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REACTION RATE KINETICS FOR IN SITU COMBUSTION RETORTING OF
MICHIGAN ANTRIM OIL SHALE

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ABSTRACT

The intrinsic reaction rate kinetics for the pyrolysis of Michigan Antrim oil shale and the oxidation of the carbonaceous residue of this shale have been determined using a thermogravimetric analysis method. The kinetics of the pyrolysis reaction were evaluated from both isothermal and nonisothermal rate data. The reaction was found to be second-order with an activation energy of 252.2 kJ/mole, and with a frequency factor of $9.25 \times 10^{15} \text{ sec}^{-1}$. Pyrolysis kinetics were not affected by heating rates between 0.01 to 0.67°K/s.

No evidence of any reactions among the oil shale mineral constituents was observed at temperatures below 1173°K. However, it was found that the presence of pyrite in oil shale reduces the primary devolatilization rate of kerogen and increases the amount of residual char in the spent shale.

Carbonaceous residues which were prepared by heating the oil shale at a rate of 0.166°K/s to temperatures between 923°K and 1073°K, had the highest reactivities when oxidized at 0.166°K/s in a gas having 21 volume percent oxygen.

Oxygen chemisorption was found to be the initial precursor to the oxidation process. The kinetics governing oxygen chemisorption is

$$\frac{dX}{dt} = 176 e^{17.9X} e^{-(42+104X)/RT} (\text{sec}^{-1})$$

where X is the fractional coverage.

The oxidation of the carbonaceous residue was found also to be second-order. The activation energy and the frequency factor determined from isothermal experiments were 147 kJ/mole and $9.18 \times 10^7 \text{ sec}^{-1}$ respectively, while the values of these parameters obtained from a nonisothermal experiment were 212 kJ/mole and $1.5 \times 10^{13} \text{ sec}^{-1}$. The variation in the rate constants is attributed to the fact that isothermal and nonisothermal analyses represent two different aspects of the combustion process.