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A COMPARISON OF MINERAL REACTIONS FOR  
TWO COLORADO OIL SHALE SAMPLES

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INTRODUCTION

Second generation surface oil shale retorting processes will undoubtedly utilize the residual char on the spent shale leaving the retort. Whether this is done by combustion (1) or steam gasification (2) the temperatures will be sufficiently high that mineral reactions can occur to a significant extent. The more common mineral reactions include dolomite and calcite decomposition as well as solid-solid reactions between mineral carbonates and quartz to form various silicates. The latter reactions proceed at surprisingly fast rates in western shale even at mild temperatures (> 950°K). This is probably due to the small grain sizes (1-10 $\mu$ ) inherent in western shale (3) which provide for unusual mobility and reactivity.

A knowledge of the mineral reaction rates is important to efficient oil shale processing because the decomposition reactions are highly endothermic and the reaction products can affect the disposal strategy for the shale ash. To date the most extensive study of mineral reaction rates in western oil shale has been conducted by the oil shale group at Lawrence Livermore Laboratory (4,5). Using a 22 GPT oil shale sample from the Anvil Points area, they developed reaction rate expressions for dolomite and calcite decomposition as well as for the formation of silicates which they took to be a reaction between quartz and calcite. Other investigators (6) however, report only the formation of calcium-magnesium silicates.

Because the behavior of calcite appears to be instrumental to the formation of silicates, we decided to investigate the mineral reactions which take place in an oil shale sample which was low in free calcite. This sample, a core sample from the C-a tract, (designated "C-a") has a higher calcium concentration than a sample from the Parachute Creek Member in western Colorado (designated "PCM"), but as Table I shows, it is primarily tied up in ankeritic dolomite. Also shown in Table I are data reported by Campbell (3) for a sample taken from the Anvil Points area.

TABLE I  
OIL SHALE SAMPLE DATA

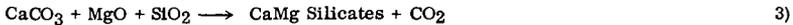
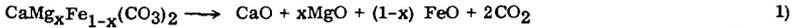
	<u>PCM</u>	<u>Anvil<sup>c</sup></u>	<u>C-a</u>
Assay <sup>a</sup>	50	22	25
<u>Mineral %<sup>b</sup></u>			
Dolomite/Ankerite	21	35.3	44
Calcite	9	19.4	2.4
Quartz	-	} 41.0	32
Silicates	-		18
<u>Elemental %<sup>b</sup></u>			
Ca	10.2	-	12.3
Mg	3.4	-	3.5
Fe	2.8	-	2.5
Al	5.0	-	4.3
Na	2.6	-	2.0
K	1.7	-	1.7
Si	18.8	-	16.2

a. gallons per ton; b. based on spent shale; c. data reported in Lit. Cited (3).

## EXPERIMENTAL

Figure 1 shows a schematic sketch of the experimental equipment. Approximately 1.5 g of spent shale (particle size  $\sim 100 \mu$ ) was placed in a 400 mesh stainless steel basket which was suspended from a recording electrobalance to provide continuous gravimetric readings as the reactions proceeded. The reactor vessel was constructed of 310 stainless steel and placed in a 3" furnace capable of reaching temperatures as high as 1200°K. Any one or a mixture of gases can be metered to the reactor via a 1/4" sparge tube and provisions are made to sample the exit gases with on-line gas chromatography. Tracer tests indicate that the design of the sparge system effectively creates an ideal back-mix state. Temperatures are monitored and controlled by means of two 1.6 mm shielded chromel-alumel thermocouples; one placed approximately 2 cm above the basket and the other so that it barely touches the shale sample.

Attempts were made to isolate the individual reactions to the degree to which it was possible. While this was not too difficult in experiments conducted on the PCM sample, it posed a serious problem with the C-a sample. The problem is best understood by referring to the three sets of reactions shown below.



In all samples the presence of  $\text{CO}_2$  can prevent calcite decomposition because of the reversible nature of (2). However, we also found that the ankeritic dolomite in the C-a sample will not decompose (Equation 1) in the presence of  $\text{CO}_2$ . As a result it was first necessary to study the silicification reactions (Equation 3) by raising the sample to the desired temperature (1000-1150°K) in the presence of  $\text{CO}_2$ . Ankeritic dolomite decomposition was investigated by measuring the decomposition rates of virgin samples in a  $\text{CO}_2$ -free environment at temperatures between 800°K and 925°K. Reversible calcite decomposition was then studied by recarbonating the CaO formed in Equation 1 and varying the  $\text{CO}_2$  pressure as well as temperature.

## RESULTS

Figure 2 shows the results obtained when a virgin C-a sample was allowed to silicate in a  $\text{CO}_2$  atmosphere at temperatures between 1000°K and 1140°K. At 1000°K, silicification ceased after about 30% of the available  $\text{CO}_2$  had been released. That is, 30% of the mineral carbonates had been converted to silicates. Interestingly, this "staging" effect proceeded as the temperature was subsequently raised. It is possible that this phenomena is due to either the formation of different silicates or, more likely, to the buildup of a silicate layer around a reactant grain. The effect of temperatures in the latter case would be to cause a dramatic increase in the diffusivity of reactants through the layer since solid-solid diffusion is known to be activated (7). However, attempts at fitting the data to various grain diffusion models were not successful and it may be that crystalline phase changes are occurring as suggested by Huang et al. (8). It is also interesting that the silicification reaction rates measured with the C-a sample are approximately 20 times lower than predicted for the Anvil Points sample (9).

Figure 3 is a comparison of first order decomposition plots for both ankeritic dolomite "labelled ankerite" and calcite in the C-a sample with that predicted for dolomite in the PCM sample. As Campbell and Burnham concluded for the Anvil Points shale (9), dolomite and calcite decomposition are indistinguishable at this temperature although the rates are about 30% higher than the C-a shale sample. Figure 4 gives the results for ankeritic dolomite decomposition in the C-a sample at two different temperatures, with and without  $\text{CO}_2$ . Note that the presence of  $\text{CO}_2$  completely prevents decomposition at the lower temperature and severely inhibits it at the higher temperature. Experiments with both the Anvil Points and PCM samples indicated no effect of  $\text{CO}_2$  on dolomite decomposition.

A series of kinetic experiments were also conducted on reversible calcite decomposition using both the C-a and PCM samples. Figure 5 shows an Arrhenius plot for calcite and ankerite decomposition in the C-a sample. The higher activation energy for calcite (171 vs. 146 KJ/mole) produces rate constants which are 2.5 times higher for calcite than for ankerite at 925°K. Table II also shows a comparison of the forward and reverse reaction rate constants for calcite decomposition on the three samples. All three have similar decomposition rate constants although Campbell and Burnham (9) report a higher activation energy for the Anvil Points shale. The rate of recarbonation of the decomposed calcite in both the C-a and PCM shales was found to be relatively insensitive to temperature but approximately first order with respect to  $\text{CO}_2$ . The fact that the recarbonation rates are high, leads one to suspect mass transport influences during recarbonation.

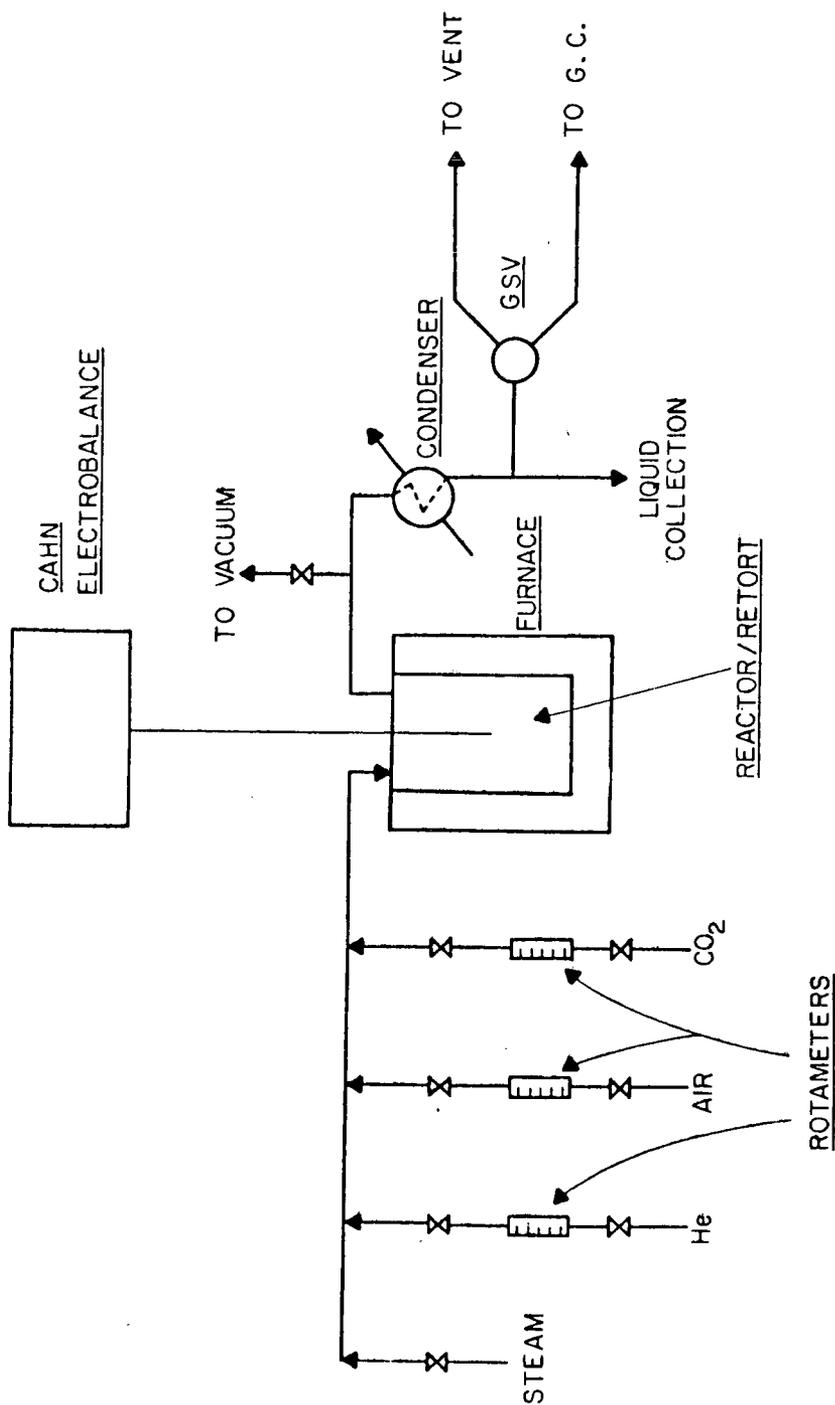


FIGURE 1: EXPERIMENTAL SCHEMATIC

Figure 2

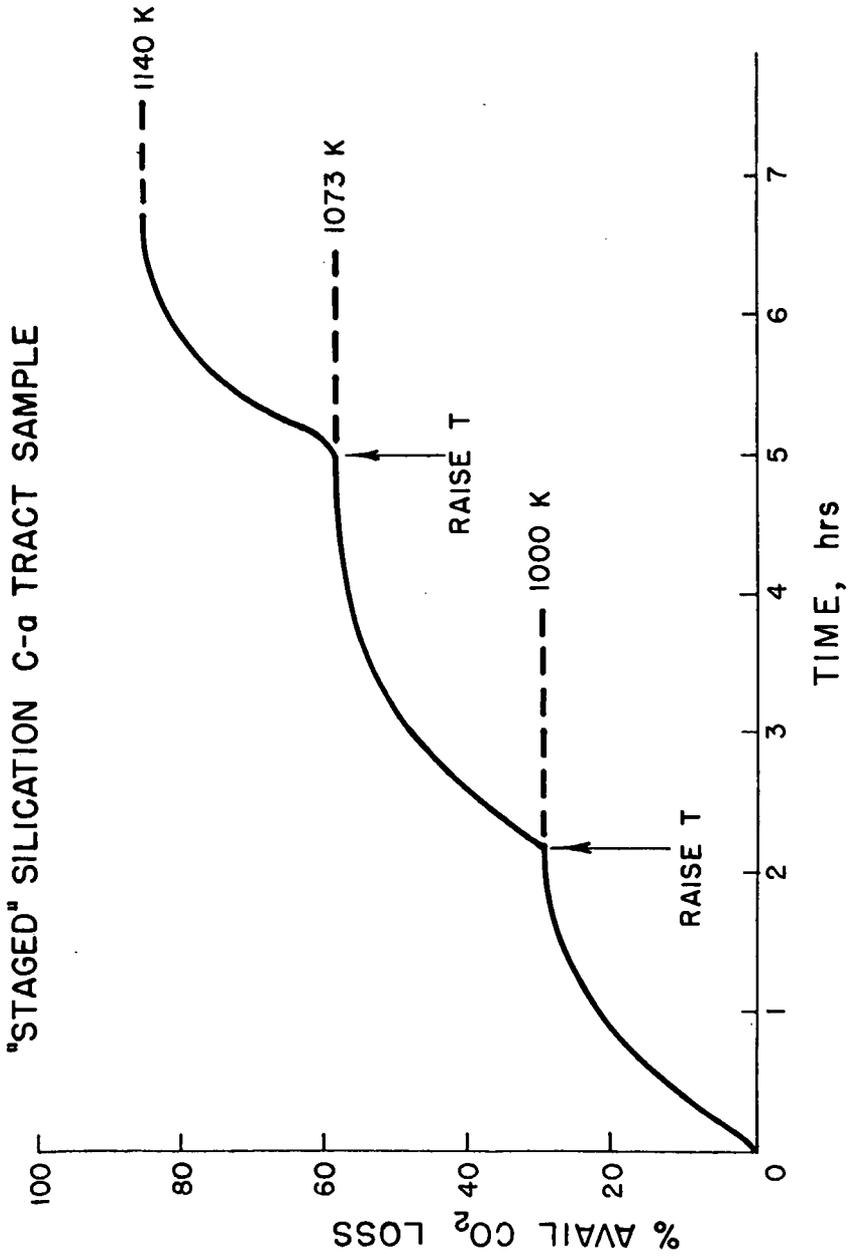


Figure 3

### MINERAL DECOMPOSITION 853 K

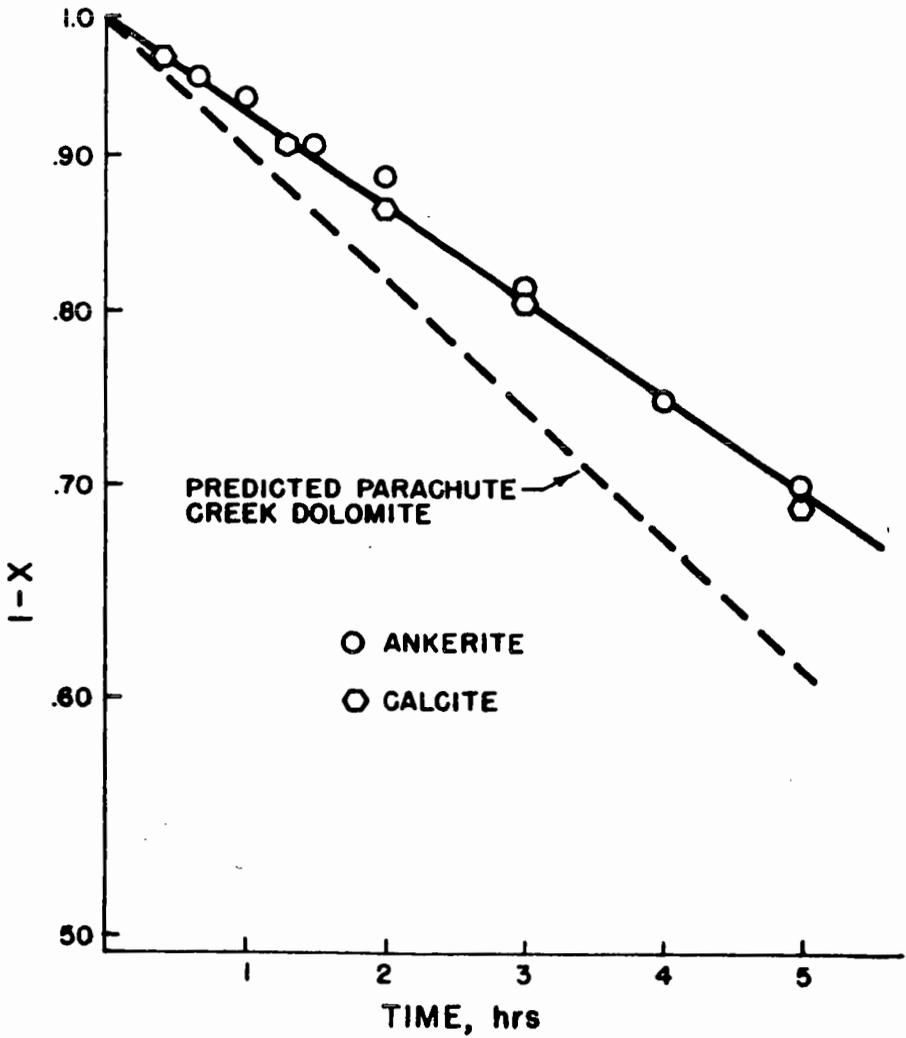


Figure 4

ANKERITE DECOMPOSITION C-a TRACT SAMPLE

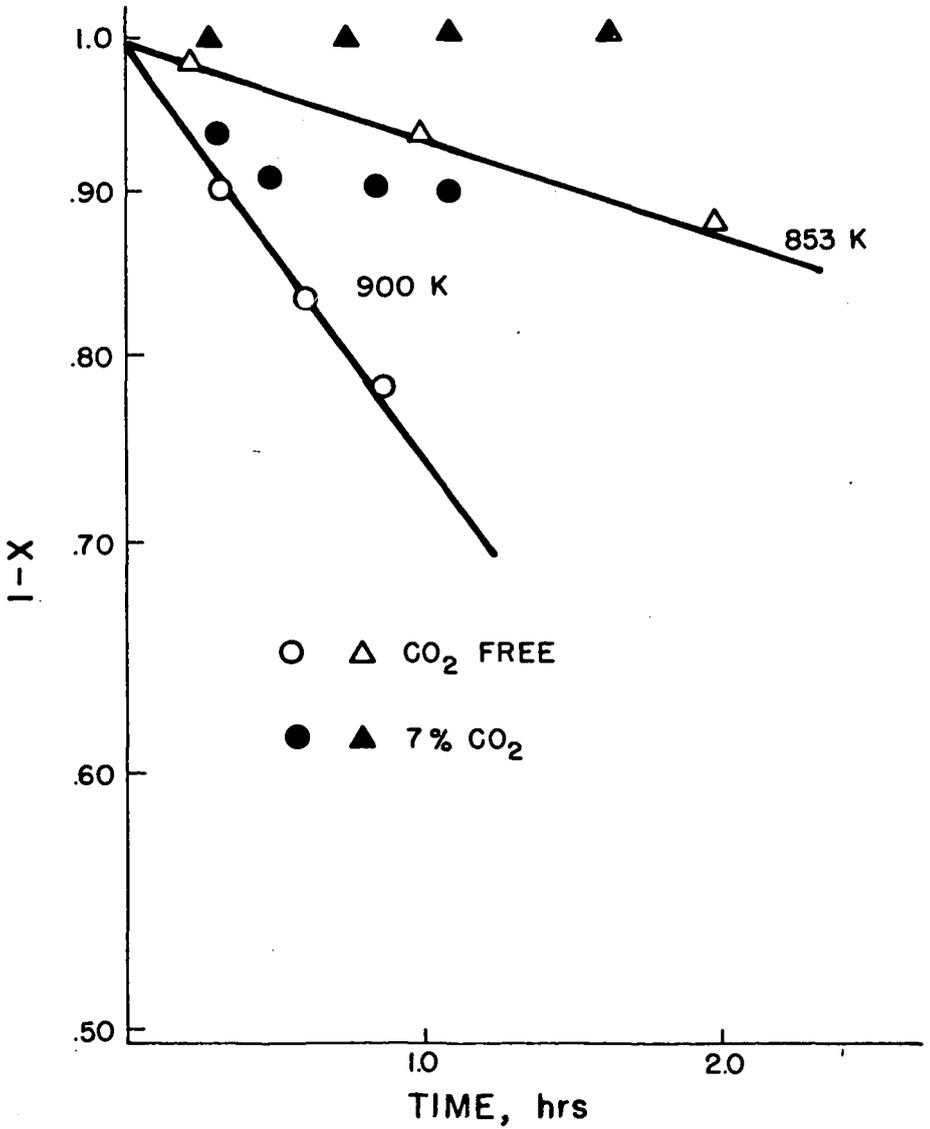
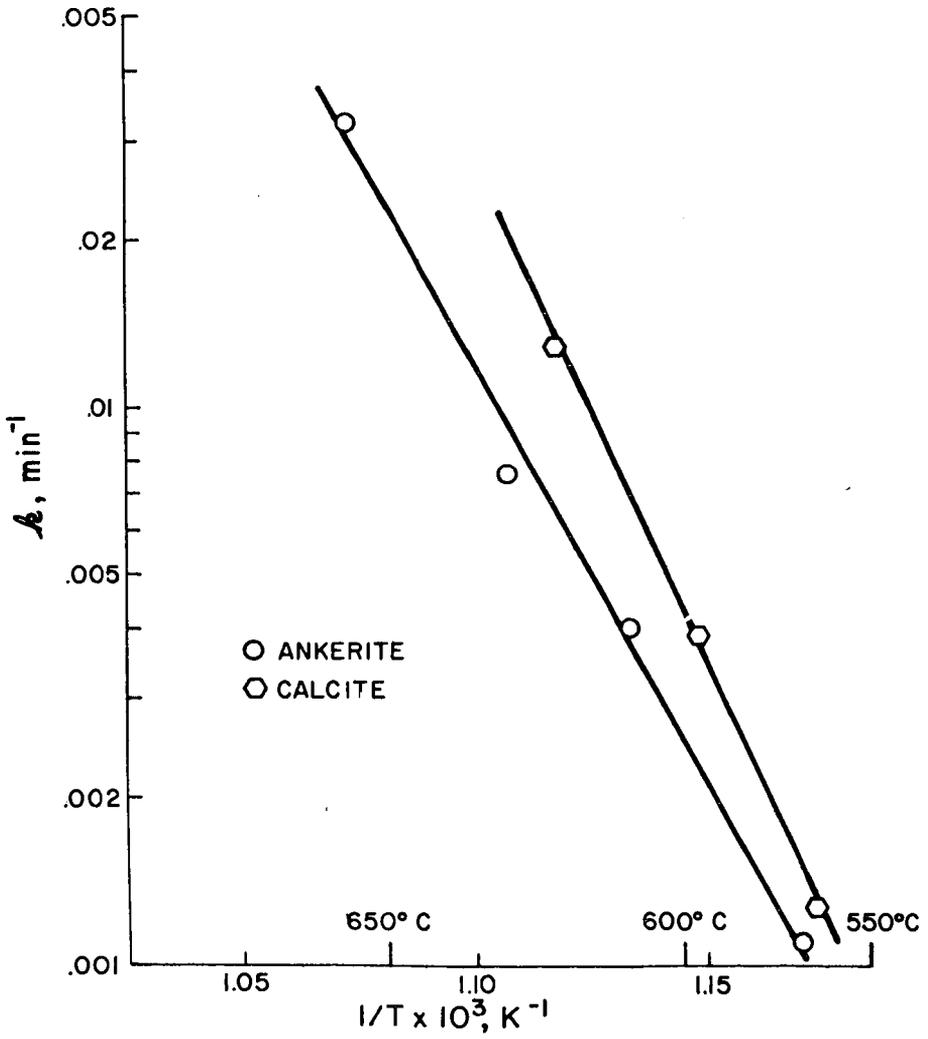


Figure 5

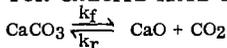
### ARRHENIUS PLOT - DECOMPOSITION



Another possibility is that the recarbonation rate is controlled by the rate of adsorption of CO<sub>2</sub>. This would be consistent with Soni and Thomson's observations (11) that recarbonation rates are ten times higher when CO<sub>2</sub> is produced on the surface due to char oxidation. If this is the case, then we would have to conclude that CO<sub>2</sub> chemisorption on shale ash is non-activated. Additional studies are now being conducted in order to distinguish between mass transport and chemisorption phenomena.

TABLE II

COMPARISON FOR CALCITE RATE PARAMETERS



$$k_{f,r} = k_{f,r}^0 \exp \left[ -\frac{E_{f,r}}{RT} \right]$$

	$k_f^a$	$E_f^b$	$k_r^c$	$E_r^b$
C-a	.0014	171	6.4	~0
PCM	.0037	171	15	~0
ANV <sup>d</sup>	.0017	242	-	-

a. at T = 855°K, min<sup>-1</sup>

b. KJ/mol

c. at T = 855°K, (atm-min)<sup>-1</sup>

d. values from Lit. Cited (9)

CONCLUSIONS

It is apparent that mineral reactions in retorted oil shale are extremely complex. The reaction rates are influenced by a combination of chemical kinetics, grain mobility, solid state crystalline behavior and mass transport. Given the dramatic differences in the dependence of ankeritic dolomite decomposition on CO<sub>2</sub>, it is obvious that future kinetic studies must also account for mineralogical structure.

ACKNOWLEDGMENT

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