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# THERMAL DEGRADATION OF OIL SHALE WITH MOLTEN NITRATES

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## ABSTRACT

The present study was conducted at the Bureau of Mines to explore the effect of a variety of molten nitrate salts on the thermal decomposition of one oil shale sample from the Green River Formation. Thermal analysis, coupled with effluent gas analysis, was used for all the tests in which the samples were heated at a constant heating rate.

Weight losses of heated oil shale in the presence of nitrates were found to be higher than similar losses in the absence of nitrates. Ammonium nitrate degraded the oil shale at a lower temperature than that at which oil shale started to decompose when heated by itself, or in the presence of sodium nitrate or potassium nitrate. From scanning electron microscopy of the heated oil shale samples, it appears that ammonium nitrate attacked both the inorganic and the organic portions of the shale.

These results indicate that a more detailed investigation of the effects of ammonium nitrate, and perhaps other nitrates, on fuel recovery from oil shale will be a worthwhile undertaking.

## INTRODUCTION AND BACKGROUND

Explosives are used in oil shale mining and in fracturing the shale for in situ combustion. To ascertain the suitability of various explosives for this purpose, the Pittsburgh Research Center of the Bureau of Mines determined the compatibility with oil shale of many explosive formulations and their ingredients. In these tests, a fast exothermic reaction occurred between a crushed oil shale sample and ammonium nitrate, a major ingredient of many explosive formulations. The reaction was initiated at ~ 170°C, the melting temperature of ammonium nitrate. This observation raised the possibility that ammonium nitrate, and perhaps other nitrate salts, might enhance oil shale degradation, thereby improving fuel recovery. It also led to the short study, consisting of thermal tests of mixtures of oil shale and nitrate salts, which is described here. The aim of this study was to observe the reaction between oil shale and a few molten nitrate salts, and to attempt to understand it in the light of information available on oil recovery from oil shales,

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on the general behavior of ionic salt melts, and on the characteristics of ammonium, potassium and sodium nitrates. A large amount of information on these topics is available, but only that which bears directly on this study is presented here.

Many oil shales are essentially non-porous and impermeable. Above ground retorting or in situ controlled combustion, is required to release the shale oils from the kerogen, the organic portion of the oil shale. At best, these methods are lengthy and costly. Unfavorable basic costs of surface shale technologies [1] decrease hopes for near-term commercialization of shale resources unless research and development offer new alternatives.

For a better understanding of the mechanism of oil shale decomposition, which will eventually simplify the recovery of oil and/or reduce recovery costs, a few melts and solvents are being investigated as decomposition media. These include a tetrachloroaluminate melt [2], hydrous pyrolysis, utilizing water with helium at 1–2 atm [3], and steam [4]. The effects of various organic solvents on the thermal decomposition of Colorado oil shale, when heated in an autoclave at 200°C under self-generated pressures, were also observed and related to the solvent properties [5].

The physical properties of ionic salt melts lie between those of molten metals and of water, more closely approaching those of aqueous systems [6]. Their good heat transfer properties, low vapor pressures, and good thermal stabilities are important to their performance as reaction and solvent media. The nitrate melts and nitrate eutectics are used extensively as constant-temperature baths and reaction media for various research purposes.

Sodium and potassium nitrates begin to decompose at about 400°C to their respective nitrites with evolution of oxygen, but at lower temperatures they remain stable for long periods. Further decomposition to the alkali oxides, with concurrent formation of oxygen and nitrogen oxides, takes place at higher temperatures. Release of oxygen by the nitrates makes them good oxidizing agents. Indeed, sodium and potassium nitrates are used for decomposing small samples of organic matter [7], though their ability to decompose or oxidize kerogen has not been assessed. Nitrate melts can act as nitrating media as well, but the extent of nitration of organic compounds is usually very small, unless certain ingredients, such as pyrosulfate ($S_2O_7^{2-}$), are added to the nitrate melt. Pyrosulfate increases the concentration of nitronium ion, $NO_2^+$, the nitrating species, in the melt. Their ability to decompose, oxidize, or nitrate kerogen is not known, nor is their capability to interact with and degrade the mineral portion of the oil shale. If the nitrate melts help break down the matrix and increase the exposed surface of the kerogen, which is intimately intertwined with the inorganic minerals, the pyrolysis rate might be increased.

Fused ammonium nitrate can dissociate to ammonia and nitric acid or decompose to various gaseous products, depending on conditions such as temperature and the presence of foreign matter. In the molten state it reacts

with certain metals, oxides and carbonates, including barium and calcium carbonates [8], and dissolves them, releasing ammonia in the process. Pure ammonia, even under pressure, cannot always bring about ammoniation and ammonolysis, but in the presence of acid catalysis, these reactions occur. In the case of fused ammonium nitrate, $NH_4^+$, the ion initially formed in the dissociation step, is the acid catalyst.

Ammonia and its vapor can change the pore structure of coals, which are similar to kerogens in some ways, and even degrade and comminute them [9]. It is also absorbed by clays, which are an important ingredient of oil shale. Thus, a variety of reactions between oil shale and fused ammonium nitrate can be expected.

## EXPERIMENTAL

### *Instrumentation*

A DuPont 990 differential scanning calorimeter (DSC) was modified to permit gas sampling directly from the DSC oven compartment via a 1/8 inch nominal stainless steel sampling tube which was inserted through the glass bell jar cover and through the stainless steel and silver covers of the oven compartment. Aluminum sample pans and covers were utilized, and the cover was lightly hand-pressed into the sample pan. A pinhole in the sample pan cover facilitated the release of any gaseous and volatilized liquid products.

A carbon monoxide meter (Ecolyzer, Model No. 2400, Energetics Science Inc., New York) and a total hydrocarbon analyzer (Bendix model 8401 total hydrocarbon analyzer), both equipped with low-flow pumps, were used to monitor some of the volatile products. The two instruments were connected to the DSC separately, one at a time, via the stainless steel sampling tube.

### *Materials*

#### *Oil shale*

The oil shale sample used in these tests came from the upper 40 feet of the Tipton Member of Wyoming's Green River Formation: the sample was from the U.S. Bureau of Mines Rock Springs site 9, Well no. 1 drilled in the NW1/4SW1/4NW1/4 of Sec. 15, T18N, R106W, Sweetwater County, Wyoming. The oil yield (Fischer assay) was close to 20 gallons of oil per ton of oil shale. The color of the shale sample, consisting mostly of marlstone and claystone, was dark to medium olive gray and brownish-gray. Minerals prevalent in the oil shale in that zone are dolomite, quartz, soda and potash feldspars and small amounts of illite and pyrite. The oil shale was crushed and blended, and stored in tightly closed glass jars.

*Nitrate salts*

The sodium and potassium nitrates were certified, reagent-grade chemicals.

Ammonium nitrate prills (Bureau of Mines Key No. X-1486; essentially pure ammonium nitrate prills, for explosive use), coated with small amounts of clay, were used. They were ground to powder, as needed, before each test.

*Procedure*

Weighed test samples were heated in the DSC cell compartment at 20°C $min^{-1}$. The atmosphere in the DSC was initially that of gently flowing ambient air, due to the pump in the gas analyzer. Upon onset of decomposition, the self-generated atmosphere was diluted by the air flow and transported continuously into the gas analyzer connected to the DSC. As soon as the test was completed, the DSC chamber was opened, and the sample was removed and weighed.

## RESULTS AND DISCUSSION

Information about the tests is given in Table 1. The final temperature reached in each test, the total weight loss and the percent weight loss for each sample are recorded in the table, as is the relative total amount of gas, either carbon monoxide or hydrocarbons, given off by each sample.

Results are presented and evaluated in four sections: thermal analysis, gas evolution, scanning electron microscopy, and weight loss. Although they are all interrelated, they are presented in this manner for simplicity and clarification.

*Thermal analysis*

*Thermograms*

The advantages and disadvantages of using thermal analysis to study fuels such as oil shales are well presented by Smith and Johnson [10]. Thermal analysis has been utilized to study various characteristics of oil shales [11–15]. It served our purposes for this initial evaluation of the effect of molten nitrates on oil shale degradation.

Thermograms for all the pure nitrate salts were also obtained but are not presented here. In the temperature range of interest for this study, none contained exotherms. The recorded endotherms are due to solid phase changes, fusion or decomposition undergone by the nitrates.

Representative thermograms are shown in Figs. 1–6. Figure 1 shows a typical thermogram for the oil shale, while Figs. 2–6 present thermograms

TABLE 1

DSC-gas evolution tests

| Test no. | Sample | | | | Final temperature (°C) | Total weight loss (mg) | %wt. loss [c] | Total relative amounts of gas given off (in equivalent units) [b] |
|---|---|---|---|---|---|---|---|---|
| | Oil shale weight (mg) | Nitrate added [a] | Nitrate weight (mg) | Nitrate wt.% in total sample | | | | |
| *Carbon monoxide evolution tests* | | | | | | | | |
| 110 | 5.5 | | | | 570 | 1.1 | 20 | 100.0 |
| 111 | 6.0 | SN | 2.8 | 31 | 600 | 2.1 | 35 | 103.5 |
| 112 | 5.4 | SN | 4.8 | 47 | 550 | 2.2 | 40 | 78.6 |
| 113 | 6.1 | KN | 4.0 | 39.6 | 550 | 2.1 | 34.4 | 53.0 |
| 114 | 6.0 | SN + KN | 2.6<br>3.3 | 49.5 | 550 | 2.3 | 38.3 | 76.8 |
| 116 | 5.5 | AN | 3.0 | 35.3 | 576 | 4.2 | [d] | 87.4 |
| *Hydrocarbon evolution tests* | | | | | | | | |
| 119 | 5.1 | | | | 591 | 1.9 | 37.2 | 63.6 |
| 121 | 11.7 | | | | 557 | 1.94 | 16.2 | 100.0 |
| 123 | 6.0 | | | | 577 | 1.1 | 18.3 | 87.6 |
| 130 | 16.9 | | | | 570 | 3.0 | 17.7 | 69.8 |
| 126 | 5.0 | SN | 4.4 | 46.8 | 576 | 2.0 | 40 | 34.3 |
| 129 | 5.9 | SN | 2.6 | 31.7 | 568 | 1.9 | 33.9 | 29.3 |
| 132 | 5.7 | SN | 4.0 | 41.2 | 575 | 2.3 | 40.3 | 22.3 |
| 124 | 9.0 | AN | 4.8 | 34.8 | 572 | 6.5 | [d] | 63.2 |
| 134 | 8.0 | AN | 4.7 | 37 | 575 | 6.3 | [d] | 38.0 |
| 136 | 8.2 | SN + AN | 1.3<br>1.9 | 28.1 | 577 | 4.5 | [d] | 55.0 |

[a] SN = Sodium nitrate, KN = potassium nitrate, AN = ammonium nitrate.

[b] Based on amount of gas given off by the neat oil shale as arbitrarily set equal to 100.0

[c] Assuming all the weight loss was from the shale.

[d] Not calculated.

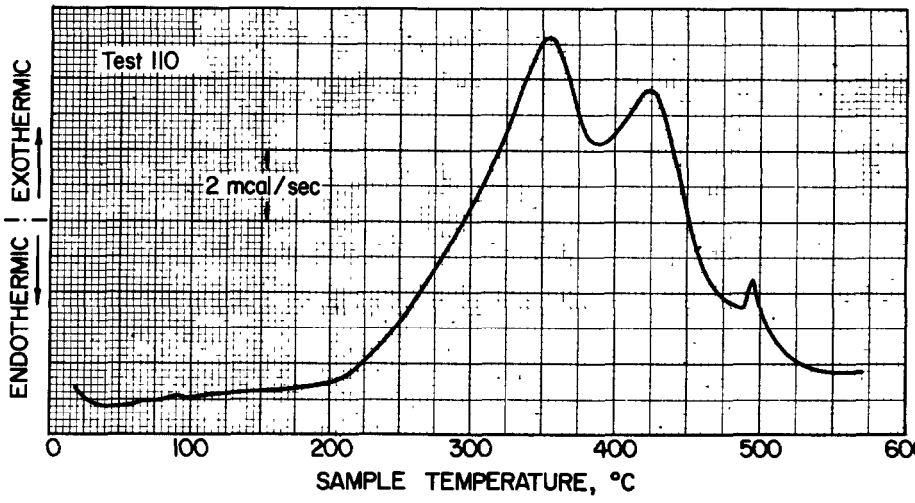


Fig. 1. Thermogram of oil shale.

obtained from oil shale heated together with the various nitrate salts or with binary mixtures of the nitrate salts.

The thermograms for the neat oil shale and for the mixtures were quite reproducible, although the relative heights of the various exothermic peaks depended on the proportions of shale and nitrate. The exothermic peaks for the oil shale sample are characteristic of oil shale and of coal thermograms obtained in ambient air. The temperatures of the exothermic peaks in the six thermograms are given in Table 2 for ease of inspection and comparison.

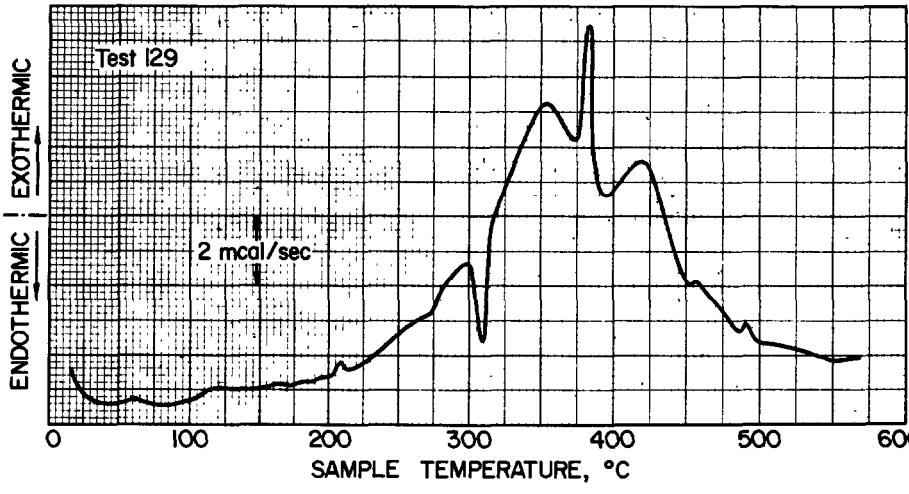


Fig. 2. Thermogram of a mixture of oil shale with sodium nitrate.

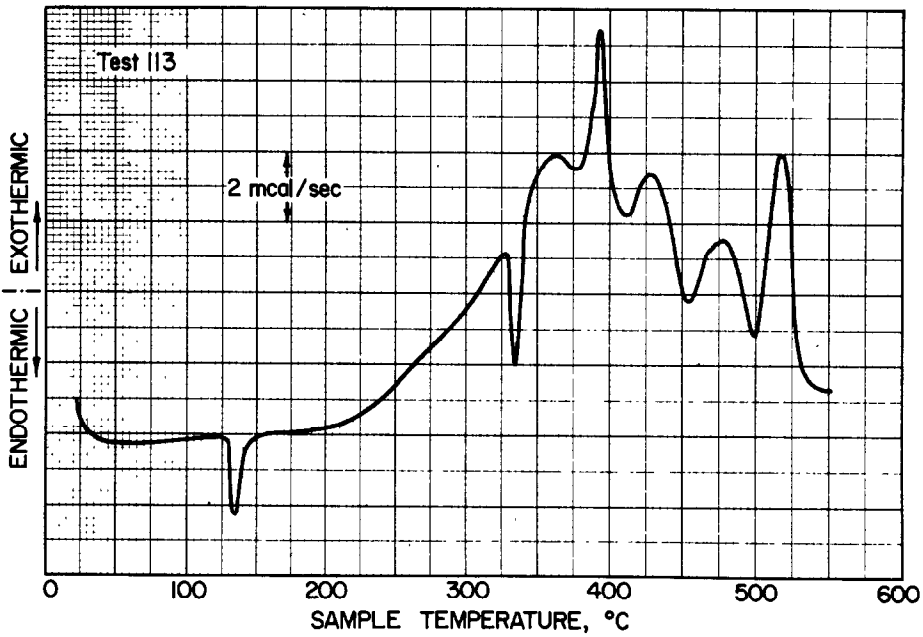


Fig. 3. Thermogram of a mixture of oil shale with potassium nitrate.

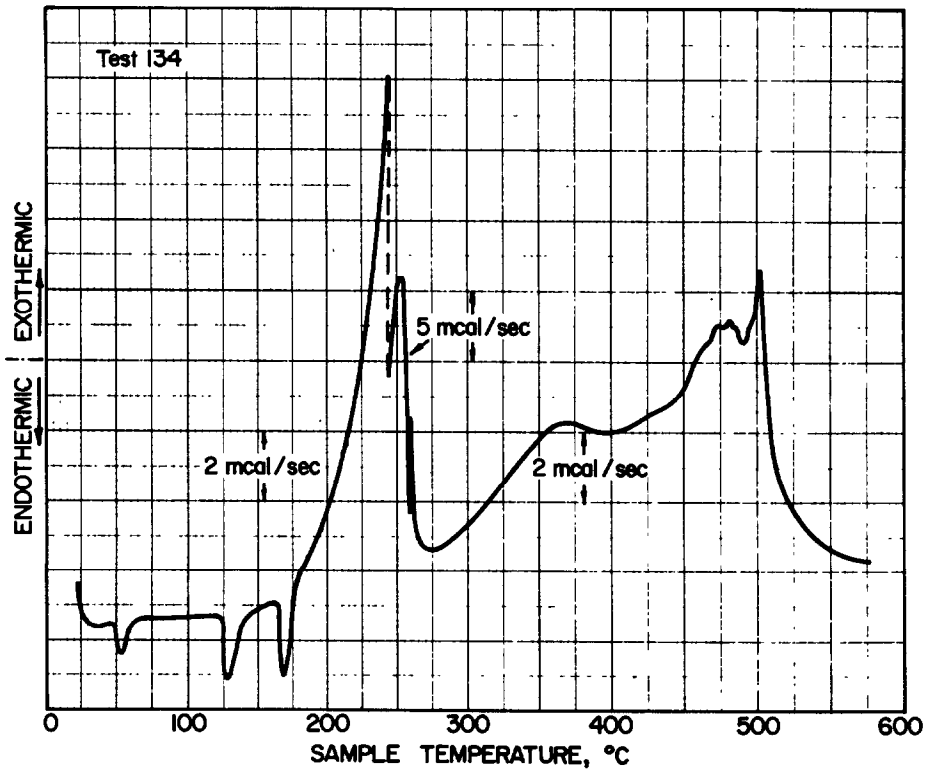


Fig. 4. Thermogram of a mixture of oil shale with ammonium nitrate.

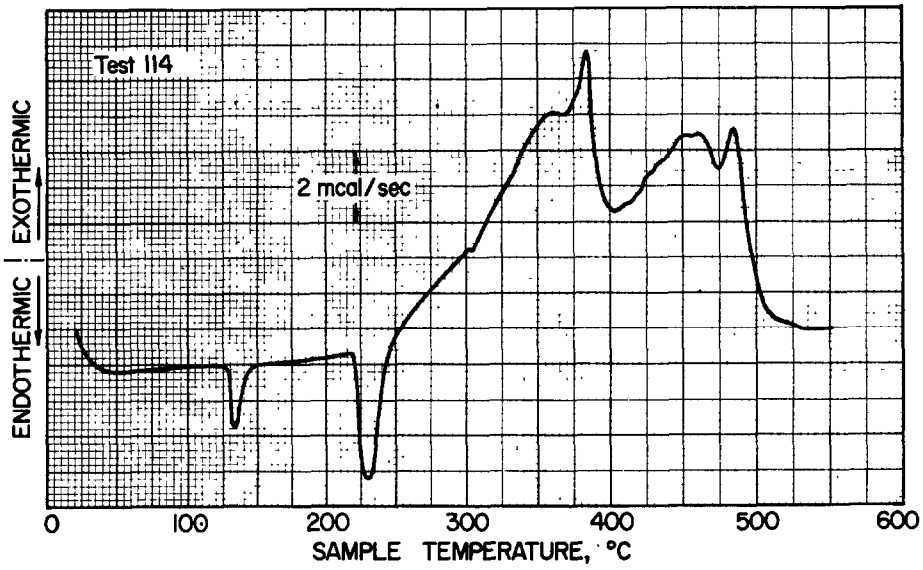


Fig. 5. Thermogram of a mixture of oil shale with sodium and potassium nitrates.

Thus, it can be seen that all the exotherms for neat oil shale are also present in the thermograms for oil shale with nitrate, at about the same temperatures, within experimental variations. The only exception is the absence of an exothermic peak at ~ 425°C in the presence of ammonium

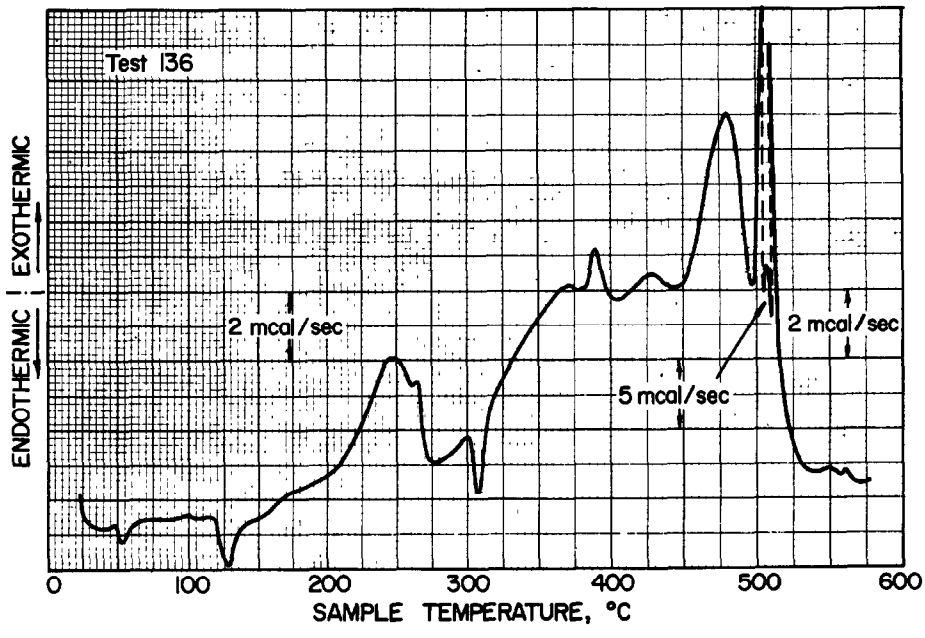


Fig. 6. Thermogram of a mixture of oil shale with sodium and ammonium nitrates.

TABLE 2

Temperatures of exothermic peaks in thermograms of oil shale samples heated without and with various nitrates [a]

| | Temperature (°C) | | | | | |
|---|---|---|---|---|---|---|
| | Oil shale | Oil shale with SN | Oil shale with KN | Oil shale with SN + KN | Oil shale with SN + AN | Oil shale with AN |
| Start of exothermic behavior | 210 | 205<br>208<br>(very small) | 210 | ~ 220 [b] | 175 | 175 |
| | | | | | 240 | 240 |
| | | 275 | | | 265 | 255 |
| 1st peak of neat oil shale | 365 | 355<br>385 | 362<br>392 | 360<br>383 | 370<br>390 | 365 |
| 2nd peak of neat oil shale | 425 | 416<br>460 | 428<br>480 | 425<br>460 | 430<br>480 | 475 |
| 3rd peak of neat oil shale | 495 | 492 | 492 | 485 | 508 | 500 |

[a] SN = Sodium nitrate, KN = potassium nitrate, AN = ammonium nitrate.
[b] A eutectic endotherm at this temperature range prevents an accurate determination.

nitrate. Also evident is the lower temperature, about 175°C, at which strong exothermic behavior is initiated in the presence of ammonium nitrate; sodium nitrate and potassium nitrate, on the other hand, essentially do not influence the initiation temperature of exothermic behavior of oil shale, at about 210°C.

The exothermic peaks at 380–390°C and at 460–480°C, which follow the peaks generated by neat oil shale, imply that a reaction takes place between the alkali metal nitrate melt and either the decomposition intermediates of the oil shale, or some of the ingredients of the oil shale, made more accessible to attack. The sodium nitrate and potassium nitrate melt at 307 and 334°C, respectively. Equimolar amounts of the two salts form a eutectic at about 225°C, but no evidence of a reaction between this melt and the oil shale, in the form of an exothermic peak, is seen in the thermogram (Fig. 5). This behavior warrants more study. The thermogram for oil shale with ammonium nitrate is not as easy to explain; perhaps different reactions occur, or similar reactions take place but at a lower temperature.

Nitrate melts are strong oxidizers and may react with both inorganic and organic portions of the oil shale and the kerogen pyrolysis–decomposition

products. The ability of the ionic nitrates to nitrate is minimal and depends on the presence and concentration of $NO_2^+$ ions in the melt which is usually low.

Various mechanisms have been postulated for oil shale pyrolysis or decomposition, including stepwise consecutive reactions from kerogen through bitumen to oil, with concurrent formation of gas and carbonaceous material. Reed and Warren [12] have observed Green River oil shale decomposition via a combined thermal-evolved gas analysis. They identified products from three thermal regimes and found that (1) up to 300°C the evolved products were very similar to products obtained from heating bitumen (which can be extracted from raw oil shale or kerogen by solvents, at room temperature); (2) the products from the second regime, between 300 and 375°C, included low-molecular-weight, non-linear hydrocarbons; and (3) low-molecular-weight hydrocarbons were most prevalent in the products from the third regime, between 375 and 475°C. Although somewhat different as to temperature boundaries, three main thermal regimes, or exotherms, were also observed in this study. The differences in the temperatures are due to factors such as differences in the compositions of the samples used in these two studies, in heating rates, and in the atmosphere in the thermal analyzers. These various thermal regions reflect the need for increased energy requirements to break the aliphatic and aromatic carbon–carbon and carbon–hydrogen bonds. Nottenberg et al. [16] found that Green River oil shale undergoes a drastic change in mechanical strength at about 380°C, the temperature at which the third thermal region starts. Such a change is indicative of some form of breakdown in the material. This extensive structural deformation is desirable for the utilization of oil shale, especially if larger surfaces of kerogen are thereby exposed to the effect of heat during retortion. In the presence of the fused ammonium nitrate, chemical reaction with the carbonate minerals likewise may help disintegrate or break apart the oil shale matrix, but at a lower temperature.

*Heating values*

Areas under thermograms obtained by differential scanning calorimetry (DSC) are often utilized to calculate heat evolution (or absorption) during phase changes or chemical reactions. Gamel and Smothers [17] showed that a linear relationship existed between heats of combustion of coals as determined by thermal analysis and by bomb calorimetry, and that the thermogram areas obtained for coal samples were a relatively good measure of the heating values of these coals, of about 7500 cal $g^{-1}$. Rogers and Bibby [14] extended Gamel and Smothers' method to 93 samples of New Zealand oil shales and found the heat of combustion of the oil shales to be in the range ~ 50–2000 cal $g^{-1}$, with the average being ~ 620 cal $g^{-1}$. They also calculated the heat of combustion of the kerogen in their samples to be about 8100 cal $g^{-1}$. Longuet [13] utilized DSC for analysis of French oil

shales and measured the areas under the resultant thermograms for heat effects. He obtained a lower calorific value of 7200 cal $g^{-1}$ for the "pure" volatiles.

Since thermograms were available for all the tests cited in Table 1, the areas under the exotherms for the various oil shale and oil shale–nitrate samples were determined and converted to heating values, or heats evolved, by a procedure described in the appendix. These calculated values are shown in Table 3. The average values for oil shale, oil shale with sodium nitrate, and oil shale with ammonium nitrate were 5000, 4500 and 4800 cal $g^{-1}$ of oil shale, respectively. These values are lower than the value of 7200 cal $g^{-1}$ given by Longuet for the French oil shales, but differences in the chemical constitution of the shales, in the atmospheres present in the thermal analyzer, and in the experimental procedures preclude any close agreement in results. Rajeshwar et al. [18], in their review on thermophysical properties of oil shales, also point out the lack of close agreement in the results of various researchers and attribute the differences in results to the same causes.

All the samples were in containers with a pinhole in the cover. One sample (Test 123) was not covered and shows the lowest heating value. This is evidence of heat loss from the sample, influencing the results and explaining the low values obtained for all the samples. These are only order-of-magnitude values.

TABLE 3

Heating values

| Test no. | Nitrate used [a] | Shale wt (mg) | Total wt (mg) | Heating value (cal $g^{-1}$ oil shale) |
|---|---|---|---|---|
| 110 | | 5.5 | 5.5 | 6230 |
| 111 | SN | 6.0 | 8.8 | 5240 |
| 112 | SN | 5.4 | 10.2 | 3830 |
| 113 | KN | 6.1 | 10.1 | 5180 |
| 114 | SN + KN | 6.0 | 11.9 | 4380 |
| 116 | AN | 5.5 | 8.5 | 5590 |
| 119 | | 5.1 | 5.1 | 5000 |
| 121 | | 11.7 | 11.7 | 4630 |
| 123 [b] | | 6.0 | 6.0 | 3720 |
| 124 | AN | 9.0 | 13.8 | 4170 |
| 126 | SN | 5.0 | 9.4 | 4090 |
| 129 | SN | 5.6 | 8.2 | 4150 |
| 130 | | 16.9 | 16.9 | 4390 |
| 132 | SN | 5.7 | 9.7 | 4980 |
| 134 | AN | 8.0 | 12.7 | 4660 |
| 136 | SN + AN | 8.0 | 11.4 | 4460 |

[a] SN = Sodium nitrate, KN = potassium nitrate, AN = ammonium nitrate.
[b] No cover was used in the test.

Of more interest to this study is a comparison between our experimental heating values for oil shale with and without nitrate. The average value for oil shale samples with nitrate is 4610 cal $g^{-1}$; the respective value for neat oil shale samples is 5060 cal $g^{-1}$. The value for test 123, in which the sample was not covered, was not used. The values for the former combinations are not much lower than the heating values for the oil shale by itself. These results suggest that the nitrates do not react to any great extent with the kerogen portion of the oil shale. The measured heating values are plotted as a function of total sample weight in Fig. 7. As can be seen, the heating values decline with increasing weight; this is suggestive of diffusion-controlled phenomena.

These heating values are rough values, not only because of the estimates and approximations made in their calculations, but also because of heat losses in the DSC. The DSC was modified to permit direct gas sampling from it; these modifications, which include a sampling tube assembly and ports for the sampling tube, are conducive to heat losses. The escaping gaseous products also carry heat with them. The samples with nitrate might have evolved more heat via the exothermic reaction of nitrate with charcoal, one of the decomposition products of kerogen, by the reactions [19]

$$4\ KNO_3 + 2\ C \rightarrow 4\ KNO_2 + 2\ CO_2 \quad (1)$$

$$4\ KNO_2 + 3\ C \rightarrow 2\ K_2CO_3 + CO_2 + N_2 \quad (2)$$

These reactions are highly exothermic and should be noticeable, but our results do not show such evidence. The temperature was not high enough to

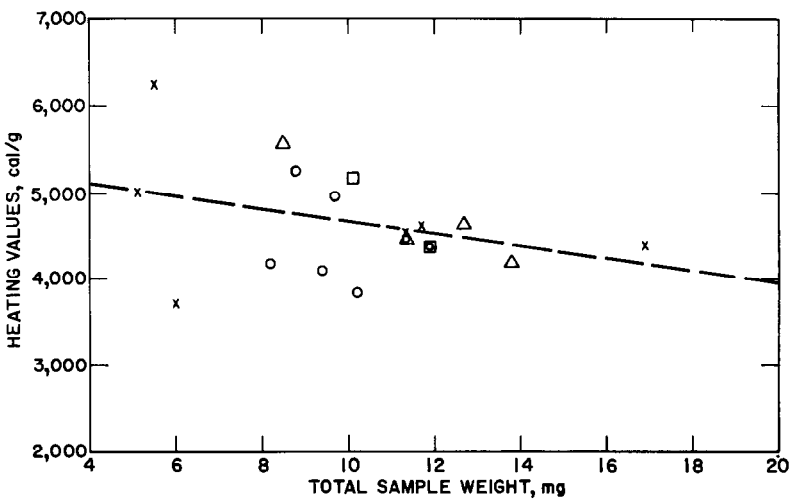


Fig. 7. Heating values of oil shale and of oil shale with various nitrates. ×, Oil shale, ○, oil shale + sodium nitrate; □, oil shale + potassium nitrate; △, oil shale + ammonium nitrate; ⊠, oil shale + sodium and potassium nitrates; ⊿, oil shale + ammonium and sodium nitrates.

decompose most of the kerogen to the char, or to decompose the nitrate to an appreciable extent.

*Gas evolution*

Initially, a gas chromatograph with columns tailored to measure carbon monoxide, carbon dioxide and various hydrocarbons was connected directly to the DSC. The results were unsatisfactory either qualitatively or quantitatively, probably due to the small size of the samples. Therefore, instruments capable of measuring some of the individual gases of interest, such as carbon monoxide or hydrocarbons, were used. An instrument to measure continuously very small quantities of carbon dioxide in the range 10–250 ppm was not available, and the evolution rate of carbon dioxide was not monitored.

*Carbon monoxide*

Evolution of gas from the heated oil shale in the relatively lower temperature range used in the DSC tests, is one indication that the kerogen is decomposing. The amount of gas evolved and the evolution rate are measures of the extent of decomposition. Decomposition of the inorganic portion of the oil shale, and especially of the carbonates, at the temperature range used in the tests is not expected. Some water loss might occur. Carbon monoxide evolution from the various samples, as a function of the temperature, is seen in Fig. 8. As is evident visually, but only qualitatively, in this

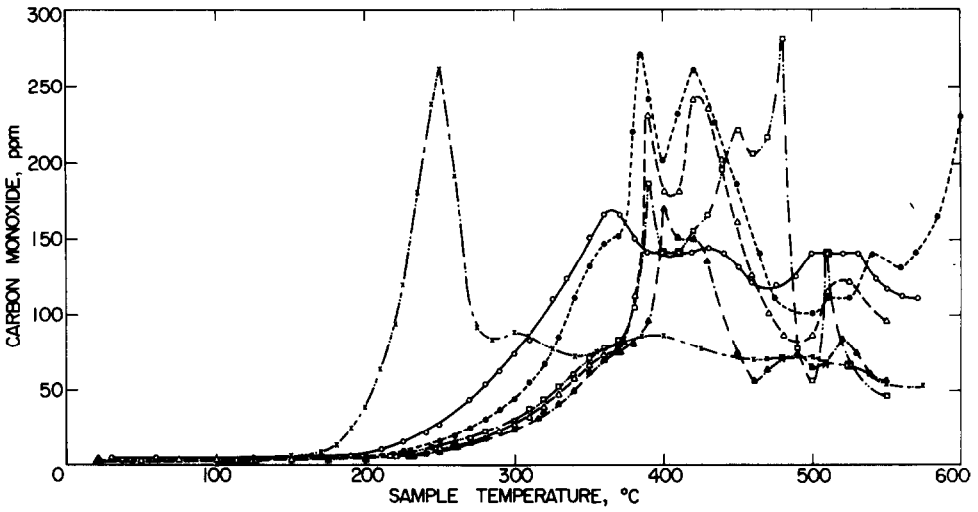


Fig. 8. Carbon monoxide evolution rate as a function of temperature for heated samples of oil shale and oil shale with various nitrates. ○——○, Test 110, oil shale; ●------●, Test 111, oil shale + sodium nitrate; △— — —△, Test 112, oil shale + sodium nitrate; ▲–·–▲, Test 113, oil shale + potassium nitrate; □–··–□, Test 114, oil shale + sodium and potassium nitrates; ×–·–·–×, Test 116, oil shale + ammonium nitrate.

figure, less monoxide was emitted from the samples containing sodium, potassium or sodium and potassium nitrates than from the oil shale without nitrate. This is especially so between 200°C, at which point carbon monoxide becomes noticeable, and about 400°C. The weight of the oil shale was about the same in all the samples, about 5–6 mg in each sample, so that comparisons are valid. Because of the variety and shape of the peaks, it is not possible to assess visually the total amount of carbon monoxide registered from each test. Therefore, the areas under the gas evolution curves were measured. In addition to integrating the complete areas under the curves in Fig. 8, fractional, 40°C interval, areas were also measured. The complete areas (in equivalent units), indicative of the total amounts of carbon monoxide evolved, are given in Table 1. The quantitative results in this table corroborate the visual results in Fig. 8; namely, that on the whole, less carbon monoxide was released from the samples with nitrate than from the neat sample, without nitrate. The cumulative yields, at 40°C intervals, for the complete temperature range are shown in Table 4.

Melting temperatures were conveniently recorded as endotherms in the thermograms. Sodium nitrate, potassium nitrate, and the mixture of sodium and potassium nitrates, in the presence of oil shale, melted at 300, 327 and 200°C, respectively. The molten nitrate, a liquid of high viscosity, understandably can impede the diffusion of the gas released from the shale. Even the unmolten, powdery, nitrates can do the same, by increasing the bulk and

TABLE 4

Cumulative carbon monoxide yields as a function of temperature

| Test no. | 110 | 111 | 112 | 113 | 114 | 116 |
|---|---|---|---|---|---|---|
| Nitrate used [a] | | SN | SN | KN | SN+KN | AN |
| Temperature range (°C) | | | | | | |
| RT–200 | 0.07 | | | | | 1.84 |
| 200–240 | 0.91 | 0.17 | 0.27 | 0.27 | 0.14 | 14.19 |
| 240–280 | 4.14 | 1.63 | 1.43 | 1.93 | 1.37 | 36.00 |
| 280–320 | 11.62 | 5.86 | 4.56 | 6.24 | 5.03 | 46.26 |
| 320–360 | 25.49 | 16.87 | 11.84 | 16.19 | 12.89 | 55.24 |
| 360–400 | 41.43 | 37.20 | 29.71 | 34.50 | 29.11 | 65.10 |
| 400–440 | 56.32 | 60.91 | 58.53 | 62.83 | 50.45 | 74.56 |
| 440–480 | 69.31 | 76.83 | 75.87 | 76.10 | 80.25 | 83.14 |
| 480–520 | 83.64 | 87.33 | 88.69 | 89.77 | 94.24 | 91.48 |
| 520–550 | | | 99.82 | 99.66 | 99.95 | 100.62 |
| 520–560 | 96.88 | 100.0 | | | | |
| 560–570 | 99.93 | | | | | |

[a] SN = Sodium nitrate, KN = potassium nitrate, AN = ammonium nitrate.

thickness of the total sample in the sample pan. As temperature increases and the viscosity of the nitrate melt decreases, carbon monoxide can escape more easily, as is seen at 400°C and above (Table 4). The sample with potassium nitrate released less carbon monoxide than all the other samples.

Results of the sample with ammonium nitrate are especially interesting. Evolution of carbon monoxide is evident at about 170°C, the melting temperature of ammonium nitrate, and reaches a peak at about 250°C. Carbon monoxide continues to evolve at the higher temperatures, but at lower levels than in the other samples. The mixture of sodium nitrate with potassium nitrate forms a eutectic with a melting point temperature not much higher than that of ammonium nitrate, but carbon monoxide evolution was not enhanced at the low temperature by the mixture. Oxidation of carbon monoxide in air is very slow throughout most of the temperature range employed in the tests described here. Various metal oxides, especially of the transition metals, accelerate the reaction but even when present in the oil shale, these oxides would not be available as catalysts until the oil shale matrix disintegrated.

*Hydrocarbons*

Hydrocarbons, especially aliphatic hydrocarbons, are the sought-after products of oil shale decomposition, by whatever mode. Gas-chromatographic analysis could perhaps have identified individual gases, as well as the relative amounts of each gas. However, the amounts released were too small for such complete analysis, and only total gaseous hydrocarbons released were measured.

The evolution of hydrocarbons from the various samples as a function of the temperature of the samples is shown in Fig. 9. Volatile hydrocarbons became noticeable in all the samples, other than those containing ammonium nitrate, at ~ 200°C. In the presence of ammonium nitrate, hydrocarbons were first observed at 175–180°C. These results, and the results of carbon monoxide evolution, show that in the presence of ammonium nitrate the oil shale decomposed at a lower temperature than in its absence.

Again of interest is the relatively larger evolution of hydrocarbons between 200 and 280°C for samples with ammonium nitrate as compared with those without ammonium nitrate or with samples mixed with other nitrates. The amount of oil shale is somewhat larger in the two samples with ammonium nitrate than in the samples with sodium nitrate.

The cumulative yields of total hydrocarbons, which were obtained in the same way as the carbon monoxide cumulative yields, were determined and are presented in Table 5. The data in Table 5 suggest that whatever amounts of hydrocarbons were evolved, more were evolved at lower temperatures when sodium nitrate was present in the sample than in its absence, when comparing like samples. For instance, tests 119 and 123 of neat oil shale, and tests 126, 129, and 132 of oil shale with sodium nitrate, all contain 5–6 mg of

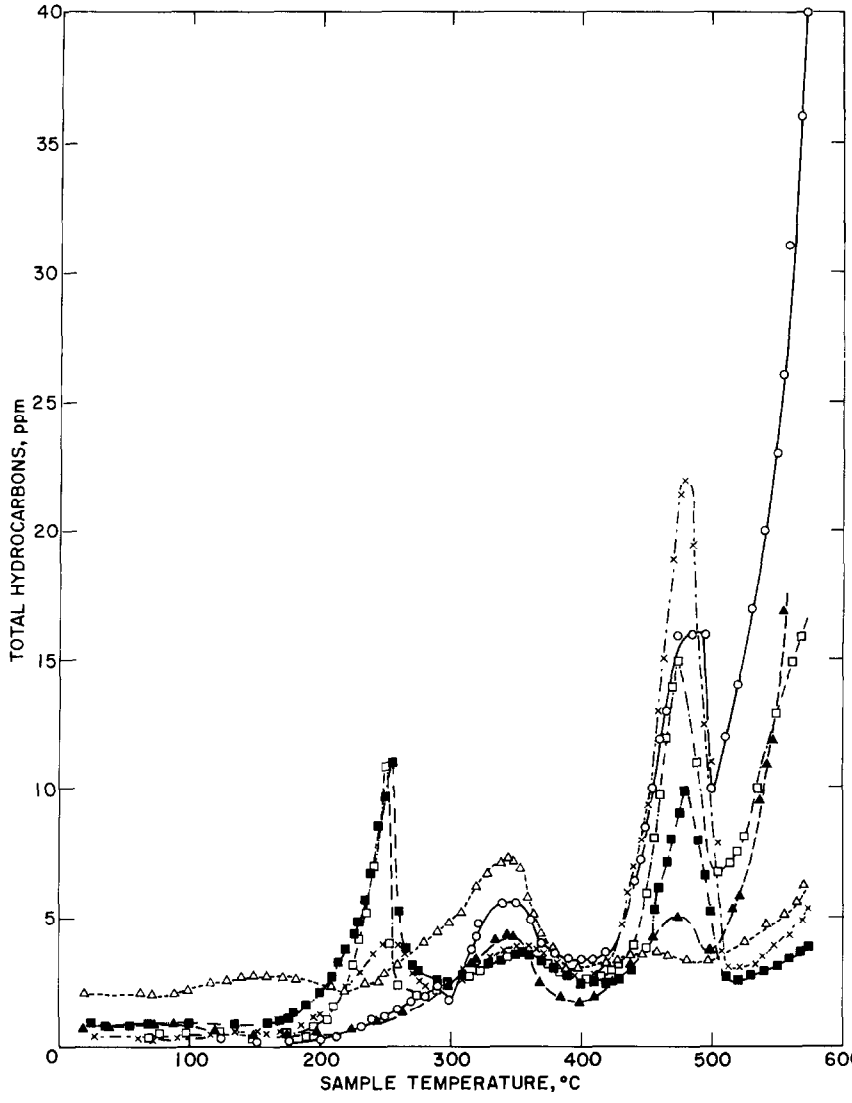


Fig. 9. Total hydrocarbons evolution rate as a function of temperature for heated samples of oil shale and of oil shale with various nitrates. ○——○, Test 123, oil shale; △- - - - -△, Test 126, oil shale + sodium nitrate; ▲— — —▲, Test 132, oil shale + sodium nitrate, □— · —□, Test 124, oil shale + ammonium nitrate; ■– · · –■, Test 134, oil shale + ammonium nitrate; × – · – · – ×, Test 136, oil shale + ammonium and sodium nitrates.

oil shale. On the other hand, the samples with ammonium nitrate and the sample with ammonium and sodium nitrates contain 8–9 mg of oil shale and differ in weight from the neat oil shale samples so that meaningful comparisons as to quantitative amounts of evolved gases cannot be made. To complicate matters even more, the ratios of weights of total nitrates to oil

TABLE 5

Cumulative total hydrocarbons yields as a function of temperature

| Test no. | 119 | 121 | 123 | 130 | 126 | 129 | 132 | 124 | 134 | 136 |
|---|---|---|---|---|---|---|---|---|---|---|
| Nitrate used [a] | | | | | SN | SN | SN | AN | AN | SN + AN |
| Temperature range (°C) | | | | | | | | | | |
| RT–200 | | | | | | | | 0.20 | 1.41 | 0.38 |
| 200–240 | 0.78 | 3.97 | 0.38 | 1.18 | 0.48 | 0.56 | 0.37 | 5.45 | 11.69 | 4.46 |
| 240–280 | 3.45 | 10.99 | 2.13 | 6.63 | 3.24 | 4.93 | 6.49 | 14.11 | 29.33 | 11.26 |
| 280–320 | 9.50 | 20.91 | 5.48 | 22.57 | 10.69 | 17.18 | 22.63 | 18.31 | 35.39 | 15.72 |
| 320–360 | 19.32 | 34.30 | 12.80 | 49.23 | 23.55 | 38.31 | 49.72 | 24.35 | 43.83 | 22.82 |
| 360–400 | 24.85 | 38.93 | 17.95 | 57.70 | 30.28 | 47.61 | 59.55 | 29.86 | 51.08 | 29.01 |
| 400–440 | 29.21 | 39.59 | 23.57 | 64.10 | 37.37 | 55.21 | 65.86 | 35.24 | 56.82 | 36.56 |
| 440–480 | 38.31 | 44.47 | 39.86 | 85.13 | 51.91 | 68.31 | 74.21 | 53.94 | 74.46 | 68.28 |
| 480–520 | 53.85 | 50.26 | 59.08 | 94.55 | 65.49 | 80.97 | 81.07 | 71.00 | 90.04 | 90.18 |
| 520–560 | 84.08 | 100.34 | 88.16 | 100.36 | 99.63 | 99.86 | 94.24 | 92.59 | 96.97 | 97.13 |
| 560–570 | 99.62 | | 99.92 | | | | 99.06 | 100.07 | 99.24 | 99.47 |

[a] SN = Sodium nitrate, AN = ammonium nitrate.

shale also vary from sample to sample, viz.

| Test no. | Wt. of nitrate/wt. of oil shale |
|---|---|
| 126 | 0.88 |
| 132 | 0.70 |
| 134 | 0.59 |
| 124 | 0.53 |
| 129 | 0.44 |
| 136 | 0.39 |

Additional experiments, in which the amounts and ratios of the ingredients are constant, are required for more specific and quantitative results, but were not called for in this study. It is clearly evident, though, that in presence of ammonium nitrate, hydrocarbons are released already at 200°C, whereas none are released from the other samples. Overall, smaller amounts of hydrocarbons were collected from the samples with nitrate than from samples without nitrate. The same behavior was observed for carbon monoxide. Again, diffusion may be a major factor. No attempts were made to control the thickness, area or geometry of the samples, because the main objective of these tests was only to determine the overall effect of molten nitrates on oil shale decomposition, and to see if decomposition, as manifested by release of products, would occur at a lower temperature. These results, of lower amounts of gases for samples with nitrates may seem puzzling, especially in light of weight loss results and of visual observations of sample residues (presented in later sections) which denote more extensive degradation in the presence of nitrates. However, rather than indicating that smaller amounts of volatiles are released, they probably indicate that the gases are oxidized.

Some atmospheric oxidation of the gaseous hydrocarbons is expected at the higher temperatures. Oxidation was suggested by Smith and Johnson [10], in their thermal studies of Green River oil shale, to explain some of their results. But atmospheric oxidation of the carbon monoxide and the hydrocarbons should not differ in the presence of nitrates, unless the sodium and potassium nitrates are decomposing and forming nitrogen oxides in the upper temperature range of the tests. Lower maximum temperatures or isothermal tests at somewhat lower temperature levels will eliminate this problem.

Both light and heavy oils form in pyrolysis of oil shales, in addition to gaseous products. The heavy oils are viscous and readily condense. Although some condensation inside the stainless steel sampling tube might have taken place, the results of hydrocarbon evolution rates were generally reproducible in the tests, and condensed products were not seen in the sampling tube which was washed after each test. However, it is possible that only the light fractions and non-condensable gaseous products reached the flame ionization detector of the hydrocarbon analyzer.

*Scanning electron microscopy*

Scanning electron microscopy photomicrographs of the oil shale, of oil shale residues from the tests of the oil shale, and of the oil shale with sodium nitrate, with potassium nitrate, and with ammonium nitrate were obtained at a magnification of 300, and are presented in Figs. 10A–E, respectively. The cohesive, solid nature of the raw oil shale is evident in the photo of the unheated sample. The sample containing sodium nitrate and the straight oil shale show a similar degree of degradation, whereas the sample with added potassium nitrate is less disintegrated and does not contain very fine loose particles. On the other hand, the sample with ammonium nitrate shows complete disaggregation. The small size and angular shape of the particles in this sample are reminiscent of inorganic minerals separated from oil shale.

X-Ray spectra of these same samples for the major elements of their minerals were also obtained and are presented in Fig. 11A–E, respectively, in units of intensity versus energy. The major peaks in the spectra, seen from left to right, are those of Si, K, Ca and Fe. Longer counting times did reveal the presence of smaller peaks for Mg, Al and S. The sample containing potassium nitrate shows a major peak for K, overshadowing the Ca peak. A sodium peak should be observed in the sample with sodium nitrate, but owing to the low sensitivity of the specific X-ray instrument to sodium, it is absent from the X-ray spectra, although a longer counting time did show the presence of a small peak for Na. The heights of the peaks, as well as their ratios, vary from sample to sample. It is not known if this is due to variations from sample to sample, or to a preferential loss of certain minerals during decomposition. Probably the former is the case.

*Weight loss*

The weight loss incurred by the samples during the test is a direct measure of the extent of decomposition undergone by the samples in the heating process and is therefore of considerable importance in assessing the overall results of these tests. The evolved gases that were measured, carbon monoxide and hydrocarbons, give only a partial view of the decomposition events. Condensed gases and heavy liquids, which were not measured, are an important part of the decomposition scheme.

All the samples were removed from the DSC oven and weighed as soon as the test was completed. Weight loss was greater from samples heated with nitrates than from samples heated without nitrate, as shown in Table 1. In these tests, the maximum temperatures were between 500 and 550°C. Decomposition rates of pure sodium and potassium nitrates at these temperatures are usually quite low. Oil shale or certain of its ingredients may, however, affect the decomposition rate of the nitrates.

The samples were exposed to the higher temperatures only briefly. When

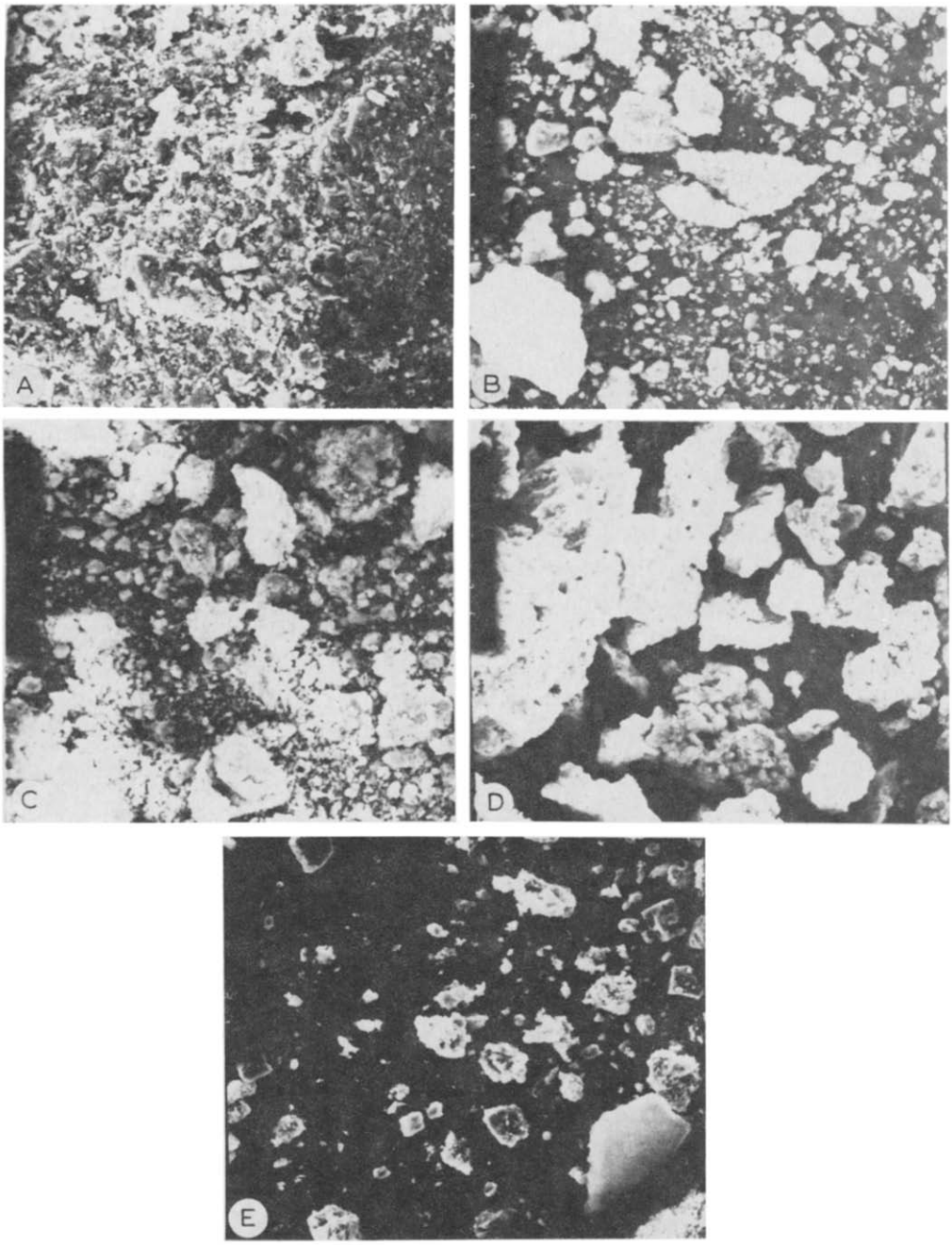


Fig. 10. Scanning electron microscopy photomicrographs of various oil shale samples (magnification 300×). A, Oil shale; B, oil shale residues from the tests of oil shale; C, oil shale + sodium nitrate; D, oil shale + potassium nitrate; E, oil shale + ammonium nitrate.

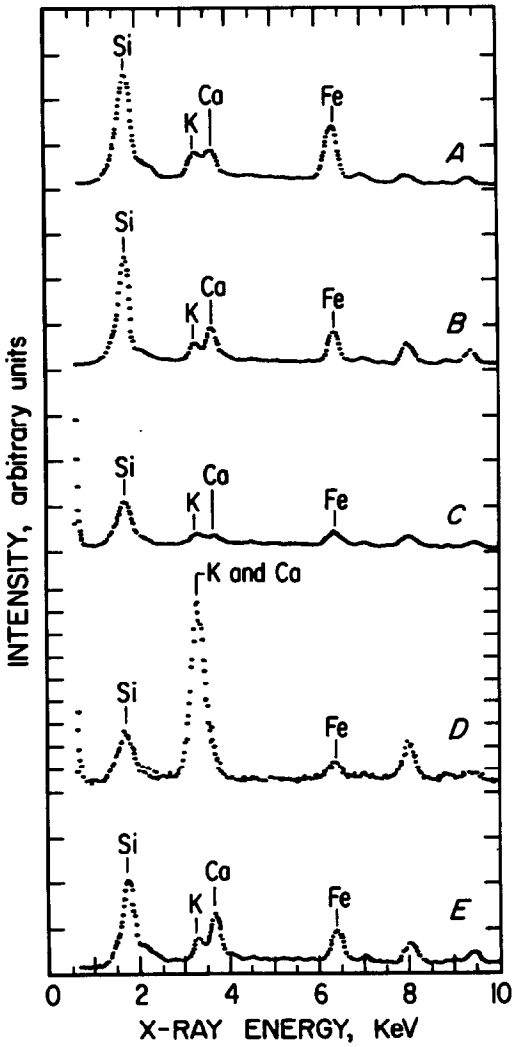


Fig. 11. X-Ray spectra of various oil shale samples. A, oil shale; B, oil shale residues from the tests of oil shale; C, oil shale + sodium nitrate; D, oil shale + potassium nitrate; E, oil shale + ammonium nitrate.

weight loss for the samples containing nitrates other than ammonium nitrate was calculated, it was assumed that most of the weight loss was due to oil shale degradation to volatile products. Even higher losses were found for samples containing ammonium nitrate, but since ammonium nitrate itself decomposes at a relatively low temperature to volatile compounds, it was not possible to assign weight loss to the oil shale alone.

The effect of oil shale on nitrate decomposition is not known. There is, on the other hand, some evidence that certain salts accelerate the decomposition

of pure carbonates. Esin et al. [20] found that sodium nitrate, as well as other sodium salts, increased the intensity of carbon dioxide evolution from pure dolomite (one of the major carbonate minerals in oil shale), at a given temperature. Jukkola et al. [21] found that dolomite and calcite in the oil shale began to dissociate at much lower temperatures than did the pure carbonates; dolomite decomposition in the shale started at about 560°C. However, this temperature is above the temperature range of the tests reported here and is probably not significant to this work.

Of more direct interest are the results shown by Bischoff [22]. He found that magnesium carbonate, which is the portion of dolomite that dissociates first, decomposes completely when heated at 500°C in the presence of gaseous ammonia, water vapor or nitric oxide. A mixture of similar gases forms when ammonium nitrate decomposes. But even the fused ammonium nitrate, which is not decomposed, can react with carbonates such as calcium carbonate, viz. [8]

$$2\,NH_4NO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + 2\,NH_3 + H_2O + CO_2 \qquad (3)$$

Due to the impervious nature of the oil shale, this reaction commences only when the ammonium nitrate is molten. Thus, ammonium nitrate is able to open up the oil shale matrix by reacting with the carbonate minerals. Decomposition of the carbonates frees the kerogen from the inorganic matter, so that it in turn can decompose more easily, and at lower temperatures.

## SUMMARY AND RECOMMENDATIONS

Molten ammonium nitrate attacks the oil shale at a relatively low temperature. Both carbon monoxide and hydrocarbons appear at lower temperatures than they do from all the other samples tested. The exact mode of attack is not known, although it is thought that reaction between the molten ammonium nitrate and the carbonate minerals takes place. The exact nature of the evolved hydrocarbons is not known either. But the nature of these hydrocarbons is of utmost importance, if nitrates are to be used to enhance oil shale degradation to valuable products. Previous attempts to analyze gases emanating from coal samples, heated in the same DSC set-up, with a gas chromatograph coupled directly to a DSC, were unsuccessful, due to the small size of the samples. For this reason, a gas chromatograph was not used in this study. A system combining thermal analysis with mass spectrometry, analogous to that described by Gibson [23], would be valuable to a more detailed study of oil shale degradation by nitrates. Another attractive test system that would yield desirable information is one that was used by Weitkamp and Gutberlet [24] in which a microretort was combined with a train of low-temperature traps and with a gas chromatograph. Larger sam-

ples, more representative of the shale being analyzed, would also be of help. If results are promising, a few other oil shales should be evaluated, as should the proportions of shale to nitrate.

Molten sodium and potassium nitrates may undergo the same reaction with the carbonate. If kept at lower temperatures to prevent the decomposition of the nitrates, they may be as beneficial as ammonium nitrate.

The reactions of nitrates with organic materials can be fast and highly exothermic, especially when confined. The possibility of explosion should also be considered. The relative amounts of these materials partly control the rate and extent of reactions; the optimum amounts for both efficient and safe performance should be determined on a small scale.

## SHORT STATEMENTS

(1) *Principal new conclusions and results*

Molten ammonium nitrate, when in contact with oil shale reacts with it, and especially with the inorganic components of the oil shale. As a result, gaseous and liquid products are evolved at lower temperatures than in the absence of the molten nitrate.

(2) *Methods and observations from which deduced*

Thermal analysis combined with evolved gas analysis was utilized to study the effects of molten nitrate salts on the overall decomposition behavior of an oil shale from the Green River Formation. The evolved gases observed were carbon monoxide and hydrocarbons. The molten nitrate salts used in the tests were ammonium, sodium and potassium nitrates.

(3) *Special limitations and assumptions*

Only one oil shale was tested. But the compounds in oil shale which react with molten ammonium nitrate, namely, calcite and dolomite, are among the major ingredients of most oil shales.

Very small samples are used in thermal analysis. The next step would be the evaluation of larger and additional samples.

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## APPENDIX

### *Determination of heat evolved using DSC thermograms*

For quantitative calorimetric measurements the thermograms have to be recorded as millicalories per second versus time. Sensitivities are chosen so as to give maximum areas.

Our thermograms were recorded as millicalories per second versus sample temperature rather than versus time. Much smaller areas result in this recording mode, but when comparisons were made of areas recorded in the two modes for the same samples, the ratios of the areas were found to be essentially constant, regardless of sample size or sample composition. Therefore, it was deemed proper to use this ratio as a conversion factor for the measured areas recorded in one mode for transposition of the other mode.

In addition to the determination of the areas under the thermograms, a calibration coefficient is required for the calculations of the heats evolved by the various samples. This coefficient can be determined at specific temperatures with materials whose heats of fusion and melting temperatures are accurately known. It can also be determined as a function of temperature with a material whose specific heat as a function of temperature is known. A

sapphire ($Al_2O_3$) standard is provided for this purpose by a manufacturer of the DSC.

The calibration coefficient of the DSC cell was obtained by both methods, with the results as given.

| Sample temperature (° C) | Calibration coefficient | | |
|---|---|---|---|
| | Sapphire | Indium | Zinc |
| 50 | 1.06 | | |
| 100 | 1.11 | | |
| 150 | 1.17 | | |
| 156.6 | | 1.20 | |
| 200 | 1.19 | | |
| 225 | 1.12 | | |
| 250 | 1.21 | | |
| 300 | 1.31 | | |
| 350 | 1.38 | | |
| 400 | 1.46 | | |
| 419.4 | | | 1.74 |
| 450 | 1.56 | | |
| 500 | 1.65 | | |
| 550 | 1.76 | | |

The range of temperatures of importance for heat evolution measurements is between 200 and 500°C, with the larger amount of heat being released between 250 and 500°C. The calibration coefficient for our DSC cell (which was used with the older model Cell Base I) was found to be a linear function of temperature, in the temperature range of interest. Newer models of DSC cell bases have improved electronic circuitry with a resultant constant calibration coefficient. An average calibration coefficient of 1.46 was chosen for the calculations. For best results, areas under the thermograms should be integrated in steps of about 100 degrees each, and averaged calibration coefficients for that temperature range should be used. Since only approximate values of heats were desired, this was not done. With all the assumptions and approximations, the calculated values are rough, at best.

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