-2	8.525	3.095	
Average Values (wt %)	7.42	2.64	

Figure 9 - Variation of Total Sulfur With Total Carbon Analysis in Raw Shale

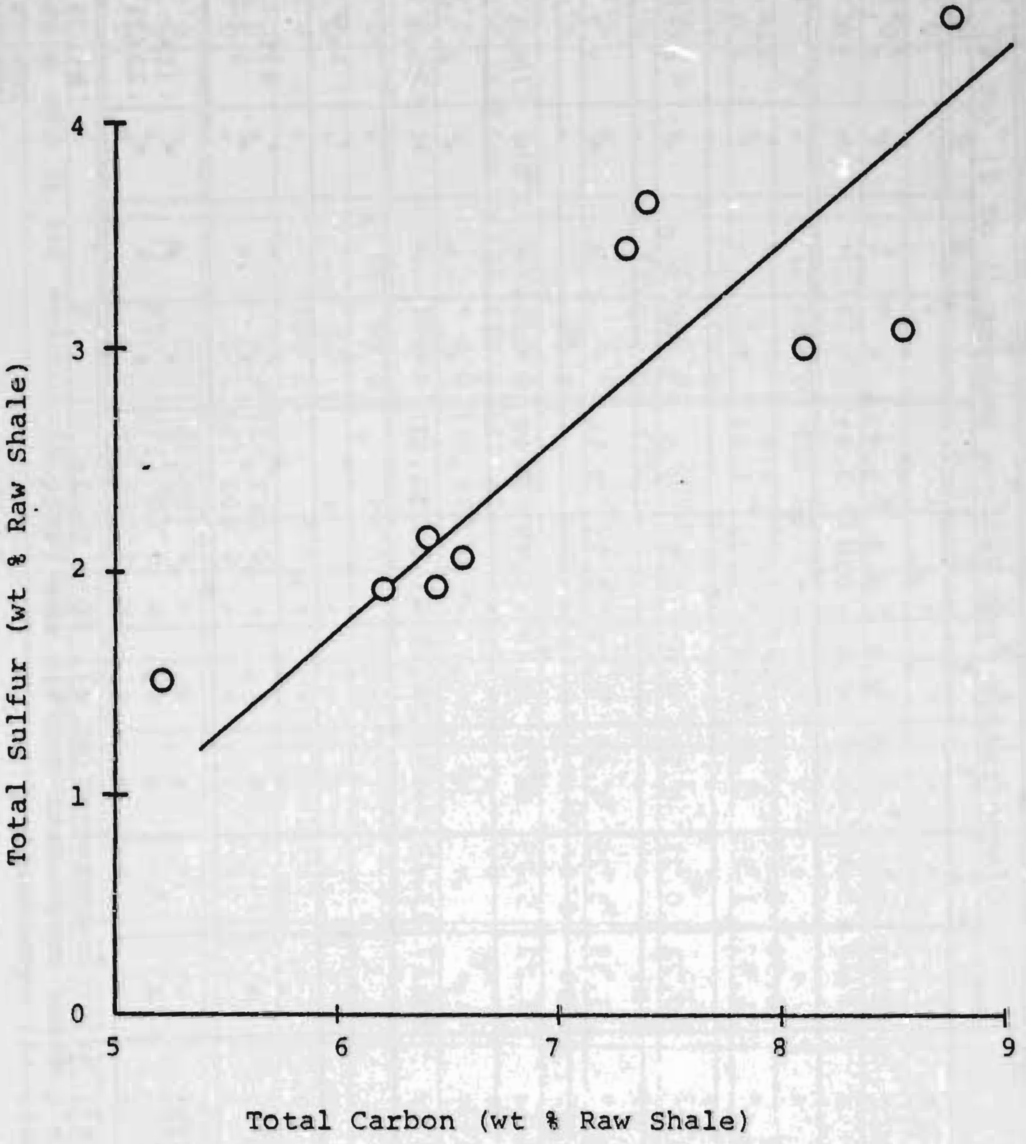


Table 20 - Elements Present More Than 0.1 wt % in Raw Antrim Shale

Group	Element	Concentration From Various Sources (1 of 2) (wt %)											Mean (wt %)
		1	2	3	4	5	6	7	8	9	11	10	
IA	H(4)	*	*	*	*	*	*	*	*	*	0.95	*	0.95
	Na	0.21	0.22	0.69	0.0	0.0	0.33	*	*	*	0.3	*	0.25
	K	3.19	3.15	0.95	0.0	0.0	2.89	*	*	*	3.6	*	1.95
IIA	Mg	0.90	0.87	1.17	1.24	1.07	0.0	*	*	*	1.4	*	0.95
	Ca	1.97	1.95	0.96	1.47	1.31	1.04	*	*	*	1.0	*	1.39
IVB	Ti	0.21	0.21	0.50	0.0	0.0	0.0	0.36	0.0	*	.5(2)	*	0.20
VIII	Fe	3.35	3.29	4.69	2.74	2.96	3.95	*	*	*	3.7	*	3.53
IIIA	Al	5.72	5.79	6.74	7.68	5.88	7.98	*	*	*	9.0	*	6.97
IVA	C(4)	*	*	*	*	*	*	*	*	*	6.35	*	6.35
	Si	23.47	23.48	24.82	25.65	21.03	24.81	*	*	*	30.6	*	24.84
VA	N	*	*	*	*	*	*	*	*	*	1.6	*	1.6
VIA	O	*	*	*	*	*	*	*	*	*	43.	*	43.
	S(4)	*	*	*	*	*	*	*	*	*	3.17	*	3.17
VIIA	H (IA)	*	*	*	*	*	*	*	*	*	(IA)	*	(IA)
	Cl	*	*	*	*	*	*	*	*	*	.22(2)	*	0.22

Total, major components (wt %), this Table	105.39	95.39
Total, minor components (wt %), See Table	0.40	0.38
Total, all components	105.79	95.77

Notes: 1) numbers in parenthesis show number of determinations, 2) see Table for identification of sources, 3) * denotes not measured, 4) see previous section.

Table 21 - Elements Present Less Than 0.1 Wt % in Raw Shale

Group	Element	Concentration in Raw Shale From Various Sources (wt %) See Notes 1-3											Mean (wt %)
		1	2	3	4	5	6	7	8	9	11	10	
IA	Li	*	*	*	*	*	*	0.006 (2)	0.0	*	0.0	*	0.006
	Rb	0.02	0.03	*	*	*	*	0.03 (2)	0.014 (2)	*	0.013	*	0.021
	Cs	*	*	*	*	*	*	0.0005 (2)	0.0	*	0.0	*	0.0005
IIA	Sr	*	*	*	*	*	*	0.003 (2)	0.0	*	0.0	*	0.006
	Ba	*	*	*	*	*	*	0.003 (2)	0.0	*	0.07	*	0.037
IIIB	La	*	*	*	*	*	*	0.0	0.0010	*	0.0	*	0.0003
	Y	*	*	*	*	*	*	*	*	*	0.005	*	0.005
IVB	Zr							0.04	0.04 (2)	*	0.14	*	0.07
VB	V	0.05	0.07	*	*	*	*	0.020 (2)	0.041 (5)	0.0117 (3)	0.03	*	0.037
VIB	Cr	*	*	*	*	*	*	0.006 (2)	0.0	*	0.0	*	0.006
	Mo	*	*	*	*	*	*	0.019 (2)	0.012 (5)	0.0033 (3)	0.008 (2)	*	0.011
	W	*	*	*	*	*	*	0.0034	0.0024 (3)	0.001 (3)	0.0	*	0.0023
VIIB	Mn	0.03	0.03	0.0	0.0	0.0	0.0	0.0	0.06	*	0.017 (3)	*	0.03
VIII	Co	*	*	*	*	*	*	0.002	0.0	*	0.0	*	0.001
	Ni	0.01	0.02	*	*	*	*	0.015 (2)	0.013 (2)	*	0.01	*	0.014
IB	Cu	0.03	0.05	*	*	*	*	0.0002	0.003 (2)	*	0.007 (2)	*	0.018
	Ag	*	*	*	*	*	*	0.0	0.0004 (2)	*	0.0	*	0.0001
IIB	Zn	*	*	*	*	*	*	*	*	*	0.003	*	0.003
IIIA	Ga	*	*	*	*	*	*	0.02 (2)	0.009 (2)	*	0.0	*	0.01
IVA	Pb	*	*	*	*	*	*	0.0	0.013 (2)	*	0.0	*	0.004
VA	As	*	*	*	*	*	*	*	*	*	0.0036	*	0.0036
VIIA	F	*	*	*	*	*	*	*	*	*	0.09	*	0.09
Rare Earth	Th	0.0087	0.0097	*	*	*	*	0.0	0.0005	*	0.0008	*	0.0049
	U	0.0017	0.0019	*	*	*	*	*	0.0	*	0.0024	0.0040	0.0015
	Total, Minor Components (wt %)										0.40		0.38

Notes: 1) Numbers in parenthesis show number of determinations (One implied if not indicated)
2) See table for identification of sources, 3) * denotes not measured.

Figure 10 - Simplified Periodic Table for Identification of Groups in Elemental Analysis

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA
1 H																1 H
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I
55 Ca	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At

Table 22 - Source of Raw Antrim Shale Analysis Used in Elemental Analysis, Tables 20 & 21

Source Number	Well Identification(a)	Depth (feet)	Remarks
1	--	--	600 gm sample from 396 feet of core from various locations and depths
2	--	--	same as above
3	--	--	Paxton quarry, upper 5 feet
4	--	--	Paxton quarry, rusty shale, upper layers
5	--	--	Paxton quarry, blue-black shale, lower layers
6	Dow #5 Salt	2740-2750	
7	Monroe #6	2700-2725	
8	Dow #5 Salt	2590-2890	
9	Dow Ludington #27	1300-1455	
10	--	--	One determination, uranium, shale of unknown origin

Notes a) See Section G for Well locations employed are assumed to have been the same within a series. The analyses were made over a number of years using samples from across the state. It was decided to average the data at a particular location over the depth ranges reported. Duplicate determinations were averaged as well. Where two methods were used, the highest precision data (most significant figures) was employed. Zero values were assumed when 1) no value was reported for the element, and 2) other sources in that series showed non-zero values for that element. Distinguishing between elements not sought and elements not detected zero concentration is critical in calculating average values for the resource. The data identified as sources 1 through 10 was (presumably) based on ashed samples, samples fired in air at 900°C to drive out the volatile and combustible components. Major component data was corrected to a raw shale basis. Minor component data may not of been and these concentrations might be 10 to 12% high in some analysis.

The data shown under source 11 was a recent attempt to get a complete component balance on a typical shale sample from Dow Bay Fee #2 including the volatile components (C, H, S, O and N) to allow a material balance closure around the analysis.

The analytical methods used are summarized in Table 23. this survey used rapid scan methods and is probably less accurate for trace components than some of the earlier work. It did give good overview and fair closure. The material balance was high for the raw shale (106%). Values obtained for silicon and aluminim look high in comparison with sources 1 - 10. The result for oxygen is not very accurate (± 1%). The overall balance seems to give better closure (94%). Unfortunately we only have one oxygen

Table 23 - Methods Used in "Complete" Elemental Analysis, Source 11, Tables 20 and 21

	Method	Source (MDAL)	Approximate Precision (wt %)	Remarks
1)	X-ray Fluorescence	Paul Himes 574 Building	0.001	fast scan of "periodic table" no organic interference
2)	Atomic Emmission	Norm Smith 1603 Building	0.01	plus 2 valence metals (and higher), precision for Si and Al poor, very low results for Fe.
3)	Neutron Activation	Gary Jewett 1602 Building	varies	direct determination of oxygen and nitrogen, and halogens. Very accurate for heavy metals.
4)	Elemental Microanalysis	Russell Nunemaker 574 Building	0.1	combustion methods for C, H and S

determination and inaccuracies in this value cannot be averaged out. Oxygen was calculated by difference to give the "average" analysis summarized in section A.

Tests for heavy metals showed no mercury or selenium down to the limits of detection (1 ppm).

One complete analysis was run on the shale used in source 11 combusted for 96 hours under air at 600°C (Table 24). The various methods used and duplicate determinations are shown (omitted from source 11, Tables 20 and 21. The oxygen analysis is in fair agreement with the value from Table 20 allowing for a 10 to 12% weight loss during combustion (see Section E1). Silicon seems a bit low. Notice that about half the sulfur is retained as discussed in Section I2.

Tests for heavy metals are shown in Table 25 for the spent shale sample. Comparison of this data with the results shown in Table 21 suggests that these materials are largely bound to the spent shale as expected. Selenium and mercury were not present down to 1 ppm, in agreement with the data on raw shale.

3) Fischer Assay

The Fischer assay method measures the water and oil (and generally gas) yield achieved when a sample of shale is heated according to a specified temperature program. It does give some idea of the relative richness of the resource. It is by no means an ultimate yield. Recoveries of 110% of Fischer assay are achieved by flash heating.(31) The gas yield would be useful for indirect heating processes or resource evaluation. However, this data is of little value

Table 24 - Elemental Analysis on Combusted Shale Sample

Group (b)	Element	Concen. (wt %)	Method (a)
IA	H	0.14	4
	Na	0.4	2
	K	4.3	1
	Rb	0.014	1
IIA	Mg	1.2	2
	Ca	0.4	1
		0.5	2
	Sr	0.01	1
	Ba	0.08	1
IIIB	Y	0.007	1
IVB	Ti	0.[illegible]	1
		0.4	2
	Zr	0.02	1
VB	V	0.04	2
VIB	Mo	0.012	1
		0.002	2
VIIB	Mn	0.01	1
		0.02	2
		0.009	3
VIII	Fe	4.4	1
		0.53	2
	Ni	0.01	1
		0.02	2

Group (b)	Element	Concen. (wt %)	Method (a)
IB	Cu	0.01	1
		0.17	
IIB	Zn	0.005	1
IIIA	Al	10.3	1
		9.	2
IVA	C	0.06	4
	Si	30.1	1
		27.	2
VA	N	1.7	
VIA	O	46.	3
	S	1.42	4
		1.5	1
VIIA	H	0.14	4
	F	0.10	3
	Cl	--	1
		0.04	3

Notes a) See Table 23 for identification of methods.

b) See Figure 10 for Groups.

Table 25 - Analysis for Heavy Metals

Element	Fresh Shale (ppm)	Spent Shale (ppm)
As	36	44
Sb	<1	4
Hg	<1	<1
Th	8	10
U	24	33
Se	<1	<1

in determining the gas yield or composition which can be obtained in a partial combustion process where dilution by the carrier gas and combustion of the volatile fractions will occur. For these reasons, carbon and energy balances have more utility than the Fischer assay when a fuel gas is desired as a major product, when the heating program is much different from that used in the assay, or in a directly heated retort where the products are mixed with a carrier.

No Fischer assays have been determined in recent studies. Earlier data by the Nuclear and Basic Research Lab on 10 foot intervals through the Dow White Fee #1 well averaged 10.75 gallons per ton (gpt) of oil and 5.51 gpt of water in nine determinations (Table 26). Additional determinations on shale from other locations is summarized in Table 27. The well locations are summarized in section G. The average over all 24 determinations was 9.58 gpt of oil with a range from 3.79 to 12.54 gpt.

Table 26 - Fischer Assay Results on Core Samples from the Dow White Fee #1 Well

Depths (H)	Oil gal/ton	Water gal/ton	Weight loss assumed to be gas - grams
1519.5-20	12.58	7.19	1.8
1529.5-30	4.72	7.67	Not determined
1539.5-40	11.78	4.79	2.04
1549.5-50	9.32	5.27	1.45
1559.5-60	13.23	5.27	2.08
1569.5-70	11.19	4.55	1.59
1579.5-80	9.56	4.79	1.42
1589.5-90	9.16	5.03	1.1
1600.5-01	15.53	5.03	2.14
Mean (gpt)	10.75	5.51	--

Table 27 - Fischer Assay on Antrim Shale Samples from Various Locations

Location	Mean Fischer Assay (gpt of shale)	Number of Determinations
Paxton quarry, Huron Cement Co.	11.10	6
Dow Canada - 2A	5.79	2
Brazos-Smith #1	8.02	6
Dow-White Fee #1 (Table 24)	10.75	9
Brazos-Midland Fee #1 (Composite)	6.81	1
Mean (24 determinations) (gpt)	9.58	24

D. THERMAL PROPERTIES

The purpose of this section is to summarize data collected on the heat of combustion, specific heat, and thermal conductivity or thermal diffusivity of Antrim oil shale.

1) Heat of Combustion, ΔH_c

The heat of combustion of raw and spent shale is of primary concern in evaluating the energy recovery achieved in any process. One determination on a raw, lean shale (5.2 wt % carbon) gave 960 (± 140) Btu/#. Data obtained in earlier studies on samples assaying 8.095 and 8.525 wt % total carbon showed 1730 (± 20) and 1770 (± 40) Btu/# respectively. Dividing the heat of combustion by the carbon concentration gives 18500, 21400 and 20800 Btu/# of carbon which seems reasonable in comparison to other high carbon fuels (eg. coke, coal). Averaging these three values, the heating value can be estimated from the carbon concentration allowing about 20,000 Btu/# of carbon. More data would be useful here.

Eleven additional determinations are summarized in Table 28. The average value over all 14 determinations is 1570 Btu/# of shale. The two extreme values shown in Table 28 seem out of line. Elimination of these values drops the average value to 1500 Btu/# of shale. At 20,000 Btu/# of carbon, this would correspond to an average carbon concentration of 7.5 wt % which seems somewhat high but is within measured values.

Table 28 - Heats of Combustion of Antrim Shale Samples from Various Locations

Shale Source	Sample Number	Heat of Combustion (Btu/# of shale)
--	193-44-1	1220
--	193-44-6	1710
--	193-44-7	1600
--	193-44-8	1660
Dow Smith #1 Well	--	1160
Dow Smith #1 Well	SSR-242-615	1564
Dow Smith #1 Well	--	1768
Dow Smith #1 Well	--	265 (a)
Dow Smith #1 Well	SSR-237-353	1492
Dow Smith #1 Well	--	1383
Paxton quarry	SSR-215-839	3704 (a)
Mean this data		1590 Btu/# of shale

Note a) Suspect values, eliminate in final average

2) Specific heat, c_p

The specific heat of a shale sample taken from 2789 to 2789.5 feet in the Dow Smith #1 well was measured in the Thermal Lab over the temperature range from 25 to 150°C (Table 29). Ground samples of raw shale and shale heated 6 hours at 200 to 250°C were run. The heat capacity of the dried shale appears much lower than the raw shale and is nearly constant over the temperature range shown. The difference is due to the volatilization of water which appears to start at about 80°C. Devolatilization of the organic fraction and removal of some hydrated water may have occured under the conditions used to dry the sample. Pyrolysis effects should be negligible at these low drying temperatures. Since volatilization was occuring at the higher temperatures, the effective heat capacities are undoubtably a function of the heating rates employed. Only the lower temperature data on the raw shale has a clear meaning.

Later work was done on "spent shale" (presumably retorted in some fashion to remove the volatile fraction). Data is shown over the temperature range from 25 to 500°C (Table 30). Data obtained on a shale with similar composition is shown for comparison. Excellent agreement is obtained.

3) Thermal diffusivity and conductivity

The thermal diffusivity, α_T, is simply $k/\rho c_p$ where k is the thermal conductivity, ρ is the density, and c_p is the specific heat. These last two properties are known from alternate determinations so that knowledge of either the thermal diffusivity or the thermal conductivity suffices

Table 29 - Specific Heat of Raw and Dried Antrim Shale at Low Temperatures

	Heat capacity, c_p (Btu/#-°F)		
Temperature (°C)	Raw Shale		Sample dried 6 hours, 200-250°C
29.2	.190	.190	.175
39.1	.195	.196	.181
49.0	.198	.202	.186
59.0	.197	.201	.191
69.0	.192	.198	.193
79.1	.185	.192	.194
89.2	.192	.197	.196
99.3	.210	.216	.194
109.4	.236	.239	.192
119.6	.267	.271	.188
129.8	.290	.302	.185
140.0	--	--	.184
150.3	--	--	.185

Table 30 - Specific Heat of Spent Shale at High Temperatures

Temperature (°C)	Specific heat, c_p (Btu/#-°F) (Antrim)	Reference 36, (Shale)[(a)]
25	0.186	0.190
50	0.198	0.199
100	0.218	0.211
150	0.235	0.224
200	0.248	0.237
250	0.260	0.248
300	0.268	0.259
350	0.273	0.266
400	0.275	0.273
450	0.275	0.273
500	0.275	0.281

Note a) Points taken from graph to nearest 0.002 Btu/#-°F.

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THE PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION OF ANTRIM OIL SHALE

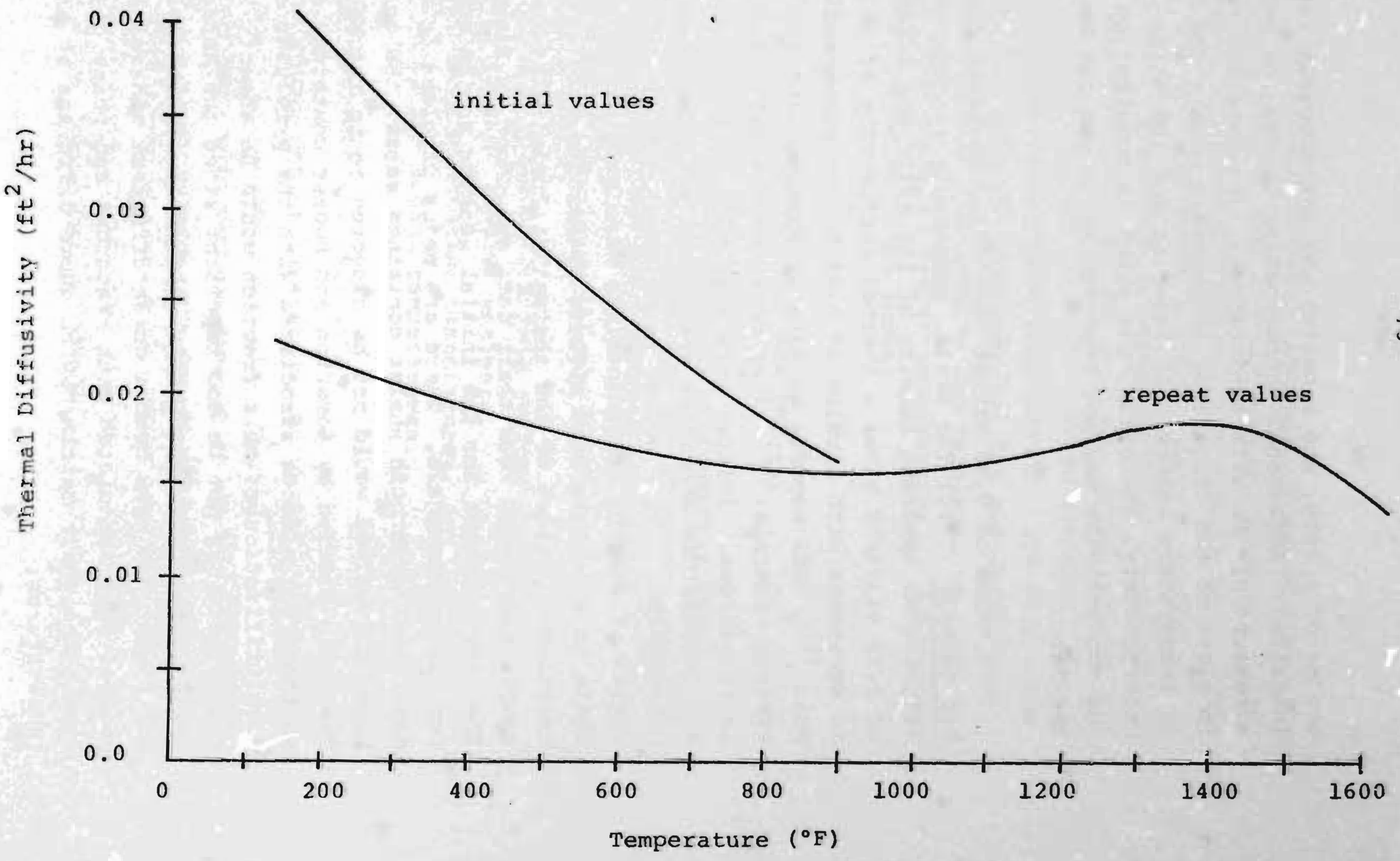
to determine the other. Two major observations are in order. First, the specific heat of a raw or partially retorted shale sample includes contributions from devolatilization of water from the pyrolysis and devolatilization of the organic fraction. Thus, it may be a function of the past history of the sample and the heating program used to determine the heat capacity. Even the heat capacity of a spent shale sample may include both irreversible and reversible heat affects associated with changes in the mineral substrate at very high temperatures. Secondly, the shale is not isotropic with regards to many of its properties (eg. permeability). In particular, the parallel orientation of the mica platelets (See Section G) should make the conductivity normal to the bedding planes much different from the conductivity along the planes. A similar situation occurs with Western shales. Barnes and Ellington assume that the conduction through the planes is only 71% of the value measured along the planes.(40) Application of this factor to the Antrim would be highly speculative since the shales are mineralogically quite different.

Two attempts have been made to measure the conductivity in raw shale along the bedding planes using radial conduction through cylindrical core samples cut normal to the planes. In one unsteady state experiment, core samples were drilled out along the centerline and a thermocouple was installed. The cores were simply placed in a muffle furnace preheated at 500°C and purged with nitrogen to avoid ignition of the samples. Some experiments were compromised when the cores split. Some reasonable data was obtained, but the thermal conductivities were not calculated and the data was lost.

A second steady-state experiment was run in earlier studies. A 3/4" diameter hole was drilled down the center of a core, and a heater and thermocouple were installed. Additional thermocouples around the perimeter gave a measure of the skin temperature. The data was reported in plots of the centerline temperature versus the difference in temperature between the interior and the skin. Unfortunately, the heat input which is required to calculate the conductivity was not reported so no use can be made of the data.

A value of 0.85 Btu/ft^2-hr-°F/ft was taken from Brown, <u>Ore Genesis</u> (1918) for shale, presumably at room temperature. Assuming an apparent density of 145 #/ft^3 and a heat capacity of 0.19 Btu/#-°F gives a thermal diffusivity of 0.031 ft^2/hr in agreement with a value of 0.03 ft^2/hr recommended by Katz.(1) Katz reports on data by Somerton and Boozer on various minerals.(42) They measured thermal diffusivities in two series. Initial runs were made to 1800°F to locate any temperature anomilies associated with reactions (eg. dehydration, to quartz transition). Then a second series of soaking determinations were made on the spent shale to eliminate heat effects associated with reversible reactions. Values of the thermal diffusivity of a shale sample calculated from their data are shown in Figure 11. The results shown for the initial heating may be appropriate for raw Antrim shale. There are major problems in using this data. Although both shales contained water, the quantity and bonding involved would not be expected to be the same. The shale studied by Somerton and Boozer contained no organic so that heat effects associated with the pyrolysis and devolatilization of this fraction would be absent. These two effects may not be too important since the Antrim is quite lean. More importantly, the shale studied by Somerton and Boozer may have been a quite different mineral so that heat effects associated with reactions and phase changes within the shale matrix may be quite different at high temperatures.

Figure 11 - Data On Thermal Diffusivity of Shales (Reference 42)



This last problem is most important in attempting to use the repeat run data to estimate the thermal diffusivity of spent shale. At high temperatures, the data is quite flat from 500 to 1500°F and shows a slight maximum at 1400°F associated with reversable reactions occuring within the mineral. This behavior was not typical. Other materials show a continuous decline to about 0.45 to 0.6 times the value at 200°F at temperatures over 1000°F. The data shown in Figure 11 was used to select values for the diffusivity up to 500°C (932°F). The results are tabulated in section A. Use of this data at still higher temperatures is highly speculative for the reasons cited above.

E. EFFECTS ON HEATING

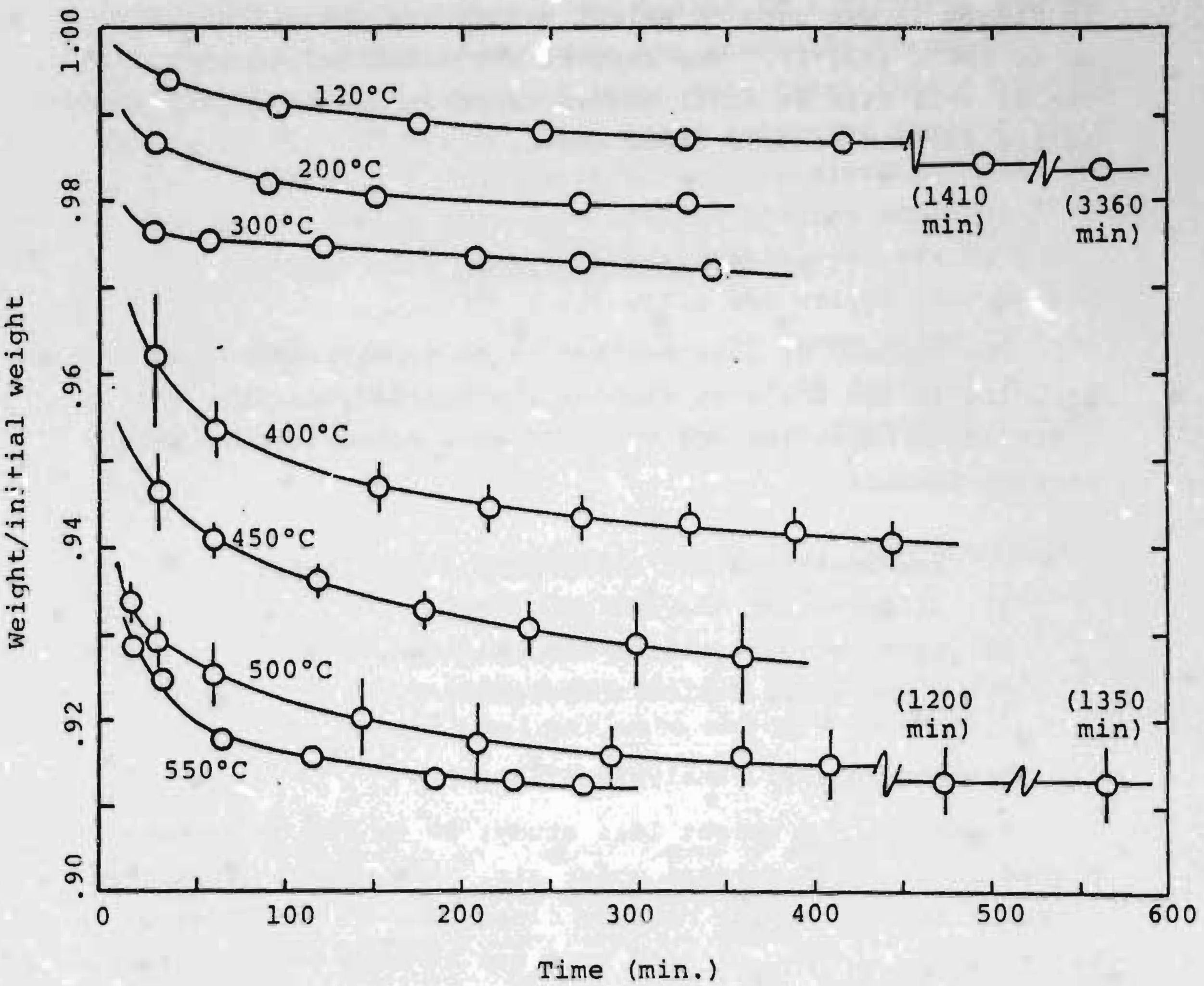
The purpose of this section is to summarize changes occuring in the shale as samples are heated under air and inert atmospheres (He and N_2). Effects summarized in this section include

1) thermogravametric analysis (weight loss),
2) differential thermal analysis,
3) spontaneous ignition temperatures, and
4) spent shale fusion temperatures.

1) Thermogravametric analysis (TGA)

In one simple weight loss study, 80 to 100 gm samples placed in a muffle furnace under air. The samples were semicircular fragments with minimum dimensions on the order of 0.8 to 1.0. Two samples were run at each temperature. The results are shown in Figure 12. There was no clear plateau at 120°C, even after 3360 minutes (2.33 days). Runs up to 300°C showed similar behavior. There was a sudden

Figure 12 - Weight loss verses Time for 80 to 100 gm
Samples at Various Temperatures



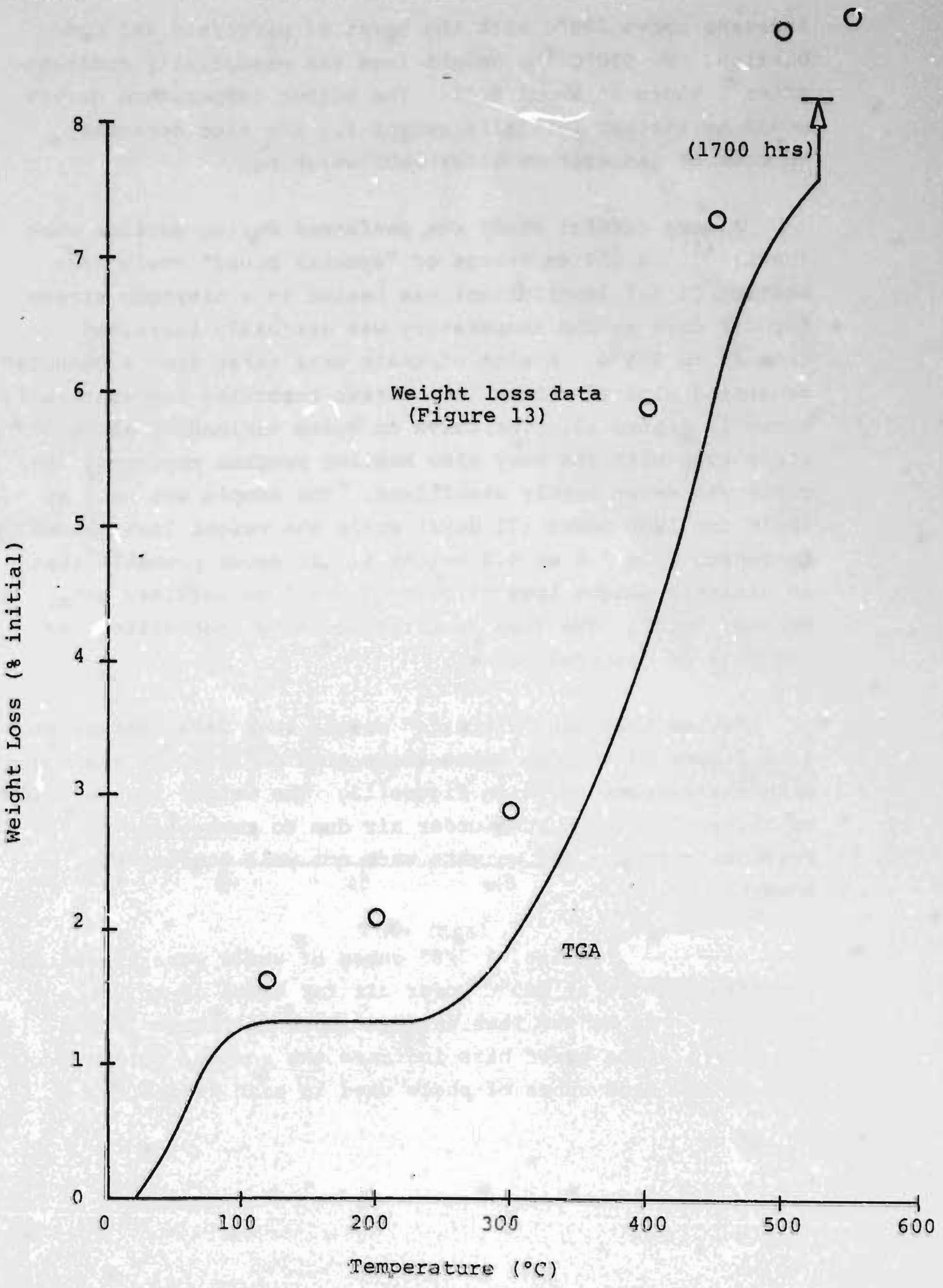
increase above 300°C with the onset of pyrolysis and combustion. By 550°C the weight loss was essentially constant after 5 hours at about 8.7%. The higher temperature curves would be steeper initially except for the time necessary to come to temperature after each weighing.

A more careful study was performed during earlier work A 650 gm charge of "special blend" shale (see Section C1 for description) was heated in a nitrogen stream for 268 days as the temperature was gradually increased from 25 to 525°C. A plot of their data taken from a computer generated plot of weight loss verses retorting temperature is shown in Figure 13. The curve is quite misleading above 300°C, since even with the very slow heating program employed, the curve was never really stabilized. The sample was held at 525°C for 1700 hours (71 days) while the weight loss gradually increased from 7.6 to 8.2 weight %. It seems probable that an ultimate weight loss of over 8% could be obtained at perhaps 400°C. The time required would be prohibitive and the data of doubtful value.

Notice that the "ultimate" weight loss data extrapolated from Figure 12 at long times shows good qualitative agreement with the results shown in Figure 13. The weight loss should be higher for these runs under air due to combustion of the residual carbon. The weights were not well stabilized, however.

In a third series, 1-3/8" cubes of shale were placed in a muffle furnace at 600°C under air for times up to 96 to 98 hours. The weight loss data is shown in Figure 14 for two series. The error bars indicate the scatter obtained between the four cubes of shale used in each series. The

Figure 13 - Thermogravemetric Analysis on Antrim Shale



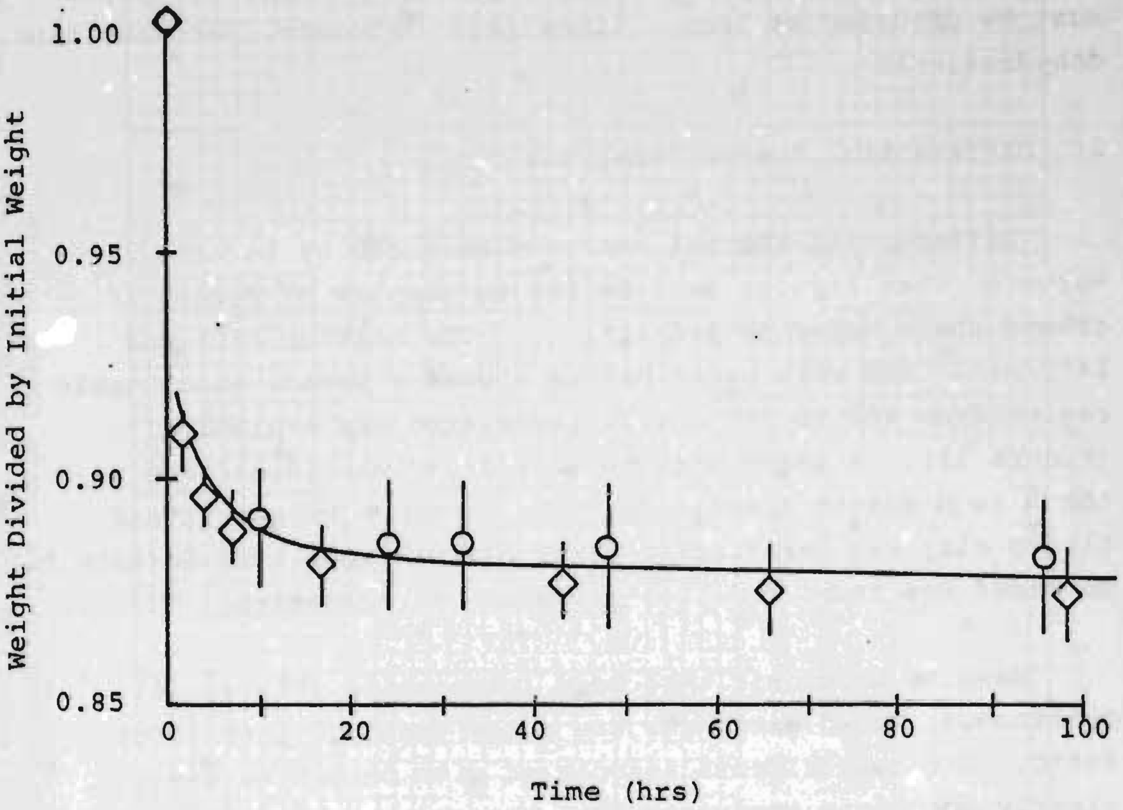


Figure 14 - Weight Loss Data For 1-3/8" Cubes of Shale
Placed in a Muffle Furnace at 600°C Under Air

weight losses are higher than the high temperature results shown in Figure 12 due to differences between the shales and the longer times envolved for the runs at 600°C. The final weight loss was about 13% in good agreement with values of 12.05 and 12.13 wt % obtained in previous work on samples of "standard blend" shale combusted at 900°C.

It is interesting that the weight appear to decline continuously in Figure 14 at very long times. Residual carbon levels were less than 0.1% after 50 hours. Other reactions must be occuring at longer times (eg. carbonate, decomposition, dehydration).

2) Differential thermal analysis (DTA)

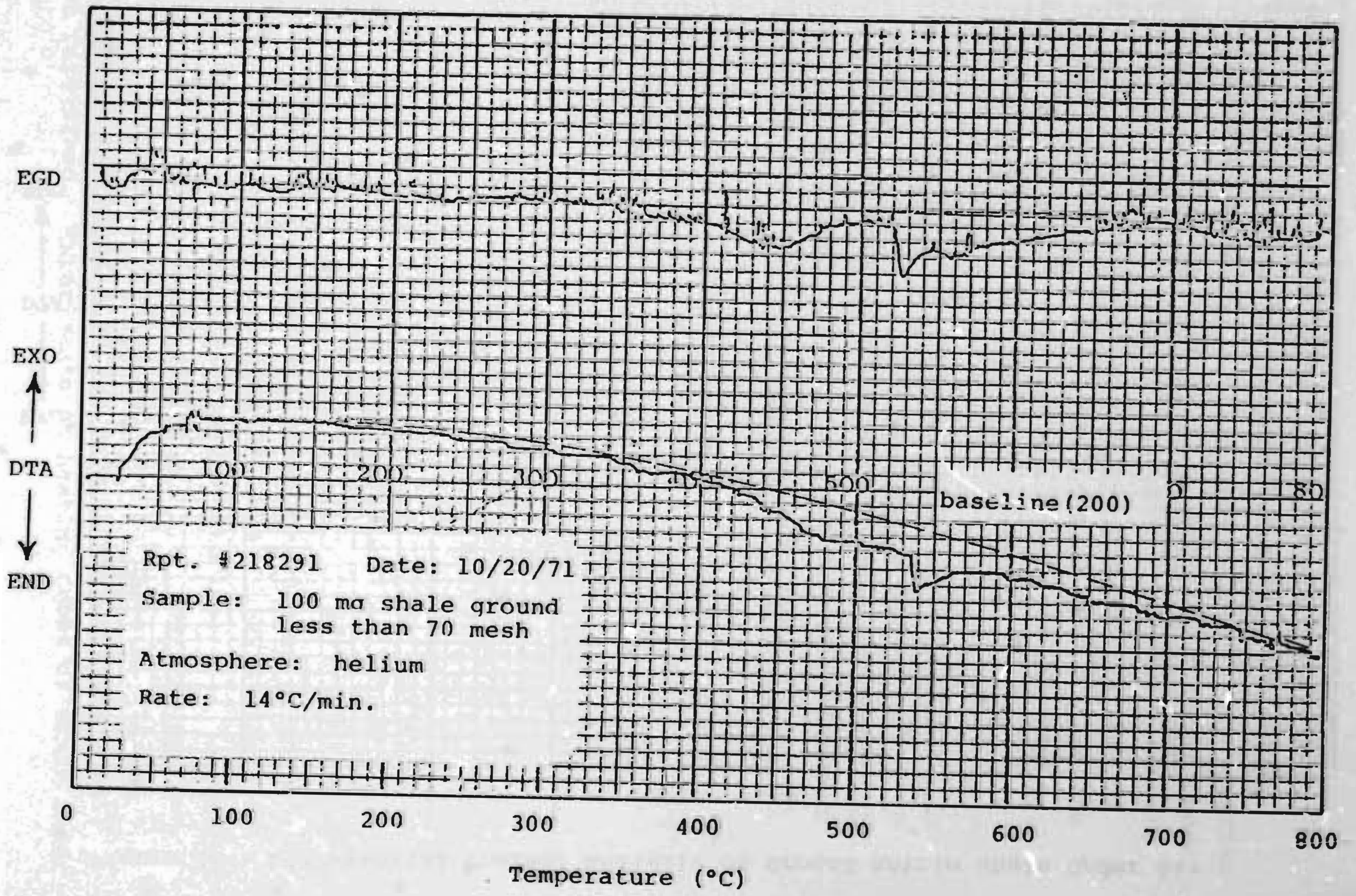
Differential thermal analyses were run on 100 mg samples of finely ground shale under He and air. The heating rate was 14°C/min. The work under helium showed a broad, endothermic region from 400 to 700°C with associated gas evolution (Figure 15). A sharp endotherm at 540°C was identified as the α to β quartz transition. The presence of quartz and illite clay was verified by x-ray diffraction. (See Section F.) No proof was found for loss of waters of hydration.

Results under air were more interesting (Figure 16). Continuous, broad exotherms are noted from 200°C to about 660°C. The heat effects associated with oxidation are clearly much more important than the endothermic cracking reactions and product vaporization.

3) Auto-ignition temperatures

The auto-ignition temperature of shale is not a simple property of the shale alone. Shale ignition probably evolves

Figure 15 - Differential Thermal Analysis and Evolved Gas Detection on Ground Antrim Shale Under Helium



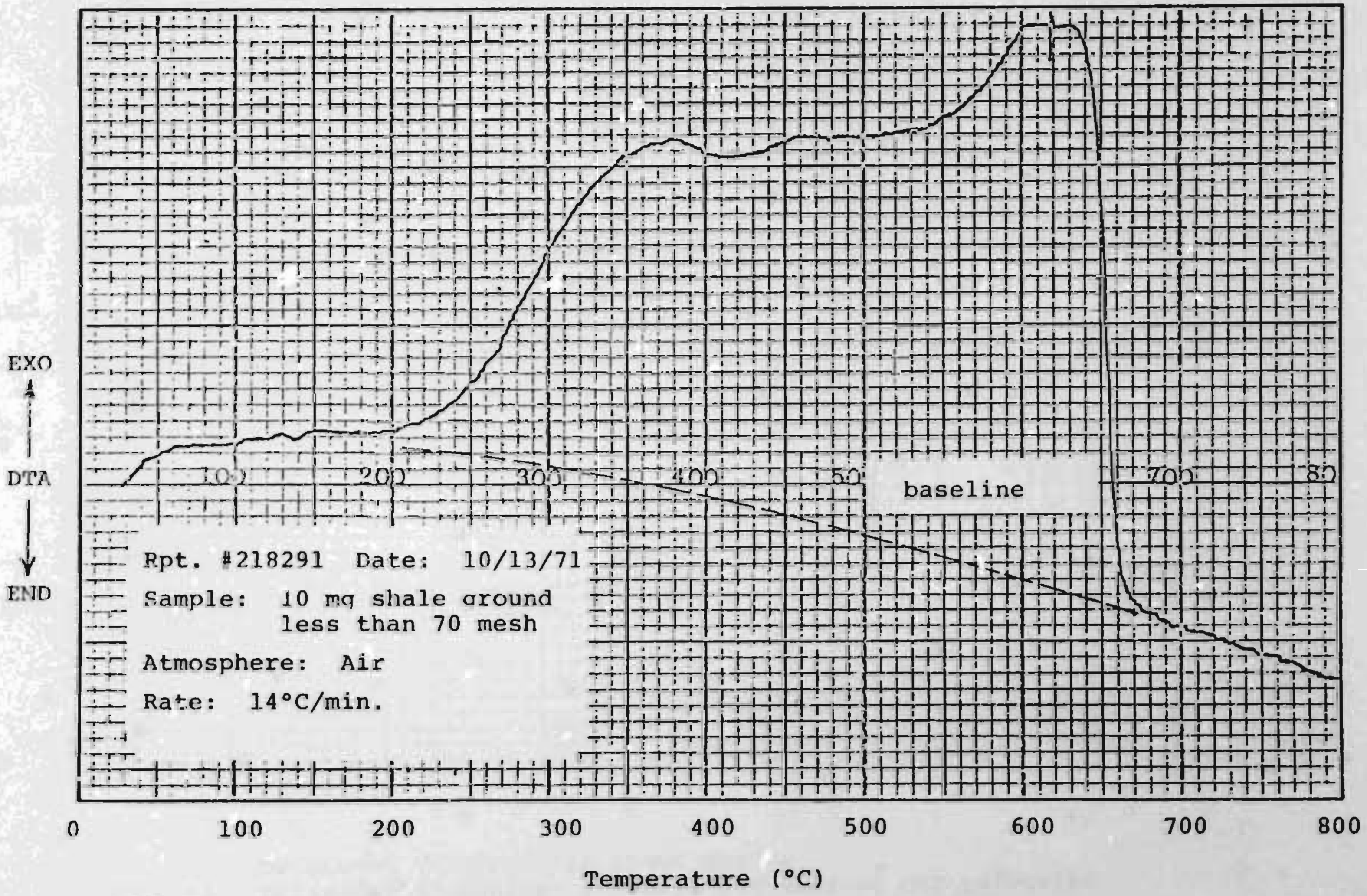
Rpt. #218291 Date: 10/20/71

Sample: 100 mg shale ground less than 70 mesh

Atmosphere: helium

Rate: 14°C/min.

Figure 16 - Differential Thermal Analysis on Ground Antrim Shale Under Air



the combustion of gases, oils, and tars evolved during heating. Some typical hydrocarbon ignition temperatures are summarized in Table 31. This data suggests that ignition could occur at temperatures down to perhaps 250°C if higher hydrocarbons are evolved rapidly enough to form a flammable mixture in air. This in turn evolves the surface area of the sample (per unit volume), the rate of heating, and the mixing of air and vapors around the sample in addition to the temperature.

Table 31 - Auto-ignition Temperatures for Typical Hydrocarbons (Reference 48)

Material	Auto-ignition Temperature (°C)
Alkanes	
Methane	630
Propane	480
Pentane	275
Regular gasoline	280
Kerosene	255
Parafin	245

Two types of ignition experiments have been performed. The first envolves the ignition of large chunks of shale rapidly heated in a furnace. Earlier studies suggested auto-ignition temperatures of 545 and 570°C for raw and retorted shales. The method used in unknown. Large core samples placed in a muffle furnace at about 500°C will burst into flame. Experiments on heating cubes of shale under air showed spontaneous ignition at 500°C at sufficiently high air rates. Ignition was not achieved under low air rates. All this data seems to suggest ignition temperatures in the range of 500 to 550°C for raw shale. The actual values would be expected to be a strong function of the test employed.

The situation is much different in a partially retorted bed of fine shale (mean particle diameter 0.24").(7) In one experiment, a 33" deep bed was burned out about half way. Then the air was turned off and the bed allowed to cool to about 60°C. The bed could be re-ignited when the temperature about 2" downstream of the original flame front location reached 300 to 310°C. Apparently, ignition occured in the tars distilled out ahead of the hot zone. This range of auto-ignition temperatures for partially retorted shale was confirmed repeatedly in alternate heat and sweat cycle operation in packed beds. Similar effects are expected in the field although the actual temperatures required may be much different in systems with radically different surface to volume ratios.

4) Ash Fusion Temperatures

Cubes of shale placed in a muffle furnace at 1000°C showed some thermal cracking but no fusion or sintering. The edges remained very sharp. Experiments were also done placing slabs of shale at various distances from methane/O_2 torch. The surface temperature was measured with an optical pyrometer.

The surfaces seemed intact at 1210°C but showed bubbling and glazing within minutes at 1230°C. One coal-type ash fusion test was run in earlier studies. A rich sample from the Paxton Quarry (3704 Btu/#) was used. The results shown in Table 30 seem consistent with the more qualitative tests summarized above.

Table 32 - Ash Fusion Temperatures for Antrim Shale

Initial deformation	1120°C (2046°F)
Soft point	1175°C (2147°F)
Fluid point, above	1433°C (2611°F)

F. MINEROLOGY AND GEOLOGY OF THE ANTRIM

The following description of the resource geology was taken from Reference 21.

Geology

"The Antrim shale is a black, bituminous shale deposited some 260 million years ago in a shallow marine sea which covered much of the east central part of the contenent during late Devonian and early Mississippian time. Other black shales, stratigraphically related and lithologically similar, are found in Illinois, Indiana, Tennessee, Kentucky, Ohio, Pennsylvania and New York. In Michigan, the black shale interval includes the black Sunbury and the Antrim with an intervening sand and gray shale wedge of Berea-Bedford in the eastern part of the lower peninsula. In the western part, there is a facies change from black shale to the gray-green shales of the Ellsworth which interfinger with the black shales in the central part of the state. The Ellsworth thickens to the west.

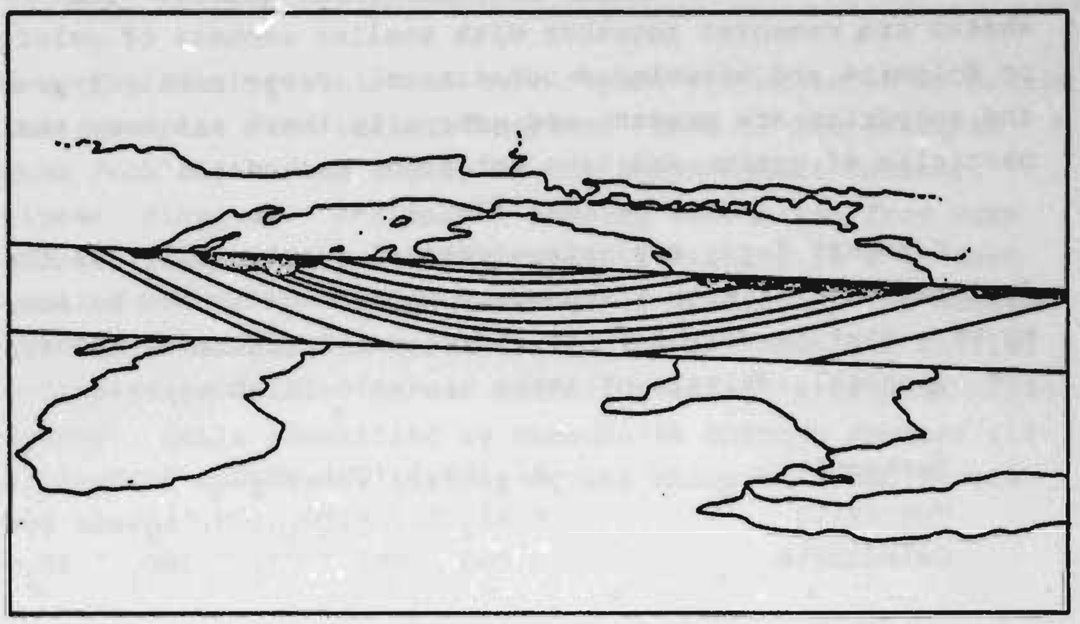
The Michigan Basin, in which the Antrim was deposited, is a large circular structural feature which was a negative area throughout early Paleozoic time, slowly settling under the weight of additional sediments. This down warping resulted in the structural basis as it is known today; deeply burried older sediments exposed at the outer rims of the basin, while the younger covering sediments are exposed near the center of the basin. (Figure 17) The Antrim outcrops at the surface in Antrim, Charlevoix, and Alpena Counties in Michigan and in Lambton County in Ontario. At Midland it is 2600 feet below the surface and dipping yet deeper to the center of the basin northwest of Midland."

Mineralogy

Continuing, from Reference 21:

"Mineralogical studies have shown the Antrim to be a very fine grained, laminated shale composed dominantly of the clay-mineral known as "illite" and quartz with minor amounts of organic matter, pyrite and carbonate. The clay-mineral mica or illite occurs as thin platelets 1 to 12 microns in thickness and about 5 to 35 microns in major diameter. Quartz and feldspar, mainly microcline and sodic plagioclase, occur as grains 5 to 30 microns in size. The organic matter occurs as a finely dispersed amorphous brown binder and as the disc shaped spore-like fossil, Tasmanites. Pyrite ranges from large concretionary masses to very finely disseminated crystals, the bulk of which range in size down to less than 0.5 microns to 15 microns. The carbonates, dolomite and calcite are in roughly equal proportions and occur as minute, irregular grains. Traces of chlorite, tourmaline and zircon have been identified."

Figure 17 - Geological cross section through Michigan Sedimentary rock basin (Reference 57)



a) orientation of cross section across lower peninsula

b) Geologic cross section of the Michigan sedimentary rock basin, showing Lakes Michigan and Huron lying in zones occupied by relatively weak rocks of the Antrim Shale and Salina Group, Green Bay and Georgian Bay lying in zones of weak Ordovician rocks, and the escarpment of the Niagaran Dolomite which separates the lakes from the bays.

"X-ray analyses by H. W. Rinn and H. C. Anderson indicate that the main mineral components of the shales tested are silicate materials which resemble muscovite (mica) but which have not been identified in all cases, and quartz. The shales are cemented together with smaller amounts of calcite or dolomite and bituminous substances. Occasionally gypsum and anhydrite are present and generally there are some small particles of pyrite and iron oxides or carbonate."

A recent X-ray analysis suggested quartz (SiO_2) as the dominant mineral with a secondary major constituent believed to be a mixture of muscovite and/or celadonite, and vashegyite. The elemental analysis of these minerals is shown below.

Vashegyite	$Al_4(PO_4)_3(OH)_3xH_2O$
Muscovite	$K\ Al_2(Si_3,Al)O_{10}(OH,F)_2$
Caledonite	$2\ CuO \cdot PbO \cdot CO_2 \cdot 3SO_3 \cdot 3H_2O$

Although muscovite (mica) seems reasonable, the elemental analysis (Section G) argues against the other two candidates except in trace quantities. No phosphorous and very little lead or copper have been found. Thermogravemetric analysis confirms quartz as a major component. There is a clear α to β quartz transition at 540°C (See Section F).

"Mineralogically, the Antrim is composed primarily of illite, a micaeous clay mineral $K_y\ (Al_4 \cdot Fe_4 \cdot Mg_4 \cdot Mg_6)\ (Si_{8-y} \cdot Al_y)\ O_{20}\ (OH)_4$ about 45% by weight, quartz (SiO_2) 30%, organic material, spore cases and amorphous matter 10%, pyrite (FeS_2) 5%, mineral carbonates $CaCO_3$ and

$CaMg(CO_3)_2$ 5%, chlorites (complex iron-magnesium-aluminosilicates) 2%, and various accessory minerals 1%. Sulfur occurs as 10% organic and 90% as pyrite."

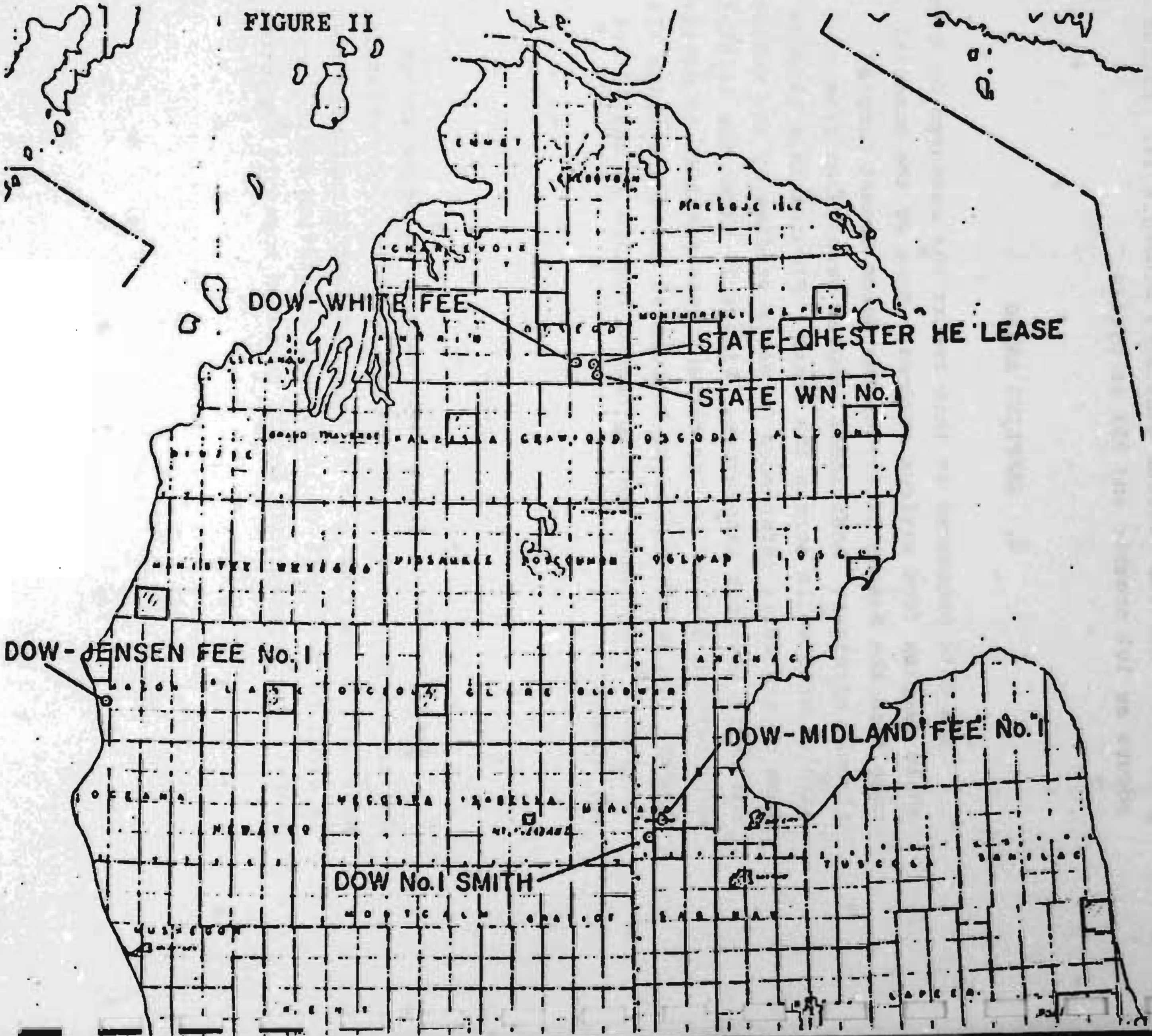
G. SAMPLING AREAS

The data presented in this report was measured on Antrim shale samples from various sources. Some of the material came from the Paxton Quarry of the Huron Cement Company, Alpena, Michigan. Additional samples were taken from core samples from wells across the state. Figures 18 & 19 show some of the wells referenced in early studies by the Nuclear and Basic Research Laboratory. Figure 20 shows the initial well pattern drilled on our current research site in Sanilac County. Wells identified as Rhoburn #5 through Rhoburn #12 drilled in subsequent testing around Rhoburn #3 and #4 are not shown.

H. SAFETY

Handling raw or spent shale should not be hazardous due to the high inert fraction and relatively non-volatile hydrocarbon fraction. It is expected that the primary risk in handling raw shale would be dust inhalation during grinding operations. Precautions should be taken to avoid exposure.

Figure 18 - Identification of Wells in earlier Project (Reference 21)



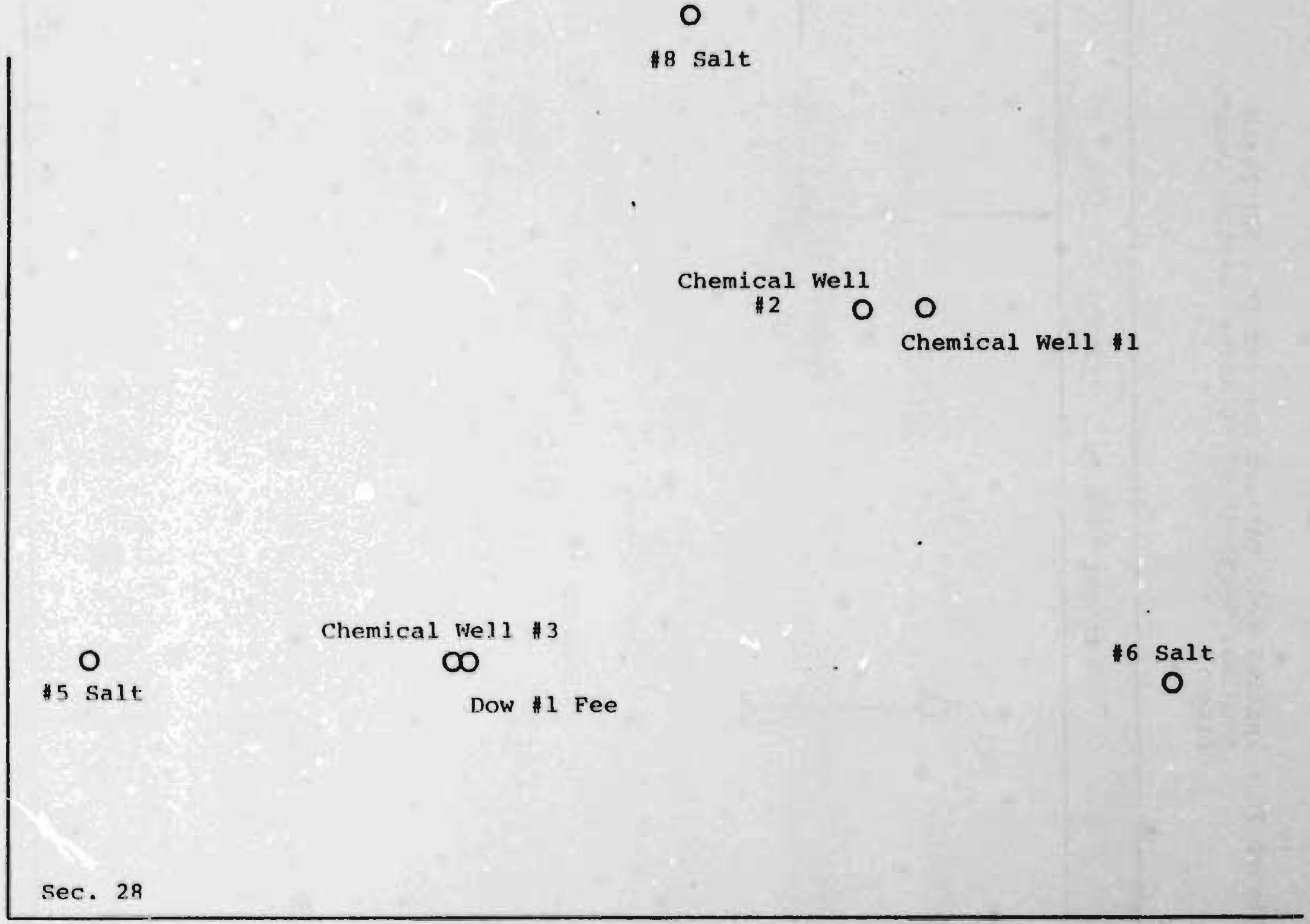
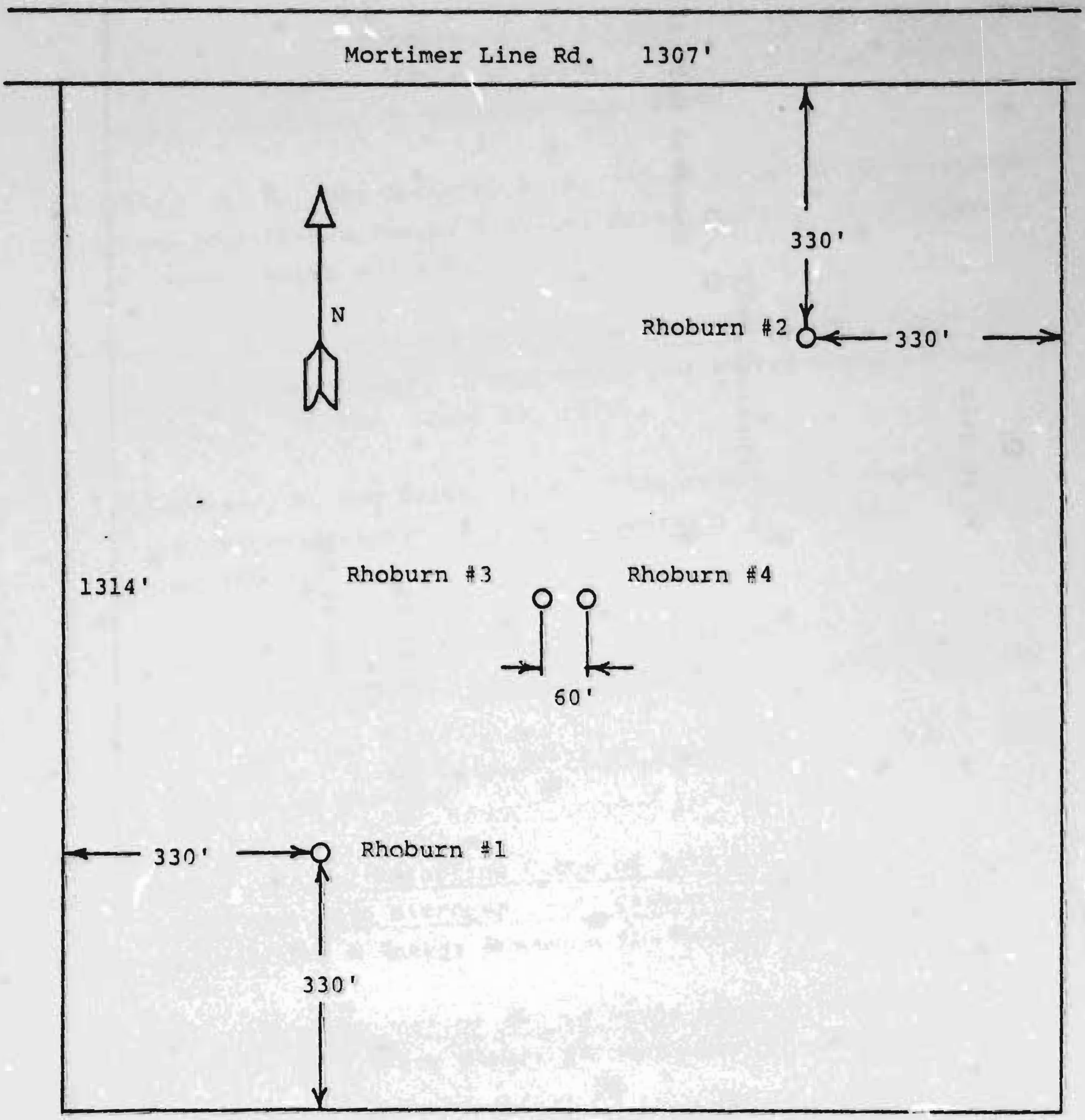


Figure 19 - Location of Wells in Midland Experiment (Reference 1)

Figure 20 - Initial Well Pattern Current (H & ER) Field Studies, North 40 of 80 Acres, Sanilac County Site.



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