



## Project Summary

# Auto-Oxidation Potential of Raw and Retorted Oil Shale

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A study was conducted to assess the potential spontaneous combustion hazard of solid waste streams produced in the processing of oil shale. In addition, the utility and precision of various test methods to assess this hazard were determined. The best methods found involved a differential scanning calorimetry test and nonadiabatic oxygen absorption test. In both cases, the sample was slowly heated in air. In the former case, exothermic activity was monitored; in the latter, changes in exhaust gas composition were monitored.

The carbonaceous retorted oil shale samples appear to present less hazard of spontaneous combustion than bituminous coal. None of the raw shales were found to present as great a hazard as Wyoming subbituminous coal. However, the two raw Utah shale samples tested were found to present hazards exceeding those of less reactive bituminous coals. These materials represent a potential hazard, but if stored and disposed of under conditions suitable for long-term storage of reactive coals, should not spontaneously combust.

The codisposal of raw and retorted shale should be approached cautiously and preferably be avoided if possible, as the presence of raw shale increases the energy contents of the mixture and in some cases decreased the temperature at which exothermic activity was observed. Codisposal of byproduct sulfur with retorted shale appears to cause no increase in risk of spontaneous combustion (but may lead to leaching problems).

*This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

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### Introduction

The main challenge in determining reactivity of solids is to measure, in the laboratory, properties of the solids which can be used to predict how full-scale storage piles will behave. Factors that influence the tendency of a storage pile to self heat and eventually ignite can be grouped into two main categories. The first category includes those properties that are peculiar to the solid itself: reactivity toward oxygen, and heat release as a function of temperature. The second group of factors relating to the pile and its construction: overall dimensions, particle size, degree of compaction, homogeneity, ambient temperature, temperature of placed material, precipitation, wind speed, etc. It is quickly seen that pile characteristics are going to be more difficult to measure and most likely subject to more variation than the properties of the solid itself.

In this study, an investigation of laboratory methods to determine spontaneous combustion tendencies was conducted. These methods were then applied to raw and retorted oil shale samples to determine the relative hazards presented by these materials. In addition, several coal samples were tested by the same methods so that the hazards of the oil shale materials could be related to the better known phenomenon of self heating in coal storage piles.

### Materials and Methods

Retorted shale samples from the Lurgi, Tosco II, Paraho direct-mode, Hytort and Union B processes were tested. A raw

shale sample from Federal lease tract C-a in Colorado, two raw shale samples from Federal lease tract Ua/Ub in Utah, Wyoming subbituminous coal, Western Kentucky #9 bituminous coal and Pocahontas #3 (Virginia) bituminous coal were also tested. Sulfur and organic carbon contents and heating values of these materials are given in Table 1. Heat capacities of these materials, as determined by differential scanning calorimetry, are given in Table 2.

### Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) involves measuring the heat evolved or absorbed by a sample at a given temperature relative to a known reference material at the same temperature. When the temperature is increased or decreased, heat effects arise from differences in specific heats, phase changes and chemical reactions. Low temperature oxidation is an exothermic reaction. When spontaneous heating occurs, the heat produced by this reaction (and other exothermic reactions including the heat of wetting) is greater than the heat which is rejected to the surroundings and the material which is oxidizing increases in temperature. As the temperature of the material increases, the rate of oxidation increases and, in some cases, a rapid temperature increase occurs.

DSC data, obtained while the temperature of the sample and reference are increased at a slow constant rate, indicate the difference in heat flow between sample and reference as a function of temperature. When the reference is an empty sample pan of equal mass and specific heat to the pan in which the sample is held, the net heat effect is that produced by the sample. When the temperature of the apparatus is restricted to eliminate the possibility of phase changes in the sample, endothermic effects are associated with the heat capacity of the sample, and with some materials, such effects as drying, desorption of gases, and devolatilization. Exothermic effects in excess of the sample heat capacity are associated with exothermic chemical reactions.

Samples were tested in a duPont Instruments Model 951\* differential scanning calorimeter equipped with a standard low pressure cell. The calorimeter was coupled to a duPont Instruments Model 1090/1092 thermal analyzer which permitted tempera-

**Table 1. Description of Samples**

Material (- 325 mesh)	Total Sulfur Weight % Dry Basis	Organic Carbon Weight % Dry Basis	Heating Value Btu/lb Dry Basis
W. Kentucky #9 Bituminous Coal	3.73	61	13050
Pocahontas #3 Bituminous Coal	0.65	69	12120
Wyoming Subbituminous Coal	0.63	64	11560
Utah Raw Shale (66 GPT)	1.85	28	6240
Utah Raw Shale (28 GPT)	0.75	11	2090
C-a Raw Shale	0.98	5.2	878
TOSCO II Retorted Shale	0.58	3.5	433
Hytort Retorted Shale	2.40	3.8	420
Paraho Retorted Shale	0.57	3.1	188
Union Shale Mixture	0.68	4.1	209
Lurgi Retorted Shale	0.86	0.13	44

**Table 2. Mean Heat Capacity of Coal and Shale Materials Based on Initial Sample Weight (J/g, - 325 mesh)**

Material	Temperature Range (°C)		
	25-200	25-400	25-600
C-a Raw Shale	0.76	0.72	0.73
Utah Raw Shale (66 GPT)	2.18	2.13	2.56
Utah Shale (28 GPT)	1.17	1.15	1.23
Hytort Retorted Shale	1.08	1.03	1.17
Pocahontas #3 Bituminous Coal	1.19	1.28	1.40
W. Kentucky #9 Bituminous Coal	0.69	0.47	0.44
Wyoming Subbituminous Coal	1.28	0.67	0.63
Lurgi Retorted Shale	0.82	0.87	0.92
TOSCO II Retorted Shale	0.39	0.89	0.86
Paraho Retorted Shale	0.73	0.71	0.66
Union Shale Mixture	2.57	1.75	1.60

ture programming and data acquisition/playback using magnetic disk storage. Samples of between 17 and 54 mg were used. Variations in sample mass for the different materials tested were primarily due to differences in bulk density. Samples were loaded into open aluminum pans; the pans were completely filled to the top edge and excess material was removed so that the sample surface was level. An empty pan of comparable mass (and heat capacity) was used as a reference.

With air flowing through the cell, a pre-weighed sample in a tared aluminum pan was placed on the sample thermocouple disk and an empty sample pan was placed on the reference thermocouple disk.

The test was conducted by programming the heater to increase the temperature of the thermoelectric disk to which sample and reference thermocouples are attached. A precisely controlled heating ramp of 2° C per minute was followed from slightly above ambient temperatures (25°-30° C). Different samples were heated to different

final temperatures (380°-550° C) but in all cases the test was continued to the end of the exotherm. Exothermic reactions were sensed by a slight lead in temperature of the sample thermocouple over the reference thermocouple. The instrument was calibrated to convert this lead into an actual heat effect.

The most important measurement relating DCS data to spontaneous heating behavior is the onset temperature of the exothermic oxidation reaction. When an exotherm is observed while a sample is being heated, this temperature is characterized by extrapolating the slope of the leading edge of the exothermic peak to the baseline. It is assumed that the lower this temperature is, the greater the tendency of the material to spontaneously heat. This provides a means for empirically ranking materials of unknown self-heating potential by comparison to materials of known heating potential. The Wyoming subbituminous and Western Kentucky bituminous coals exhibited the earliest exothermic onset tem-

\*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

peratures followed by the 66 gallon/ton raw Utah shale. The low volatility bituminous Pocahontas #3 coal was less reactive than any of the raw western shales that were tested. The carbonaceous retorted shale samples exhibited considerably higher exothermic onset temperatures than the raw shale, indicating that they present less of a spontaneous heating hazard than the raw shale and much less than the coal. Decarbonized shale from the Lurgi process was also tested but absolutely no exothermic reaction was observed at temperatures up to  $550 \pm ^\circ\text{C}$ . The Hytort retorted shale was extremely unreactive, exhibiting an exothermic onset temperature higher than that of any of the retorted shale samples except for the Lurgi retorted shale.

### Nonadiabatic Oxygen Absorption Test

The materials described above were also subjected to a nonadiabatic oxygen absorption test.<sup>1</sup> In this test, 100 g samples of material were placed in a glass cell. Humidified air at 60 cc/min was passed through the cell and the temperature of the cell and contents were increased at a rate of  $25^\circ\text{C}/\text{hour}$ . The exhaust gas from the cell was analyzed chromatographically; the depletion of oxygen and increased levels of carbon dioxide were used as an indicator of reactivity.

Based on the gas analysis, a spontaneous combustion liability index (the S index) was calculated. The formula for this index was devised by Schmeling<sup>1</sup> and is based on the conversion of oxygen in the inlet gas to  $\text{CO}_2$ .

$$S = \frac{h_1 + h_2}{2} (x_1) + \frac{h_2 + h_3}{2} (x_2)$$

where S = the spontaneous combustion index

$h_1$  = 21 - oxygen concentration at  $125^\circ\text{C}$

$h_2$  = 21 - oxygen concentration at  $150^\circ\text{C}$

$h_3$  = 21 - oxygen concentration at  $175^\circ\text{C}$

$x_1$  = carbon dioxide concentration at  $150^\circ\text{C}$   
- carbon dioxide concentration  $125^\circ\text{C}$

$x_2$  = carbon dioxide concentration at  $175^\circ\text{C}$   
- carbon dioxide concentration at  $150^\circ\text{C}$

All concentrations are expressed in volume percent.

The test indicated that the Wyoming subbituminous coal was the most reactive

material with an S index of 108 in the  $-48 + 100$  particle size test and an S index of 165 when tested in the  $-325$  particle size. This is consistent with the generally observed phenomena of spontaneous heating in low rank coals. The criterion, adopted by Schmeling, that materials with S indices greater than 30 (for the  $-48 + 100$  mesh size) are dangerous, also puts the Western Kentucky No. 9 bituminous coal ( $S = 37.5$ ) in this category. As would be expected from historical observations of spontaneous combustion, the bituminous coals are much less dangerous than the subbituminous coal.

The tests indicated, as expected, that the retorted shales are less likely to spontaneously combust than any of the coals or raw shales. The three coals rank in the order expected from past experience and larger scale testing. The raw shales exhibit oxygen absorption behavior which ranks with their energy content. (The richer Utah shale has a higher S index than the leaner Utah shale and the three western shales follow the same order in S index as in higher heating value.)

While none of the raw shales rank as high as the subbituminous coal, the richer (66 GPT) Utah shale ranks intermediate between it and the high volatility Western Kentucky #9 bituminous coal and the leaner (28 GPT) Utah shale ranks intermediate between the Western Kentucky #9 coal and the low volatility Pocahontas #3 bituminous coal. On the basis of this test, the raw shales present a hazard of spontaneous combustion on the order of bituminous coals, and the greater the energy content of the shale, the greater the tendency for spontaneous combustion. All of the retorted shales tested rank well below the bituminous coals in spontaneous combustion risk based on Schmeling's index.

In the course of the study, four other experimental methods were tried to determine their suitability as spontaneous combustion hazard indicators.

These tests were:

- (a) a method based on weight loss data from thermogravimetric analysis of samples in air using a  $2^\circ\text{C}/\text{min}$  temperature ramp.
- (b) a method based on exothermic oxidation of samples by hydrogen peroxide.
- (c) a method based on isothermal high pressure differential scanning calorimetry.
- (d) an adiabatic test similar to the non-adiabatic test described earlier.

These tests were found to be unsuitable for both technical and practical reasons.

### Conclusions

*It must be noted that the results reported here are based on a very limited number of samples of raw and retorted shale. Substantial variations in composition of raw shales occur with geographic and stratigraphic location. The retorted shale samples came from pilot plant operations which may not be completely representative of commercial operations. Hence, it is strongly recommended that actual samples of waste materials proposed for field disposal be tested to determine their actual spontaneous combustion hazard.*

Retorted shales investigated in this study are unlikely to present a spontaneous combustion hazard. These include retorted shales from the Paraho direct, TOSCO II, Hytort, and Lurgi processes and a mixture of retorted shale, raw shale "fines" and sulfur from the Union B process. These materials proved to be far less reactive than Pocahontas #3 low volatility bituminous coal which is generally regarded at the low end of the spectrum of coals susceptible to spontaneous heating. This conclusion was reached on the basis of both the exothermic onset temperature, as determined by differential scanning calorimetry, and the nonadiabatic oxygen absorption test, and supported by TGA weight loss data. The Lurgi retorted shale is noncombustible and could not burn even if an attempt was made to ignite it.

The raw western shales, while not as liable to ignite as the Wyoming Smith-Roland subbituminous coal (which is generally placed at the higher end of the spectrum of coals susceptible to spontaneous heating) present a potential hazard. The richer of the Utah shale samples (66 GPT) is particularly reactive, falling between the Wyoming subbituminous and the Western Kentucky high volatility bituminous coal (of intermediate reactivity with regard to coal) in the nonadiabatic oxygen absorption test. In the DSC test, it falls below the Western Kentucky coal but above the relatively unreactive Pocahontas #3 coal. In the TGA weight loss test (based on mass remaining after heating to  $300^\circ\text{C}$ ) a greater weight loss is observed with this sample than with the Western Kentucky bituminous coal.

The leaner Utah shale (28 GPT) is intermediate in tendency to autoignite between the Western Kentucky coal and the Pocahontas #3 coal in both the nonadiabatic oxygen absorption test and the DSC test (ranked by exothermic onset temperature). This material falls below the coal samples in the TGA weight loss tests. By Schmeling's criteria, (S index  $< 30$ ), this is

also a potential hazard. The C-a shale has about the same exothermic onset temperature as the leaner Utah shale (i.e., intermediate between the Western Kentucky and Pocahontas bituminous coals, but ranks considerably lower than the Pocahontas coal in the nonadiabatic oxygen absorption test with an S index of about 6). This is probably the least reactive of the three western raw shales tested but should still be regarded as posing potential problems.

The results of the study suggest that carbonaceous retorted oil shale poses less hazard of spontaneous combustion than bituminous coal and it is logical that the more severe the retorting process and the more complete the removal of the organic matter, the less reactive the resulting waste product will be. This does not imply that the risk of spontaneous combustion can be ignored but rather that the risk should be low if proper disposal practices are followed. Good practices would likely include cooling before disposal, compaction in lifts, and excluding air flow into the pile. Decarbonized shales, such as the Lurgi decarbonized retorted shale, are essentially inert, since substantially all of the energy content has been removed. Such shales should present no hazard of spontaneous combustion.

On the basis of DSC testing, codisposal of byproduct elemental sulfur with retorted oil shale will not increase the hazard of spontaneous combustion of the mixture. The mixing of raw shale fines with retorted oil shale for disposal should be approached very cautiously and preferably be avoided. The addition of as little as 5% raw shale fines, appears to lower the exothermic onset temperature of the mixture to approximately that of the fines themselves. Although the energy available in the mixture is much less than that of the raw shale fines, the potential for spontaneous combustion may be significantly increased as compared to the retorted shale alone and may in fact be as great as that of the raw shale fines alone. For example, the addition of as little as 5 percent raw shale fines (Utah 28 GPT) lowered the exothermic onset temperature to that of the raw shale fines alone. However, it must be emphasized that the data on this point are somewhat conflicting. The Union B shale mixture which contained 5.47 weight percent raw shale fines behaved in a manner similar to other carbonaceous retorted oil shales which did not include admixture of raw shale fines. Hence, it is recommended that anyone proposing disposal of retorted and raw shale mixtures should evaluate their particular mixture to define its properties. It is considered likely that for

each specific retorted/raw shale mixture, there is a unique value of raw to retorted shale ratio which, if exceeded, will cause the mixture to assume the properties of the raw shale.

The raw western shales present a potential hazard, but if stored and disposed of under conditions suitable for long term storage of reactive coals, then they should pose no greater risk than such coals. Ideally, however, raw shales should be processed for energy recovery to the greatest extent possible. Material produced during crushing operations that is too small for retorting would be preferably subjected to combustion for production of process heat, or if feasible, agglomerated with a binder to a size where it could be retorted for maximum energy recovery.

The differential scanning calorimetry test and the nonadiabatic oxygen absorption test appear to be the most meaningful test methods used in this study. These tests were reproducible and, when the tests were applied to coal samples, the results conformed to generally observed rankings of spontaneous combustion potential. Of the other tests considered, the peroxide test was technically unsound; pressure differential scanning calorimetry and adiabatic oxygen absorption tests did not produce

useful, reproducible results in the course of this particular study. These methods may, however, after further development, be made useful. The thermogravimetric analysis weight loss test, while potentially useful in characterizing samples was found unsuitable as results for coal samples did not conform to generally observed spontaneous combustion rankings and the retorted shale samples produced an insufficient response to evaluate.

A summary of results obtained in the differential scanning calorimetry and nonadiabatic oxygen absorption testing is given in Table 3. As no reference standards are available for the test parameters which were determined, the accuracy of these tests cannot be determined. However, the ranking of the materials can be used as an indicator of relative spontaneous combustion hazard.

## Reference

- Schmeling, W.A., et al., "Spontaneous Combustion Liability of Subbituminous Coals: Development of a Simplified Test Method for Field Lab/Mine Application," In: Analytic Chemistry of Liquid Fuel Sources, Uden, P.C., et al. eds, ACS 1978.

**Table 3.** Summary of Results From Differential Scanning Calorimetry and Nonadiabatic Oxygen Absorption Testing

Material	DSC*		Nonadiabatic test S index
	onset °C	exotherm J/g	
Wyoming Subbituminous Coal	190	10900	165
Western Kentucky #9 Bituminous Coal	193	13800	60
Utah Raw Shale (66 GPT)	211	8320	86
C-a Raw Shale	226	920	5.6
Utah Raw Shale (28 GPT)	227	2990	44
Pocahontas #3 Bituminous Coal	230	15700	42
Paraho Retorted Shale	300	480	0.27
TOSCO II Retorted Shale	306	560	1.4
Union Shale Mixture	321	860	4.6
Hytort Retorted Shale	357	1340	3.8
Lurgi Retorted Shale	**	~0	0.00

\*Tested in dry air, particle size: - 325 mesh

\*\*No exotherm observed to 550° C.



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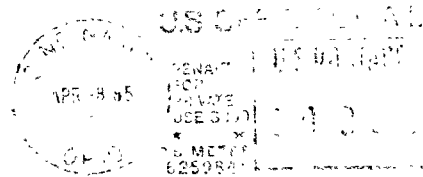
*The complete report, entitled "Auto-Oxidation Potential of Raw and Retorted Oil," (Order No. PB 85-156 248/AS; Cost: \$16.00, subject to change) will be available only from:*

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