

CORRELATION OF OIL SHALE PARTICLE SIZE
TO RATE OF DISSOLUTION OF MINERAL MATRIX

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The kerogenic material present in the Green River shale (Eocene Age) is bound to a mineral matrix composed of carbonates, quartz, clays, and other minor minerals. The isolation of this organic material can, therefore, be carried out in two ways: 1) The complete disaggregation and dissolution of the mineral material, thereby freeing the largely intact kerogen. Concentrated hydrofluoric acid is the most widely used reagent in this case (1,2) since it is still the only reagent that can effectively solubilize the silicate mineral (clay and quartz) that is resistant to most chemical treatments, 2) The partial cracking of the kerogen into smaller more soluble components while leaving the majority of the mineral matrix intact. Processes such as oxidation (3), pyrolysis (4), and hydrogenation (5) all belong to the latter category.

Methods whereby the kerogen can be isolated, preferably in the form of a more directly usable fuel, from raw shale with a minimal amount of pretreatment and handling, is of obvious economic interest. Knowledge of the physical structure of the intact raw shale would supplement in the design of such methods. In particular, increase of the porosity of the raw shale, without causing extensive disaggregation of the mineral matrix, would facilitate the movement of materials through the mineral matrix. For instance in oxidation and hydrogenation the reactants (i.e., the oxidant or hydrogen) must somehow come in contact with the kerogen entrapped in the mineral matrix, while smaller organic fragments that have been broken off from the kerogen 'nucleus' (6) must somehow be released to the outside.

Scanning electron micrographs (SEM) of bioleached shale (e.g., shale that has been leached with the acid produced by sulfur oxidizing bacteria) have revealed a more pitted, spongy-appearing surface texture (7). Bioleaching removes, primarily, the carbonate minerals (dolomite and calcite) which are apparently deposited in pits (7) throughout the rest of the mineral matrix; the removal of the carbonate would therefore be expected to increase the porosity of the raw shale. The results of SEM reveal the surface effect of bioleaching only, however, the effect of bioleaching on the structure inside the raw shale could only be inferred from such results. In order to increase the understanding of the internal structural changes we have measured the kinetics of this dissolution process using several different mesh sizes of oil shale.

EXPERIMENTAL

All shale samples used are collected from the Mahogany Ledge of the Green River formation. The shale rock was crushed and sized into three ranges, 42/60, 60/100, and 150/200. Since the effect of bioleaching is essentially that of dilute acid reaction with the carbonate material, hence for better accuracy in monitoring the acid concentration reagent grade hydrochloric acid was used instead of the acid produced by the sulfur oxidizing bacteria. The rate of dissolution of the carbonate mineral was followed by direct measurement of the weight loss and by atomic absorption measurement.

For each of the mesh size used several containers, each with 0.3 gm of raw shale and 50 ml of a HCl-KCl buffer (ionic strength ~0.1, pH ~1.28), were prepared. The reaction was allowed to progress; after a specific period of time the shale from one of the containers was quickly separated from the acid by vacuum filtration and washed thoroughly with deionized water. The shale was then dried at 100°C for at least 2 hours before weighing. The results of the weight loss in time for 42/60, 60/100, and 150/200 mesh size shale are presented in Fig. 1. Atomic absorption measurement, at 285 mμ, of the magnesium ions released, as a result of the breakdown of the dolomite portion of the raw shale, was also followed in order to confirm the results obtained from direct weight loss measurements.

RESULTS AND DISCUSSION

The results shown in Fig. 1 can be fitted, empirically, to the following equation

$$\frac{P}{P_0 - P} = Kt \dots\dots\dots 1)$$

where P is the percent weight loss at time, t, P₀ is the maximum percent weight loss, and K is a constant. By rearranging this equation into the form $P = P_0 - P/Kt$ and plotting P versus P/t, straight lines are obtained (Fig. 2). The values of P₀ and K for each of the mesh ranges, as can be estimated from the y-intercept and the slope respectively, are listed below:

<u>Mesh Ranges</u>	<u>P₀</u>	<u>K</u>
42/60	40.7	0.59
60/100	41.0	1.10
150/200	42.8	13.3

The maximum amount of carbonate mineral (P₀) that can be removed by dilute acid is apparently independent of the size of the shale particles, this is evident from the closeness of the value of P₀ for the different mesh ranges. The increase of the surface area, by mechanical crushing, seems only to accelerate the rate of carbonate removal while the maximum amount eventually removed by dilute acid remains relatively constant. This would indicate that the carbonate mineral is deposited at sites, presumably interspersed in the rest of the 'dilute acid resistant' mineral matrix, which are not inaccessible to chemical species (such as hydrogen ions and water molecules) in an aqueous medium. These carbonate deposit sites are therefore not isolated but can perhaps be thought of as interconnected by channels built from the 'dilute acid resistant' mineral.

The dilute acid (hydrogen ion) could come into contact with the carbonate minerals through these channels and the products (carbon dioxide, magnesium ion and calcium ions) can likewise be released to the outside. The rate of reaction of the acid with the carbonate mineral would be controlled by diffusion, of the reactant into and the products out of the shale particles, and not only by the availability of the surface of contact between the acid and carbonate. If the reaction is controlled by surface availability then the rate of carbonate removal is, for spherical particles of pure carbonate mineral, proportional to 2/3 powers of the amount of still unreacted mineral or $dP/dt \propto (P_0 - P)^{2/3}$. However, the presence of the 'dilute acid resistant' mineral, which separates the carbonate mineral into isolated sites connected by channels, would retard the rate of carbonate

removal so that $dP/dt \propto (P_0 - P)^n$ where $n > 2/3$. The empirical Equation (1) used to fit the data for carbonate removal can be derived from $dP/dt \propto (P - P_0)^2$.

Atomic absorption measurements of the magnesium released, as a result of carbonate removal from shale, can also be fitted to the empirical equation $P = P_0 - P/Kt$, (Fig. 3). Therefore the rate of carbonate removal by diluted acid is not dependent on the surface of contact alone (such as a mothball sublimation model would predict) but that other controlling factors could be involved (diffusion was suggested as one such possible factor). Due to the obvious complexity of the controlling factors that may be involved, we shall not attempt at present to elucidate them. The existence of interconnecting channels was postulated from scanning electron micrographs of bioleached shale surface (7) and is supported by evidence from the present study. The increase of porosity by removing the carbonate mineral with dilute acid would, presumably, improve the permeability of certain chemical species into and out of the remaining shale structure.

ACKNOWLEDGEMENT

This work is supported by NSF Grant No. GI-35683.

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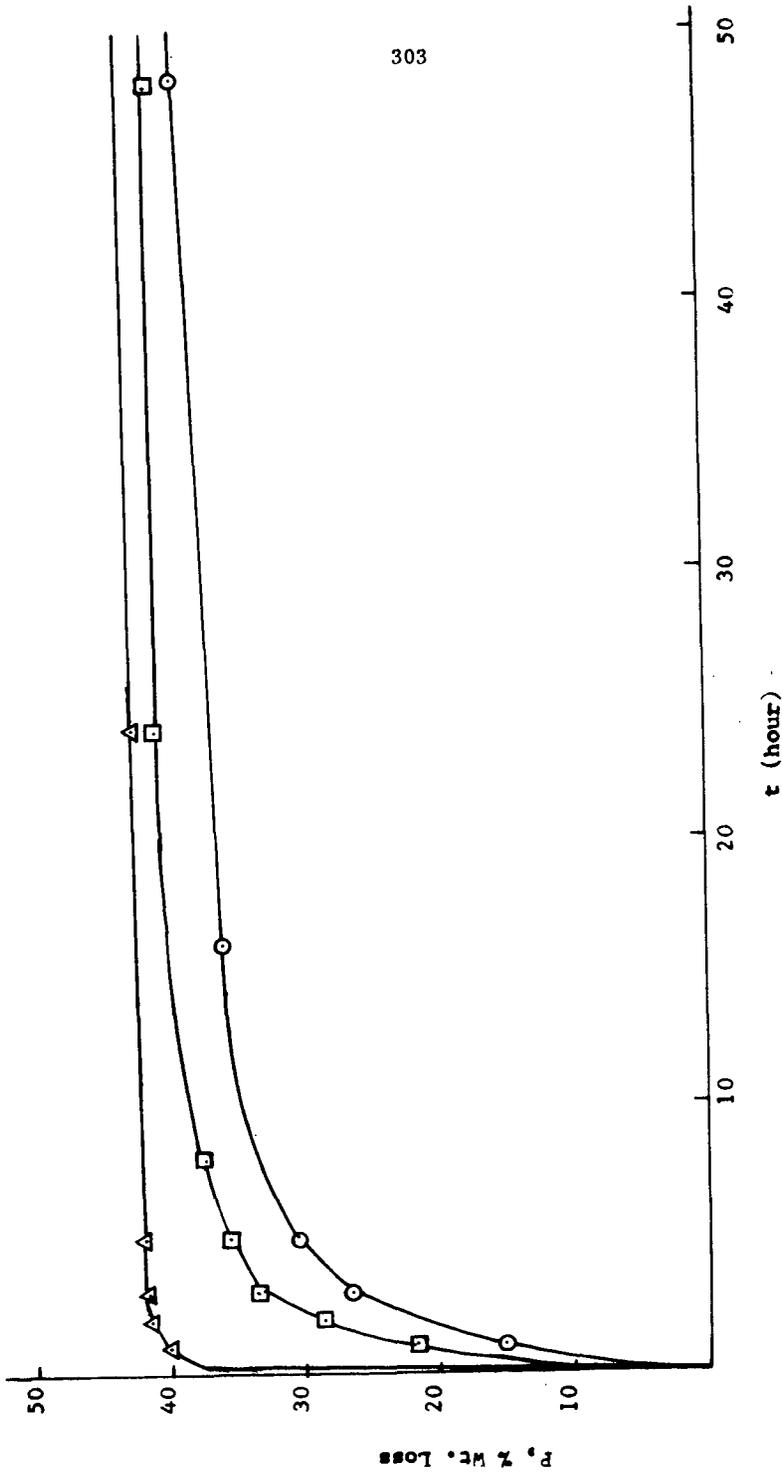


Fig. 1. Rate of weight loss of Green River Oil Shale in dilute acid (the round points indicate 42/60; the square points indicate 60/100; and the triangular points indicate 150/200; all in mesh sizes).

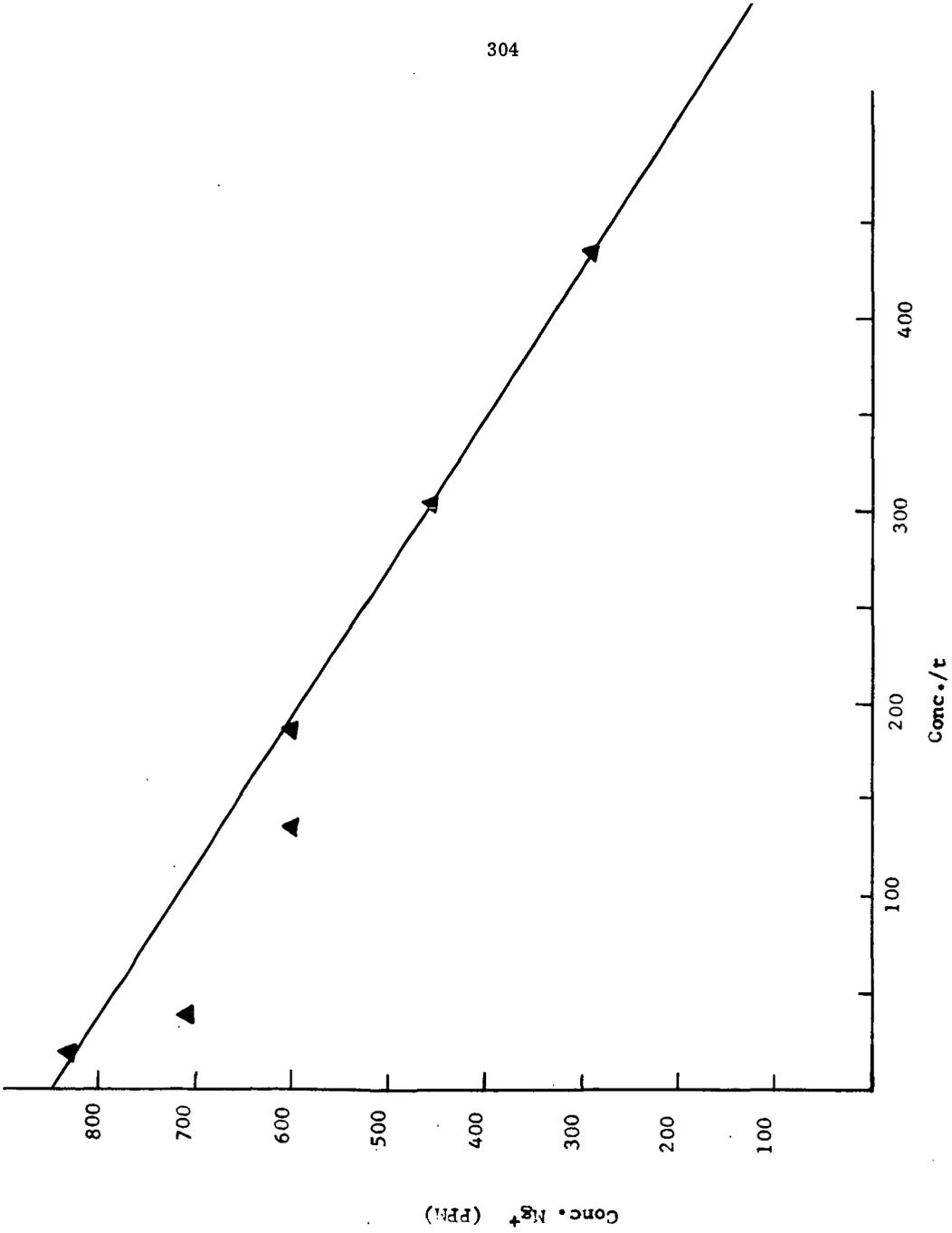


Fig. 3. Magnesium ion released from Green River oil shale by leaching with HCl. The mesh size used is 16/42. Concentration is determined by atomic absorption method.

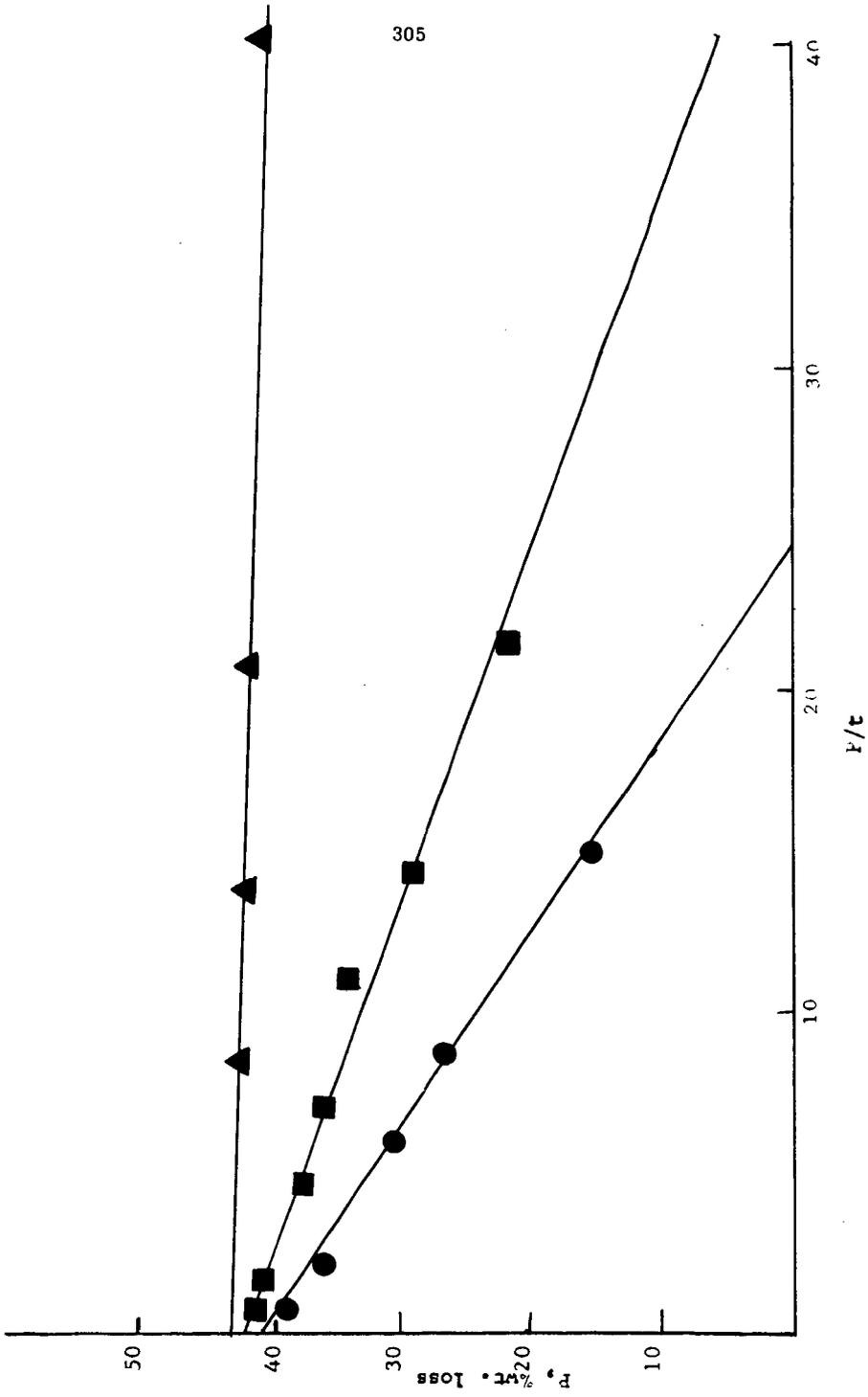


Fig. 2. Rate of dilute acid leaching fitted to the equation $P = F/kt = F$, where F is maximum percent weight loss. (The round points denote 42/60; the square points denote 60/100; and the triangular points denote 150/200; all in mesh sizes).