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Inhibition of Spontaneous Combustion of Coal

By Alex C. Smith, Yael Miron, and Charles P. Lazzara

BUREAU OF MINES

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Å	Angstrom	m^2/g	square meter per gram
Btu	British thermal unit	μm	micrometer
Btu/lb	British thermal unit per pound	mL	milliliter
cal/g-°C	calorie per gram-degree Celsius	mg	milligram
cm	centimeter	mW/cm-K	milliwatt per centimeter-kelvin
cm^3/min	cubic centimeter per minute	pct	percent
°C	degree Celsius	ppm	part per million
°C/min	degree Celsius per minute	vol pct	volume percent
g	gram	wt pct	weight percent
h	hour		

INHIBITION OF SPONTANEOUS COMBUSTION OF COAL

By Alex C. Smith,[1] Yael Miron,[2] and Charles P. Lazzara[3]

ABSTRACT

This report describes laboratory studies conducted by the Bureau of Mines to evaluate the effectiveness of 10 additives to inhibit the self-heating of coal. Aqueous additive solutions were applied to a bituminous coal with a high spontaneous combustion potential, and the minimum self-heating temperatures (SHT's) of the dried coal-additive mixtures were determined in the Bureau's adiabatic heating oven. The relative effectiveness of the additives was determined by the observed changes in the minimum SHT's of the mixtures, or by the time required for the sample temperature to reach 150° C, compared with the untreated coal and a coal-water blank. Sodium nitrate, sodium chloride, and calcium carbonate were found to be the most effective inhibitors, followed by ammonium dihydrogen phosphate, calcium chloride, ammonium chloride, sodium acetate, and potassium chloride. Two additives, sodium formate and sodium phosphate, promoted the self-heating process.

Differential scanning calorimetry experiments on the coal-additive mixtures showed that reactions occurred between the coal and some of the additives, but these reactions did not influence the self-heating process.

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INTRODUCTION

In the United States, approximately 18 pct of underground coal mine fires are attributed to spontaneous combustion (*1*).[4] The incidence rate is expected to increase with the increased use of longwall mining methods and greater consumption of lower ranked coals. In addition, spontaneous combustion continues to be a problem in the storage and transport of coal (*2*).

Spontaneous combustion occurs when heat, which is produced by the low-temperature oxidation of the coal, is not adequately dissipated. This results in a net temperature increase in the coal mass that can lead to a fire.

Present methods employed to prevent or inhibit spontaneous combustion include compaction and inerting of the atmosphere with CO_2 or N_2 (*3-4*). However, such techniques are not always practical for long-term in mine use, gob areas, or abandoned mines. European workers have investigated the impregnation of coal pillars, prior to extraction, with various gels, aqueous solutions, and powders to inhibit oxidation. Powders, such as carbamide and diammonium phosphate, were injected under pressure into drilled holes in the upper interhorizon barrier over the pillar to be extracted (*5*). After mining, increasing temperatures in the gob cause the powders to decompose, absorbing heat, while releasing ammonia that acts as an inerting gas. Gel solutions prepared from water glass (sodium silicate), ammonium sulfate, and water have also been injected into coal pillars. The freshly prepared gel solutions had the consistency of water and penetrated easily into small voids. After thickening, a plastic mass formed, which limited the access of O_2 to the coal. The effectiveness of these powders and gels was evaluated by monitoring the coal temperature and gas content of mine air in gob areas. Aqueous solutions of inorganic salts and salt-clay mixtures have also been tested and found effective in preventing spontaneous combustion fires by injection into coal seams (*6-8*).

Laboratory tests to evaluate the effectiveness of various boron compounds and calcium chloride ($CaCl_2$) in inhibiting coal oxidation were conducted by Chamberlain (*9*). In that study, compounds were added to coal in powder form and as aqueous solutions, and the rates of O_2 adsorption and CO generation were used to evaluate the relative effectiveness of the inhibitors. Boric acid and ammonium hydrogen tetraborate powders were the most effective inhibitors at temperatures above 125° C, while at lower temperatures aqueous solutions of these compounds were the most effective.

This Bureau of Mines report describes laboratory studies on the inhibition of the spontaneous combustion process of coal by additives. An adiabatic heating oven was used to evaluate the effectiveness of 10 additives in suppressing the self-heating process. Aqueous solutions containing the additives were applied to a bituminous coal with a high spontaneous combustion potential, and the minimum SHT of the coal-additive mixture was measured. The minimum SHT is the minimum initial temperature that produced a sustained exothermic reaction, or thermal runaway, and has been used to rank a coal's relative self-heating tendency compared with those of other coals (*10*). The lower the minimum SHT, the higher the self-heating potential of the coal. Thus, an increase in the minimum SHT of a coal due to the presence of an additive should be an indication of the effectiveness of the additive as an inhibitor of the spontaneous combustion of that coal. The relative effectiveness of the additives was determined by the observed changes in the mixture's minimum SHT compared with those of untreated coal and a coal-water blank.

The effectiveness of additives that when mixed with the coal produced the same minimum SHT was evaluated based on the time required for the coal-additive mixture to reach 150° C, starting from its minimum SHT. Above 150° C, the O_2 concentration falls below that required to supply sufficient O_2 to the reacting system (*10*). In addition, the relative effectiveness of one additive applied as a dry powder was determined to evaluate the effect of the application procedure.

The major heat releasing reaction in the self-heating of coal is oxidation. The process is not completely understood, but it is generally agreed that O_2 is adsorbed onto the coal and reacts with the oxygen-containing groups of the coal, releasing CO and other gases. Thus, the rate of O_2 adsorption and CO evolution should be indicative of the rate of coal oxidation. CO and O_2 concentration measurements were obtained in the self-heating tests, and the relative effectiveness of the additives based on these parameters was compared to the results of the evaluation based on the mixtures' minimum SHT's.

Tests were also conducted in the adiabatic heating oven on the coal-additive mixtures at 60° C to determine the relative effectiveness of additives when tested at an initial temperature at which all mixtures would undergo thermal runaway. If the resulting order of effectiveness agreed with that based on the determination of the minimum SHT's of the mixtures, then other additives could be evaluated in just one test.

Next, the effect of additive concentration was determined for two of the most effective inhibitors, NaCl and $CaCO_3$. Lastly, the effect of removing trace inorganic species found in the coal, which may contribute to the self-heating process, was evaluated.

Differential scanning calorimetry (DSC) experiments were also conducted on the coal-additive mixtures. A DSC thermogram indicates the amount of energy adsorbed or released by a sample as it undergoes physical and/or chemical changes, as a function of temperature. By comparing thermograms of the coal-additive mixtures with those of the coal and a coal-water blank, changes in the coal or reactions between the coal and the additives may

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[4] Italic numbers in parentheses refer to items in the list of references at the end of this report.

be discerned. Also of interest in the DSC tests was the identification of the temperature at which the onset of exothermic behavior occurs. If the additive interferes with the adsorption of O_2, the interference might be reflected in an increase in this temperature.

The effect of the additive application procedure on the results of the self-heating tests is then discussed. This is followed by a discussion of the possible thermal, chemical, and physical effects that the additives had on the coal that contributed to their behavior and relative effectiveness at promoting or inhibiting the self-heating of coal.

EXPERIMENTAL APPARATUS AND PROCEDURES

ADIABATIC HEATING OVEN EXPERIMENTS

Test Apparatus

The relative effectiveness of various additives in suppressing the self-heating process in coal was evaluated in an adiabatic heating oven. Figure 1 is a schematic of the oven and sample container. The oven is designed to minimize heat losses from the coal sample during the self-heating stage of the test.

The sample is contained in a brass wire mesh basket, 7.6-cm diam by 5 cm high, which is enclosed in a stainless steel assembly. Preheated, humidified air enters the bottom of the assembly, passes through the sample, and exits at the top. A stainless steel cylinder surrounded by a nickel-chromium wire resistance heater serves as the sample oven. The cylinder surrounds the sample assembly and is attached to an insulated top cover in which another resistance-type heater wired in parallel to the sample oven is located.

The oven assembly is contained in a 15-cm-ID Dewar flask that is surrounded by a 5-cm layer of insulation in which another heater is embedded. The apparatus is instrumented to record sample and oven temperatures, and O_2 and CO concentrations of the exit gas stream. A more detailed description of the apparatus is found in reference 10.

Test Materials

No. 80 seam coal, a high-volatile C bituminous coal from Wyoming, was used in all the tests. Table 1 shows the coal's as-received proximate and ultimate analyses, dry ash-free oxygen content, and heating value.

Ten additives were evaluated and are shown in table 2. Calcium carbonate ($CaCO_3$), sodium chloride (NaCl), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), potassium chloride (KCl), calcium chloride ($CaCl_2$), and ammonium chloride (NH_4Cl) were chosen because they have been found to be effective at inhibiting coal dust explosions (*11*). Calcium chloride and ammonium compounds have also been found to be effective at inhibiting self-heating (*5, 9*). Sodium phosphate (Na_3PO_4), sodium formate (NaOOCH), sodium acetate ($NaC_2H_3O_2$), and sodium nitrate ($NaNO_3$) were tested to evaluate the effect of varying the anion of the sodium salts on inhibitor effectiveness.

Experimental Procedures

The evaluation of the effectiveness of additives in suppressing the self-heating process was made by determining the minimum SHT's of coal samples impregnated with 15 pct by weight of the various additives in the adiabatic heating oven, and comparing them with the minimum SHT's of the untreated coal and a coal-water blank. In cases in which the coal additive mixtures had the same minimum SHT, their relative effectiveness was based on a secondary parameter, the time for the sample to reach 150° C.

TABLE 1. - Analysis of as-received No. 80 seam coal

Proximate analysis, wt pct:	
Moisture	11.0
Volatile matter	39.5
Fixed carbon	43.9
Ash	5.6
Ultimate analysis, wt pct:	
Hydrogen	5.9
Carbon	65.2
Nitrogen	1.6
Sulfur	0.7
Oxygen	21.0
Oxygen, DAF	13.5
Heating value ...... Btu/lb	11,350

DAF Dry ash-free.

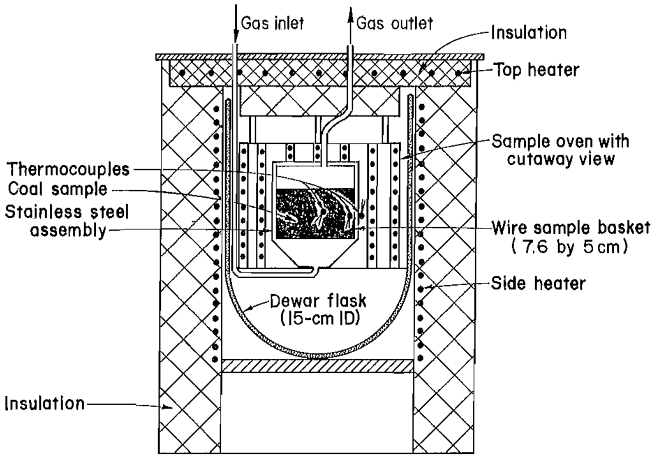

Figure 1. - Schematic of adiabatic heating oven.

TABLE 2. - Additives evaluated in self-heating tests

Additive	Formula	Description
Calcium carbonate . . .	$CaCO_3$	Limestone dust, used in coal mines for prevention of coal dust explosions.
Sodium chloride	NaCl	Certified ACS.
Ammonium dihydrogen phosphate	$NH_4H_2PO_4$	Do.
Potassium chloride . . .	KCl	Do.
Calcium chloride	$CaCl_2 \cdot 2H_2O$	Do.
Ammonium chloride . .	NH_4Cl	Do.
Sodium phosphate . . .	$Na_3PO_4 \cdot 12H_2O$ . .	Do.
Sodium formate	NaOOCH	Do.
Sodium acetate	$NaC_2H_3O_2 \cdot 3H_2O$.	Granular, meets ACS specifications.
Sodium nitrate	$NaNO_3$	Crystals.

ACS American Chemical Society.

The minimum SHT's of the samples were determined using the standard conditions and methods described in reference 10. Briefly, the coal was first pulverized and sieved. The minus 100- plus 200-mesh (74- by 150-μm) fraction of the coal was then dried in an oven at 67° C with a 200-cm^3/min flow of dry N_2. A 100-g sample was placed in the adiabatic heating oven and brought to a preselected initial temperature under a 200-cm^3/min flow of dry N_2. The coal was then exposed to a 200-cm^3/min flow of humidified air. A series of tests were made, each with a fresh sample, in 5° C increments, until the minimum initial temperature that produced a sustained exothermic reaction, or thermal runaway, was determined.

In the tests on coal-additive mixtures, 17.6 g of additive was dissolved in 75 mL of deionized water. In the tests using the three hydrated salts, the weight of additive added to the coal was increased to compensate for the water of hydration, so that the weight of the anhydrous additive was 17.6 g. In tests to determine the effect of additive concentration on the self-heating process, the amount of additive was varied to yield the desired concentration. A few of the less soluble additives required additional water for dissolution. One additive, $CaCO_3$, is insoluble. It was mixed with the water and added to the coal as a slurry.

The additive solutions or slurries were then added to 112 g of undried coal in a 21- by 21- by 5-cm glass laboratory dish and mixed. The dish was placed in an oven under a flow of dry N_2 at 67° C for a period of time sufficient to drive off most of the water. The sample was then transferred to a drying tower and dried to a constant weight at 67° C under a flow of dry N_2. The resulting sample contained 100 g of dried coal impregnated with 15 pct by weight (17.6 g) of anhydrous additive. A coal-water blank was also prepared using the same procedure without an additive.

In addition, the relative effectiveness of $CaCO_3$ was evaluated when applied as a dry powder. For those tests, 17.6 g of powder was mixed with the coal and dried in the drying tower to a constant weight in the manner described previously.

Agglomeration and/or swelling of the coal particles occurred during many of the sample preparations. To ensure a uniform particle size, all samples were placed on a 100-mesh sieve, and the portion that did not pass through the sieve was reduced in size by grinding until it passed through the sieve. The sample was then placed in the adiabatic heating oven and tested under the standard conditions.

Experiments were also conducted in the adiabatic oven using a coal sample washed with deionized water and another washed with an aqueous solution of nitrilotriacetic acid (NTA), a complexing agent. The washed samples differed in preparation from that of the coal-water blank in that most of the water was removed by aspiration before final drying in the tower.

DIFFERENTIAL SCANNING CALORIMETRY EXPERIMENTS

A DuPont[5] 990 DSC was used in all the tests. The samples, weighing 20 to 40 mg, were taken from mixtures prepared for the adiabatic oven tests. They were placed in aluminum pans, covered, and heated in an atmosphere of static air in the DSC at a rate of 10° C/min.

The resultant thermograms indicate changes undergone by the samples either as endotherms or exotherms. Endotherms, due to heat adsorption by the sample, are seen as downward deviations in the thermogram, whereas exotherms, caused by heat generation, are seen as upward deviations.

RESULTS

ADIABATIC HEATING OVEN

Evaluation of Inhibitor Effectiveness

The minimum SHT's of 8 of 10 coal-additive mixtures, the coal-dry $CaCO_3$ mixtures, a coal-water blank, and the untreated coal were determined in the adiabatic heating oven. Two of the additives acted as promoters of the self-heating process, and their minimum SHT's were not obtained.

Table 3 shows the additives and the minimum SHT's of the coal-additive mixtures, the coal-water blank, and the untreated coal, along with the times required for the sample temperature to reach 150° C. Also included are the times for the concentration of CO and O_2 in the exit gas to reach 400 ppm and 19 pct, respectively, in the tests starting at the mixture's minimum SHT.

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[5] Reference to specific products does not imply endorsement by the Bureau of Mines.

TABLE 3. - Experimental minimum SHT's and times to reach 150° C, 400 ppm CO, and 19 pct O_2 of coal-additive mixtures in the adiabatic heating oven

Additive	*Minimum SHT, °C*	*Time, h, to reach* 150° C	*Time, h, to reach* 400 ppm CO	*Time, h, to reach* 19 pct O_2
Na_3PO_4	≤40	[1]17.6	[1]15.0	[1]16.2
NaOOCH	≤40	[1]18.9	[1]16.2	[1]16.4
None	45	17.4	12.3	15.5
H_2O (blank)	50	20.5	14.8	18.8
KCl	50	36.3	29.3	35.5
$NaC_2H_3O_2$	50	46.0	42.2	44.8
NH_4Cl	50	70.1	66.7	69.4
$CaCO_3$ (dry)	50	92.1	87.3	89.4
$NH_4H_2PO_4$	55	26.7	22.3	25.3
$CaCl_2$	55	55.8	50.1	53.8
$CaCO_3$	60	13.4	11.2	11.8
NaCl	60	14.1	7.5	12.3
$NaNO_3$	60	68.6	61.3	67.7

[1] Values obtained in tests at initial temperature of 40° C.

Na_3PO_4 and NaOOCH are also included, although their minimum SHT's were not determined.

The minimum SHT of the No. 80 seam coal was 45° C. Figure 2 shows the temperature-time traces of the tests to determine the minimum SHT of the No. 80 seam coal. At a starting temperature of 45° C, there was a large initial heating rate over the first 5 h of the test, primarily due to the heat-of-wetting effect. The rate then decreased as the heat of wetting decreased until the temperature curve reached an inflection point at about 8 h. This was followed by an exponential rise in temperature, due to the heat of oxidation, from the inflection point until the end of the test. This type of temperature-time profile is typical for lower ranked bituminous coals and indicates the different competing mechanisms involved in the self-heating of dried coal exposed to moist air (*10*). In another test, with a fresh sample at an initial temperature of 40° C, there was a rise in temperature to 84° C in 16 h after exposure to humidified air. The temperature then leveled off and eventually the sample cooled. Thus, the coal had a minimum SHT of 45° C and a high spontaneous combustion potential.

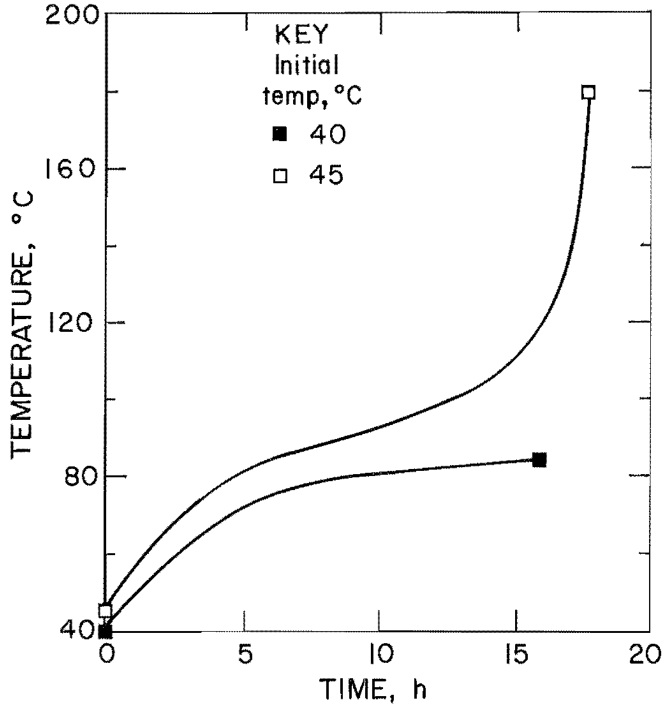

Figure 2. - Temperature histories in self-heating tests with No. 80 seam coal at initial temperatures of 40° and 45° C.

The first two additives in table 3 promoted self-heating. At an initial temperature of 40° C, both the coal-Na_3PO_4 and coal-NaOOCH mixtures self-heated, reaching 150° C in 17.6 and 18.9 h, respectively.

The temperature-time traces for the tests with the coal-additive mixtures, which had minimum SHT's of 50° C, are shown in figure 3. Included in this group is the coal-water blank, indicating that the application procedure itself had an inhibiting effect upon the self-heating of the coal. The KCl, $NaC_2H_3O_2$, NH_4Cl, and dry $CaCO_3$ additives showed a small degree of inhibition. The additives did not raise the minimum SHT above that of the coal-water blank, but the times to reach 150° C were increased. Of this group, $CaCO_3$ applied as a dry powder was the most effective inhibitor based on the time to reach 150° C, 92.1 h. Of the additives in this group applied in solution, NH_4Cl was the most effective based on the time to reach 150° C, followed by $NaC_2H_3O_2$ and KCl.

The temperature-time traces for the tests with those additives that raised the minimum SHT of the coal to 55° C are shown in figure 4. $CaCl_2$ was more effective than $NH_4H_2PO_4$; the sample took 55.8 h to reach 150° C compared with 26.7 h for the $NH_4H_2PO_4$ treated sample.

The temperature-time traces for the tests with the coal-additive mixtures that had minimum SHT's of 60° C are shown in figure 5. These additives were the most effective at inhibiting the self-heating process. The addition of NaCl, $NaNO_3$, and $CaCO_3$ resulted in an increase in the minimum SHT of the coal of 10° C above that of the coal-water blank, to 60° C. The coal-$NaNO_3$ sample took 68.6 h to reach 150° C, $NaNO_3$ proving to be the most effective additive at inhibiting the spontaneous combustion process tested. The coal-$CaCO_3$ and coal-NaCl mixtures reached 150° C in 13.4 and 14.1 h, respectively, showing that these additives had about the same relative effectiveness, but less than $NaNO_3$. The $CaCO_3$ applied as a slurry had a much greater inhibiting effect on the self-heating process than when applied as a dry powder.

Thus, of the additives tested under these conditions, the relative order of effectiveness at inhibiting the self-heating process of No. 80 seam coal in the adiabatic heating oven is

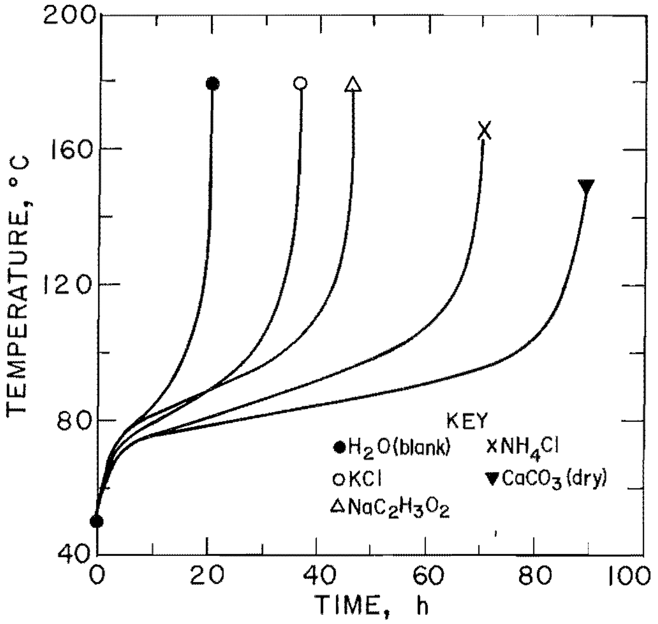

Figure 3. - Temperature histories for coal-additive mixtures with minimum SHT's of 50° C.

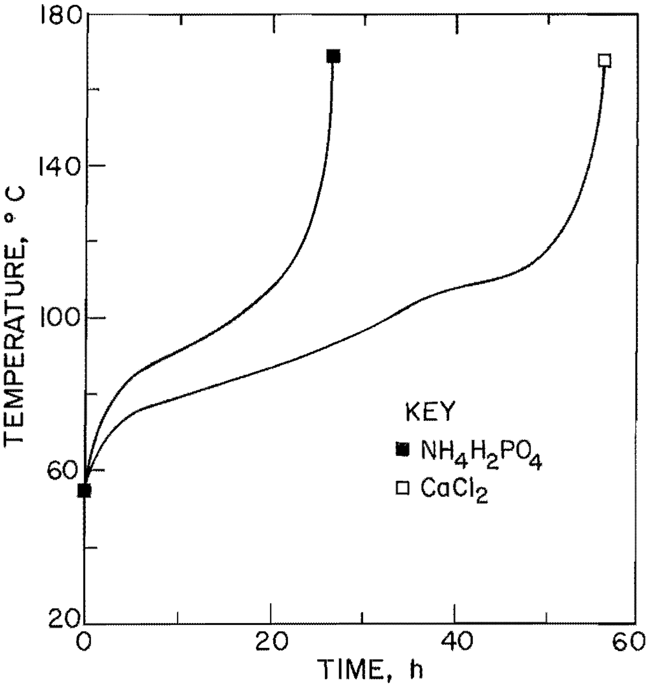

Figure 4. - Temperature histories for coal-additive mixtures with minimum SHT's of 55° C.

$$NaNO_3 > NaCl = CaCO_3 > CaCl_2$$

$$> NH_4H_2PO_4 > CaCO_3(dry)$$

$$> NH_4Cl > NaC_2H_3O_2 > KCl.$$

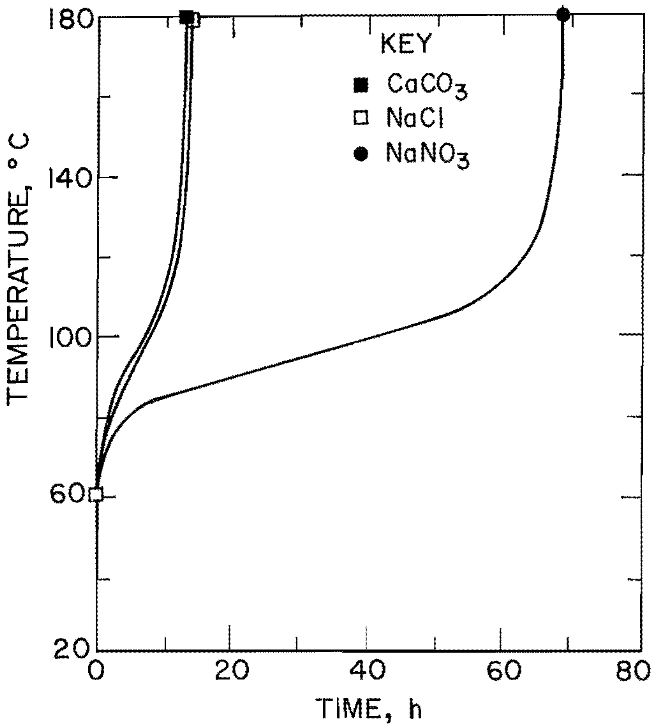

Figure 5. - Temperature histories for coal-additive mixtures with minimum SHT's of 60° C.

NaOOCH and Na_3PO_4 were also tested, but were found to promote rather than inhibit the self-heating process. Although $NaNO_3$ was found to be the most effective additive tested, it cannot be considered as a practical or viable inhibitor. When molten, which occurs at 306° C, it reacts exothermally with the coal.

Oxygen Adsorption and Carbon Monoxide Evolution

Oxygen and CO concentration profiles of the exit gas stream were also recorded for each test. The temperature, O_2, and CO concentration profiles in the self-heating test of No. 80 seam coal at an initial temperature of 45° C are shown in figure 6. The rate of CO evolution and temperature rise were similar over the first 10 h of the test, after which the CO concentration increased dramatically relative to the coal temperature. The concentration reached the limits of the analyzer (1,000 ppm) at 16 h, when the sample temperature was 112° C. The sharp drop in O_2 concentration coincided with the onset of rapid temperature rise. The O_2 concentration did not drop below 19 pct until 15 h, when the sample temperature was 108° C.

Similar O_2 and CO profiles were obtained in the tests on the coal-additive mixtures at their minimum SHT's. Increases or decreases in the time required to reach thermal runaway due to the inhibiting or accelerating effect of an additive resulted in similar changes in the time

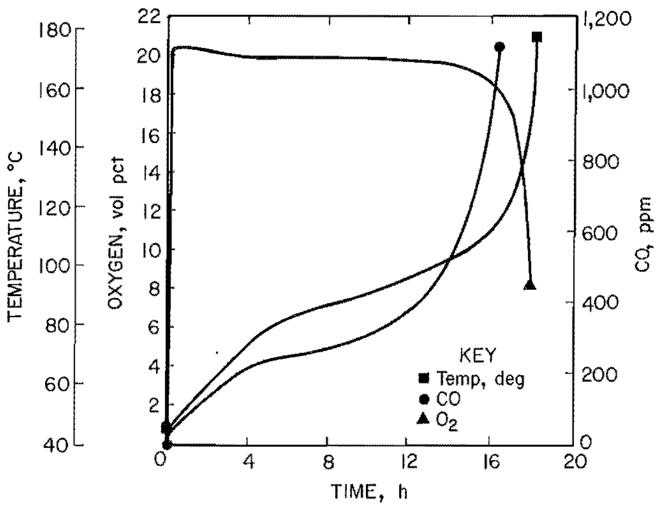

Figure 6. - Temperature, O_2, and CO concentration profiles in self-heating test of No. 80 coal at 45° C.

for O_2 and CO concentrations in the exit stream to reach levels indicative of thermal runaway. This is seen in table 3 for CO concentrations of 400 ppm and 19 pct O_2. These concentrations occurred in the tests at points where thermal runaway was imminent. The order of effectiveness within a group of additives with the same minimum SHT correlated well with the O_2 adsorption and CO evolution data, with the exception of the coal-NaCl mixture. In that test, the CO concentration reached 400 ppm in a shorter time, 7.5 h, than in the test with $CaCO_3$, 11.2 h, even though the time to reach thermal runaway and 19 pct O_2 was slightly longer.

Effect of Additive Concentration

The effect of additive concentration on the inhibition process was examined for two of the most effective additives based on minimum SHT, NaCl and $CaCO_3$. Experiments were conducted on 5, 15, and 25 pct additive-coal mixtures at an initial temperature of 60° C, the minimum SHT of the 15 pct additive-coal mixtures. The times for the sample temperature to reach 150° C and the sample exit gas concentrations to reach 400 ppm CO and 19 pct O_2 are shown in table 4.

The effectiveness of $CaCO_3$ increased with increased concentration, although not enough to increase the minimum SHT of 60° C. The relative effectiveness of NaCl showed a concentration dependence. Increasing the amount of NaCl added to the coal from 5 to 15 pct resulted in a decrease in the time to reach 150° C from 16.3 to 14.1 h. Even more notable was the decrease in the time for the CO concentration to reach 400 ppm, from 14.8 to 7.5 h. However, increasing the concentration of NaCl from 15 to 25 pct increased its effectiveness based on these parameters.

TABLE 4. - Times to reach 150° C, 400 ppm CO, and 19 pct O_2 in tests to evaluate the effect of additive concentration at an initial temperature of 60° C

Additive, wt pct	*Time, h, to reach*		
	150° C	*400 ppm CO*	*19 pct O_2*
NaCl:			
5	16.3	14.8	14.8
15	14.1	7.5	12.3
25	19.5	18.0	17.9
$CaCO_3$:			
5	12.6	6.0	11.3
15	13.4	11.2	11.8
25	18.5	15.0	17.1

TABLE 5. - Times to reach 150° C, 400 ppm CO, and 19 pct O_2 in tests at initial temperature of 60° C

Additive		*Time, h, to reach*		
		150° C	*400 ppm CO*	*19 pct O_2*
None		10.3	6.8	8.0
H_2O (blank)		11.9	3.7	9.3
$CaCO_3$	(3)[1]	13.4	11.2	11.8
NaCl	(2)	14.1	7.5	12.3
$CaCl_2$	(4)	15.6	8.3	13.4
KCl	(7)	16.3	8.3	14.4
NH_4Cl	(5)	19.8	17.3	18.0
$NaC_2H_3O_2$	(6)	36.0	30.8	34.5
$NaNO_3$	(1)	68.6	61.3	67.7

[1] Order of ranking based on minimum SHT parameter and time for sample temperature to reach 150° C.

Evaluation of Additives at 60° C

Tests were conducted on seven coal-additive mixtures, a coal-water blank, and the untreated coal, at an initial temperature of 60° C, to determine the relative effectiveness of the additives when tested from an initial temperature at which all the mixtures would undergo thermal runaway.

The times to reach 150° C, 400 ppm CO, and 19 pct O_2 are shown in table 5. The additives are listed in order of increasing effectiveness based on the time to reach 150° C. The order of additive effectiveness in these tests was consistent for all three parameters, with the exception of the time to reach 400 ppm CO for $CaCO_3$.

The coal-water blank reached thermal runaway in 11.9 h compared with 10.3 h for the untreated coal when both were tested at 60° C, consistent with the results based on the minimum SHT values. The time to reach 19 pct O_2 also increased, from 8.0 to 9.3 h. However, the CO evolution was much faster for the coal-water blank, reaching 400 ppm in 3.7 h, compared with 6.8 h for the untreated coal.

Again, $NaNO_3$ proved to be the most effective inhibitor of the self-heating process. However, the next two most effective additives based on minimum SHT, NaCl and $CaCO_3$, were the least effective when evaluated under these conditions. $NaC_2H_3O_2$ was the only other additive tested at 60° C that had a large effect on the self-heating compared to the coal and coal-water blank. However, in the ranking based on the minimum SHT's of the coal-additive mixtures, it showed little effectiveness. $CaCl_2$ and KCl had about the same relative effectiveness, increasing the time to reach 150° C by about 60 pct compared with the coal-water blank, even though $CaCl_2$ was much more effective than KCl based on the minimum SHT criteria. Based on these results, the ranking is

$$NaNO_3 > NaC_2H_3O_2 > NH_4Cl$$

$$> KCl = CaCl_2 > NaCl = CaCO_3.$$

Effect of Inorganic Species

The coal sample washed with water was tested at 50° C. The coal self-heated, reaching thermal runaway in about 56 h, almost three times longer than the coal-water blank. Analysis of the wash water showed that it contained, in order of decreasing concentration, Ca, Mg, Na, and Fe ions.

The coal sample washed with the aqueous NTA solution was tested at an initial temperature of 60° C. The sample underwent thermal runaway, reaching 150° C in 15.2 h, compared with 11.9 h for a coal-water blank tested at an initial temperature of 60° C, a 28-pct increase. The wash solution also contained Ca, Mg, Na, and Fe ions, along with Mn and Al ions, all in increased concentrations compared with the wash water from the coal sample tested at 50° C.

DIFFERENTIAL SCANNING CALORIMETRY

Thermograms were obtained in the DSC for the coal-additive mixtures and are shown in figures 7 through 9. A DSC thermogram indicates the amount of energy adsorbed (endotherm) or released (exotherm) by a sample as it undergoes physical and/or chemical changes, as a function of temperature. An endotherm is seen in the 25° to 100° C temperature region for No. 80 seam coal (fig. 7). This endotherm is attributed to the evaporation of tightly bound water that is not driven off during the drying process at 67° C, as well as trace water that is readsorbed during the final sample preparation. This endotherm is present in all the thermograms that follow, making the observation of the temperature at which the onset of oxidation occurs impossible. Two exotherms are evident in the thermogram for No. 80 seam coal, one beginning at 125° C, and a larger one beginning at 375° C, with a shoulder at 430° C, and a peak at 530° C. The thermogram for the coal-water blank, is similar to that for the untreated coal. The main exothermic peak is at 505° C, slightly shifted from that for the untreated coal. This may be a factor of the sample size, which can influence the peak temperatures.

The thermograms for the coal-$CaCO_3$ mixtures (fig. 7) are very similar to that of the untreated coal. Subtle variations are noticed in the shapes of the peaks at 540° C, which are not as pronounced as in the coal thermogram. This may be due to the decomposition of the $CaCO_3$, which can occur at temperatures as low as 500° to 550° C when mixed with coal (*12*). The evolved CO_2 may slow down coal decomposition and shift the peak temperature.

The thermogram for the coal-KCl mixture (fig. 8) contains a small endotherm at 186° C. This is probably due to the loss of the water of hydration from potassium thiosulfate ($K_2S_2O_3 \cdot H_2O$), a hydrolysis product of the reaction between pyrite in coal and KCl.

The same reaction would be expected to occur when NaCl is used as an additive. However, an endotherm is not seen in the thermogram for coal-NaCl since sodium thiosulfate ($Na_2S_2O_3$) decomposes at 48° C and therefore is lost during the drying stage of the sample preparation process. There are two distinguishable endotherms in the thermogram, a large one with a minimum at 455° C, and a smaller one at 535° C. Phase changes causing these endotherms have not been identified because the exact onset temperatures of the endotherms, needed for identification, are masked by the coal decomposition-oxidation exotherm.

The thermograms for the other coal-chloride salt mixtures, $CaCl_2$ and NH_4Cl, show several small endotherms, attributed to the presence of various sulfates and dithionates formed by the reaction between the additives and the pyritic compounds found in the coal. The endotherms are caused by the dehydration, melting, or decomposition of these compounds.

Evidence of reactions between the additives and the coal are found in the thermograms in figure 9 for the coal-$NaNO_3$, coal-Na_3PO_4, coal-$NaC_2H_3O_2$ and coal-NaOOCH mixtures. In the coal-$NaNO_3$ thermogram the endotherm caused by the melting of the $NaNO_3$ at 306° C is immediately followed by a sharp exotherm due to the reaction between nitrate and the coal. Most of the coal is consumed by this reaction; thus, the coal decomposition-oxidation exotherm usually present from 375° C to 570° C is very small. In the presence of Na_3PO_4 (fig. 9), the coal undergoes two fast reactions, at 430° C and 500° C. In the presence of the organic sodium salts, $NaC_2H_3O_2$ and NaOOCH (fig. 9), respectively, the coal oxidation exotherms at 500° C are either absent or reduced.

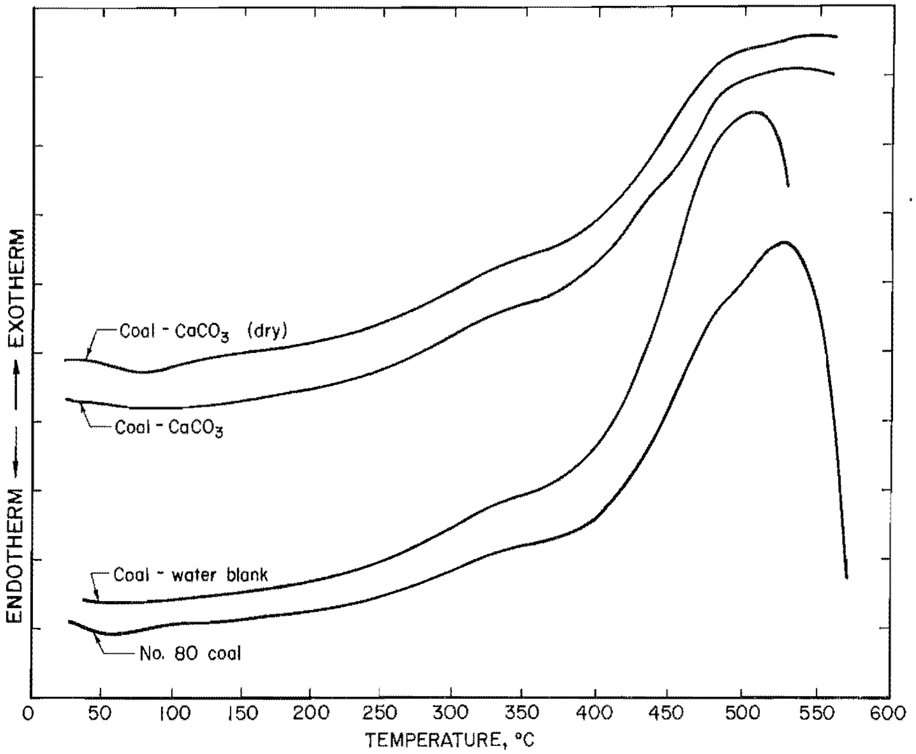

Figure 7. - DSC thermograms for No. 80 seam coal, coal-water blank, coal-$CaCO_3$, and coal-$CaCO_3$ (dry).

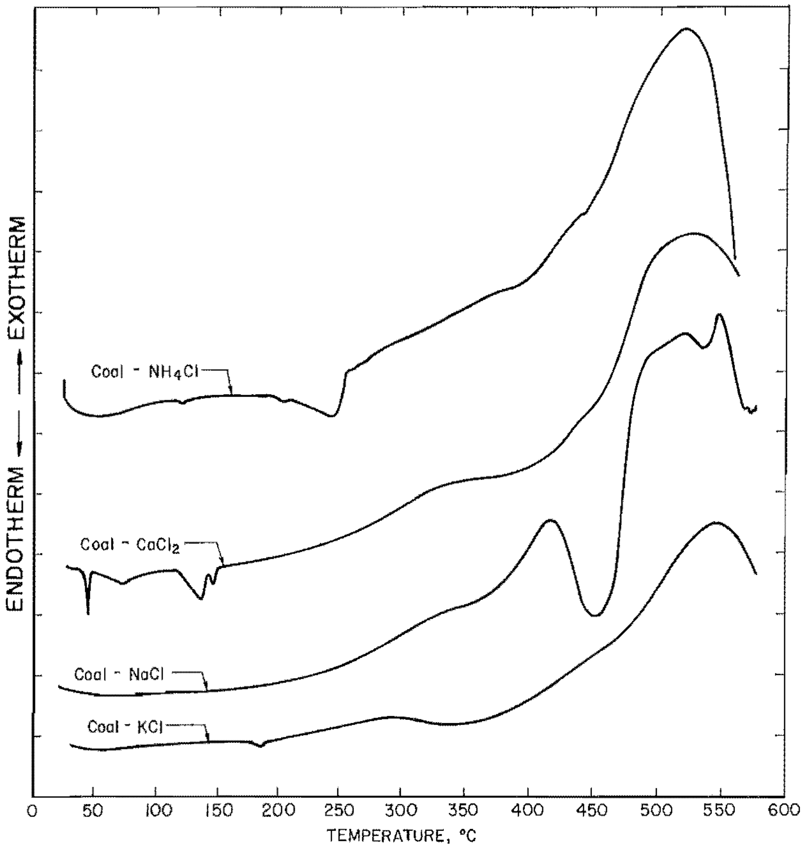

Figure 8. - DSC thermograms for coal-KCl, coal-NaCl, coal-$CaCl_2$, and coal-NH_4Cl .

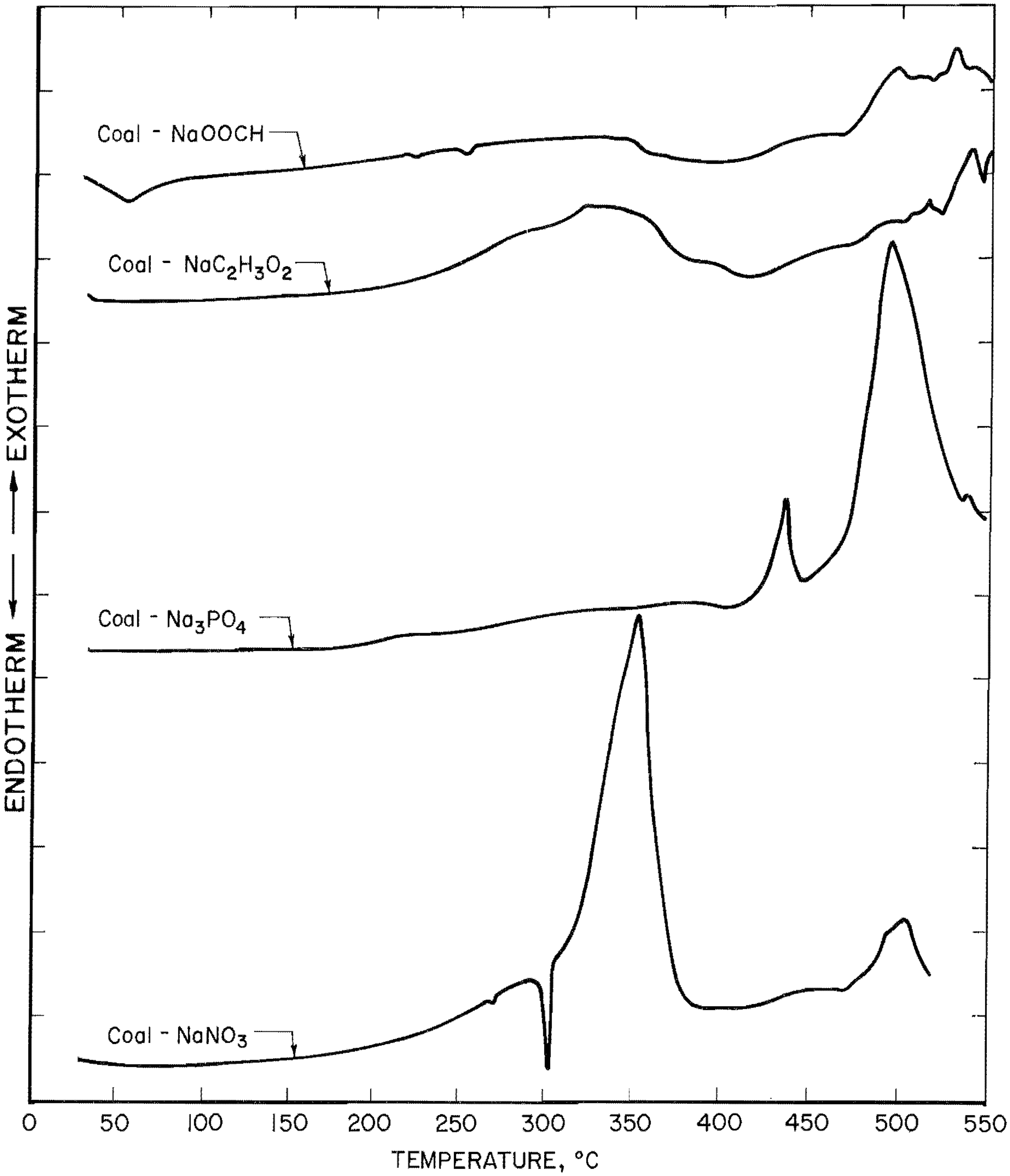

Figure 9. - DSC thermograms for coal-$NaNO_3$, coal-Na_3PO_4, coal-$NaC_2H_3O_2$, and coal-NaOOCH.

DISCUSSION

KINETICS AND MECHANISM OF COAL OXIDATION

The self-heating rate ($\dot{q}$) of a coal mass may be expressed as the sum of the heat release reaction rates ($\dot{q}_1$), the heat of oxidation and the heat of wetting, and the heat loss rate ($\dot{q}_2$), conduction and convection. Under nearly adiabatic conditions, the heat loss term is negligible, and $\dot{q} \simeq \dot{q}_1$. The oxidation of coal is a temperature-dependent reaction that obeys an Arrhenius-type rate law of the form

$$\frac{dT}{dt} = A\exp(-E/RT),$$

where the rate coefficient A includes the heat of reaction, the specific heat of the coal, and a specific rate constant, E is the activation energy, R is the molar gas constant, T is the temperature, and t is time. The heat of wetting is the heat generated by the adsorption of water vapor by the coal surface. No generally accepted rate equation for the heat of wetting is in use, but it is a function of temperature, time, and rank (*10*).

To understand and explain the effects of additives on the self-heating process, it is necessary to examine the effects that the additives have on these heat releasing reactions. These effects will be controlled by the following three parameters: (1) thermal properties of the additives, since both heat release mechanisms are temperature dependent, (2) chemical reactions between the additives and coal that reduce or increase the active reaction sites in the coal, and (3) physical effects of the additives on the coal, which can increase or decrease the access of the oxidant to the active sites of the coal. Also of some consequence and importance in this investigation is the additive application procedure. Although the procedure was selected to ensure intimate contact of the additive with the coal surface, it may have also had an inhibiting effect on the self-heating process of the coal. These parameters will be examined individually, although there may be some overlap because of their interrelationships.

EFFECT OF ADDITIVE APPLICATION PROCEDURE

Evidence that the application procedure had an inhibiting effect on the self-heating process in the coal is seen in comparing the minimum SHT of the untreated coal, 45° C, with that of the coal-water blank, 50° C. In addition, a comparison of the self-heating results of the untreated coal and coal-water blank in tests from an initial temperature of 60° C, seen in table 5, shows that the coal-water blank took longer to reach thermal runaway, 11.9 h compared with 10.3 h for the untreated coal, also indicating a decreased self-heating potential.

Residual changes in the coal structure were evident after the wetting and drying phases of the coal-water blank preparation, when the dried coal did not pass completely through a 100-mesh (150-μm) screen. Tests have shown that coal immersed in water does swell, with volume increases ranging from 2 to 25 vol pct, depending on the rank of coal (*13*). The effect of this swelling on the self-heating tendency of the coal is unclear. The swelling changes the internal pore structure of the coal, restricting some pore openings while enlarging others.

Results of coal wetting tests have also shown that water interacts with hydroxyl groups (-OH) in coal (*14*). Since the propensity of coal to self-heat is dependent on the oxygen-containing species of the coal (*10*), modification of these groups during the wetting and drying phases of the sample preparation step may reduce the coal's spontaneous combustion potential. Comparison of the thermograms for the No. 80 seam coal and coal-water blank (fig.7), indicates that no such changes occurred in the coal as a result of the coal preparation process. However, more sensitive analysis methods, such as Fourier transform infrared spectroscopy, are needed to detect modifications of this type at the active site regions of the coal.

The results from the tests on the coal sample washed with water and the sample washed with NTA solution indicate that removal of inorganic ions from the coal occurred during the sample preparation phase of these tests, and this may have had an inhibiting effect on the self-heating process. Possibly the cations acted as catalysts in the active site regions of the coal and their removal reduced the reactivity of the coal. Evidence that these cations, as well as some anions, were also removed in the coal-additive sample preparations are seen in the DSC thermograms of the coal-KCl, coal-$CaCl_2$, and coal-NH_4Cl samples (fig. 8). These thermograms contain endotherms indicating new compounds, probably formed from reactions between the leached cations and the additives, as described in the DSC section.

Another indication that the additive application procedure had an inhibiting effect on the self-heating process is seen in the results on the coal-$CaCO_3$ tests. $CaCO_3$ was the only additive tested that was not water soluble. When $CaCO_3$ was added to the coal as a dry powder, the sample had a minimum SHT of 50° C, 10° C less than when the $CaCO_3$ was added as a water slurry. The DSC thermograms in figure 7 showed no indication of chemical reaction between the coal and $CaCO_3$ in either applied form. In addition to those factors described earlier, the greater inhibition seen in the slurry addition was probably due to a physical effect caused by greater penetration of the $CaCO_3$ into the coal pores and better contact with the coal surface, blocking access of O_2 and moisture to the active sites.

THERMAL EFFECTS

The thermal properties of additives, such as thermal conductivity and heat capacity, can influence the self-heating of coal. These parameters are shown in table 6 for five of the additives and for Pittsburgh seam coal, which would be expected to have thermal properties close to those of dry No. 80 seam coal.

The thermal conductivities of the additives are larger than that of the coal; thus heat produced by the oxidation process in a coal mass containing the additives would be dissipated faster, resulting in a lower rate of oxidation. In a nonadiabatic system this heat would, in turn, be lost to the surroundings. Thus, additives with higher thermal conductivities would be expected to be more effective in preventing self-heating. In an adiabatic system, however, thermal conductivity does not play a role. Since this system is designed to minimize heat losses, and is thus nearly adiabatic, there should be a minimal, if any, effect of the thermal conductivity of the additives on the results.

This minimal effect is evident when comparing the thermal conductivities of the additives to the minimum SHT's of the coal-additive mixtures. Mixtures of coal and KCl, which has the highest thermal conductivity of the additives listed, and NH_4Cl, which has the lowest, both self-heated from a minimum initial temperature of 50° C. NaCl has a thermal conductivity similar to that of KCl, and yet the coal-NaCl mixture had a minimum SHT of 60° C, 10° C higher than the coal-KCl mixture. Thus, it appears from these data that the thermal conductivity of the additives is not an important parameter in inhibiting the self-heating of coal in the adiabatic heating oven.

The heat capacities of several of the additives are shown in table 6. The addition of an additive to a reacting coal system requires that the temperature of the additive be raised as the coal temperature rises. Assuming that the additive is inert to the oxidizer, the additive acts as a heat sink. This lowers the reaction rate and therefore should reduce the self-heating potential of the coal. In an adiabatic system, the effect would be to increase the time for the self-heating of a sample, but not to influence the self-heating temperature. Thus, the larger the heat capacity of an additive within a group of additives with the same minimum SHT, the more effective it should be at delaying the self-heating process.

This is seen when comparing the heat capacities of NH_4Cl and KCl (0.357 and 0.162 at 0° C) and their respective times to reach 150° C in the tests in the adiabatic heating oven at 50° C (70.1 and 36.3 h). The same is also true when comparing the heat capacities of $NaNO_3$, NaCl, and $CaCO_3$ (0.248, 0.204, and 0.195), which self-heated at a minimum initial temperature of 60° C, and their respective times to reach 150° C (68.6, 14.1, and 13.4 h).

TABLE 6.- Thermal properties of some additives used in self-heating tests and Pittsburgh seam coal

Additive and temperature[1]	*Thermal conductivity mW/cm-K*	*Heat capacity, cal/g-°C*	*References*
KCl:			
0° C	75-96	0.162	15-16
100° C	NA	.172	16
NH_4Cl: 0° C ...	25	0.357	15-16
NaCl:			
0° C	71	0.204	15-16
100° C	NA	0.217	16
$CaCO_3$: 0° C ..	NA	0.195	17
$NaNO_3$:			
0° C	NA	0.248	16
100° C	NA	0.294	16
Pittsburgh seam coal:			
28° C	NA	.286	18-19
50° C	2	NA	18-19

NA Not available.

[1] Temperature at which values were obtained.

Another thermal effect that may be present in the coal-$NaC_2H_3O_2$ and coal-$CaCl_2$ mixtures is the loss of water of hydration from the additives, which being an endothermic process, would remove heat from the reacting coal. Sodium acetate crystallizes as a trihydrate and $CaCl_2$ as a dihydrate at ambient temperature. This could account for the increased time for these coal-additive mixtures to reach 150° C compared to the coal-water blank.

CHEMICAL EFFECTS

Chemical reactions between coal and an additive can have a bearing on the relative effectiveness of the additive to inhibit the self-heating process. In addition to reactions that irreversibly alter the coal's structure, reactions may occur at the coal's active sites that reduce the coal's reactivity. Reactions may also occur between the additives and other portions of coal that affect the region around the active sites, thus influencing the coal's self-heating behavior.

The results from the DSC tests indicate that reactions do occur between coal and a few of the additives. In figure 9, the coal was consumed by its reaction with the $NaNO_3$ at 306° C, and a reaction between the coal and Na_3PO_4 occurred at 430° C. The two coal decomposition-oxidation exotherms usually seen are either absent or reduced in the thermograms for coal-$NaC_2H_3O_2$ and coal-NaOOCH, indicating that a reaction occurred between the coal and additive. However, these reactions occurred at temperatures well above the region where self-heating occurs in the adiabatic oven.

Evidence of reactions occurring between the metal ions leached out of the coal during the sample preparation process and the additives was discussed in the "Effect of Additive Application Procedure" section.

The increased reactivity of the coal-Na_3PO_4 and coal-NaOOCH mixtures compared to that of the untreated coal may be due to reactions that alter the region around the active sites. Hydrolysis of these additives during the test when exposed to moist air results in a basic condition

$$PO_4^{3-} + H_2O \longrightarrow HPO_4^{2-} + OH^-$$

$$COOH^- + H_2O \longrightarrow HCOOH + OH^-.$$

Since coal is more susceptible to oxidation in basic media, this may have contributed to the increased reactivity seen for the coal-Na_3PO_4 and coal-NaOOCH mixtures (*20*). In addition, basic conditions may result in the tests on the coal-Na_3PO_4 from the release of NaOH from the crystal structure of the Na_3PO_4 at temperatures above 70° C. Alkali phosphates are usually prepared by the addition of phosphoric acid to the alkali hydroxide or alkali carbonate solution, and subsequent crystallization. Some Na_3PO_4 crystals prepared in this manner may contain from 2 to 5 pct NaOH in the crystal lattice (*21*). The Na_3PO_4 used in this study contained 4.2 pct NaOH.

PHYSICAL EFFECTS

Two major physical effects impact on the ability of the additives to inhibit self-heating: (1) the tendency of the coal to swell when wetted by the aqueous salt solutions, and (2) the coating of the coal surface and sealing of the micropores and macropores in the coal by the crystallizing additives during the drying stage of the preparation procedure.

The swelling of the coal by water was discussed in the "Effect of Additive Application Procedure" section. The effects of salt solutions on the degree of coal swelling have not been studied. During the additive application procedure, many of the samples did not pass through a 100-mesh sieve after drying and required some grinding, as was the case for the coal-water blank. The increased coal particle size, in addition to being a result of swelling by the saline solution, may have been due to the precipitated salts on the outer surfaces of the coal particles. The degree to which the increased particle size depends on these two factors is unknown.

The second physical effect of the additives on the self-heating process occurs from the coating of the coal surfaces and sealing of the coal's pores by the additives. Bituminous coals have specific internal surfaces in the range of 30 to 100 m^2/g. Over 50 pct of the surface area is in the ultrafine capillaries (<40 Å). These capillaries are thought to be accessible through constrictions a few angstroms in width. Larger capillaries and cracks form about 20 to 50 pct of the total free volume (*20*). It was assumed that dissolution of the additives in the sample preparation, with the exception of $CaCO_3$, would allow better penetration of the additives into the internal structure of the coal particles, where they would recrystallize upon drying. The additive would then slow diffusion of O_2 and moisture to the active site regions, reducing the coal's reactivity. However, the ability of the additives to penetrate the coal pores and recrystallize has not been studied. The kinetics of crystallization of salts from solution and their size distributions depend on various factors, such as the degree of saturation of the solution, crystal nucleation and growth rate, temperature, and solution viscosity.

The results from the $CaCO_3$ tests showed that there was a definite effect when $CaCO_3$ was applied to the coal as a water slurry compared to when it was applied in dry form, as evidenced by the 10° C increase in the minimum SHT. This change is attributed to the physical coating of the coal surface and blockage of the macropores of the coal.

A parameter that may be important in determining the ability of an additive to penetrate the coal pores and recrystallize is the ionic radii of the anions and cations. Tests were made on various sodium and chloride salts during this study, and a correlation between the additives' cationic and anionic radii and the minimum SHT's of the coal-additive mixtures was attempted. Table 7 shows the apparent ionic radii of some of the anions and cations.

The Na^+ and Ca^{++} ions are essentially the same size, but NaCl was a more effective inhibitor than $CaCl_2$. The Na^+ and Ca^{++} are about 25 pct smaller than K^+ and 33 pct smaller than NH_4^+, and both NaCl and $CaCl_2$ were more effective than KCl and NH_4Cl. The K^+ ion is about 10 pct smaller than NH_4^+, but the coal-KCl mixture self-heated in a much shorter time than the coal-NH_4Cl mixtures. So there is no correlation between ionic size and self-heating potential for KCl and NH_4Cl, and for NaCl and $CaCl_2$, where the size differences are small. However, there does seem to be a size dependence when comparing the KCl and NH_4Cl with the NaCl and $CaCl_2$, where the size difference is appreciable.

The minimum SHT's of five sodium salt-coal mixtures were also determined. Of this group, $NaNO_3$ and NaCl were the most effective additives, raising the minimum SHT of the coal to 60° C, 10° C higher than the coal-water blank. $NaC_2H_3O_2$ had a smaller effect on the self-heating of the coal, increasing the time to reach thermal runaway compared with that of the coal-water blank from

TABLE 7. - Apparent ionic radii of cations and anions, angstroms

Ion	*Apparent ionic radius*	*Reference*
Na^+	.97	15
Ca^{++}	.99	15
K^+	1.33	15
NH_4^+	1.43	15
$HCOO^-$	1.58	22
CH_3COO^-	1.59	22
Cl^-	1.67	22
NO_3^-	1.89	22
PO_4^{3-}	2.38	22

20.5 to 46.0 h. Na_3PO_4 and NaOOCH acted as promoters, lowering the minimum SHT of the coal.

There is no apparent correlation between the anionic radii of these additives and their effectiveness as inhibitors. $NaNO_3$ was more effective than NaCl based on their times to reach thermal runaway, but the Cl^- ionic radius is less than that of the NO_3^- ion. The larger ionic radius of the PO_4^{3-} ion and corresponding lower SHT of the coal-Na_3PO_4 mixture compared with the coal-$NaNO_3$ and coal-NaCl mixtures correlate, but the effect of Na_3PO_4 on the self-heating of this coal is more likely related to the increased reactivity due to the basic conditions described earlier.

The CH_3COO^- and $HCOO^-$ ions were the smallest anions of the sodium salts, but with the exception of Na_3PO_4, $NaC_2H_3O_2$ and NaOOCH were the least effective sodium salts evaluated. So although ionic size could be an important parameter, there is no direct correlation between it and the effectiveness of an additive at inhibiting the self-heating of coal. Other aspects such as crystallization rate, size and shape of the crystals formed, ionic charge, and ionic strength of solution probably have a greater influence on the ability of the salts to penetrate the coal pores and inhibit the self-heating process.

When water was added to the coal during the coal-water blank preparation, the water was completely adsorbed by the coal, whereas when the water-additive solutions were added to the coal, the solution's adsorption was not complete in most cases. The results of the tests on the 5-, 15-, and 25-pct NaCl-coal mixtures indicated that the effectiveness of the NaCl as an inhibitor was dependent on the concentration, increasing when the concentration of NaCl was decreased to 5 pct. Observations made during these sample preparations were that the 5-pct solution was more readily adsorbed by the coal than the 15- and 25-pct solutions. This suggests that the ability of the solution to penetrate the pore openings of the coal particle is more important than the concentration for this additive, and that the ability to be adsorbed may be a function of the ionic strength of the solution. The ionic strength effect at the 25-pct concentration was probably masked by the inhibiting effect due to the large thermal mass of the salt in that test, causing the thermal effect to be more important.

An example of another type of physical phenomenon that minimizes the diffusion of oxidant to the coal's active sites may be present in the coal-NH_4Cl mixture. NH_4Cl begins to dissociate at 100° C (*23*)

$$NH_4Cl \xrightarrow{\Delta} NH_3\uparrow + HCl.$$

Ammonia vapor in the vicinity of the coal particles could act as a protective blanket to slow down diffusion of O_2 into the coal pores, resulting in a lower heating rate.

CONCLUSIONS

In this study, the minimum self-heating temperatures and the times to reach thermal runaway of eight coal-additive mixtures were determined in an adiabatic heating oven. These values were then used to rank the relative effectiveness of the additives to inhibit the self-heating process in coal. The results showed the combined effects of the thermal, chemical, and physical effects of the additives on the self-heating process. An analysis of these effects showed that no one single factor could account for the relative effectiveness of the additives, but some effects appeared to be more significant in certain cases.

$NaNO_3$, $CaCO_3$, and NaCl were found to be the most effective additives tested. However, $NaNO_3$ cannot be considered as a practical inhibitor because of its highly exothermic reaction with coal at elevated temperatures.

The evaluation of the relative effectiveness of additives in this study is specific to the apparatus and test method, and this was clearly evident when the ranking of the additives based on minimum SHT's was compared with the ranking obtained when the coal-additive mixtures were tested from an initial temperature of 60° C. The authors believe that the minimum SHT criterion is a more stringent criterion on which to base the evaluation, in that an additive that can raise the minimum SHT of a coal is more effective. However, in applications where elevated temperatures already exist, then an additive that delays the spontaneous combustion process may be needed.

The main conclusions from this investigation are summarized below.

1. The relative effectiveness of eight additives to suppress the self-heating process was evaluated in an adiabatic heating oven by determining the minimum SHT and time to reach 150° C of coal samples coated with 15 pct by weight of the additives and comparing their SHT's and times with those of untreated coal and a coal-water blank.

The relative order of effectiveness was

$$NaNO_3 > NaCl = CaCO_3 > CaCl_2$$
$$> NH_4H_2PO_4 > CaCO_3(\text{dry})$$
$$> NH_4Cl > NaC_2H_3O_2 > KCl.$$

However, $NaNO_3$ is not a practical inhibitor because of its reactivity with coal at higher temperatures (>300° C).

Two additives tested, NaOOCH and Na_3PO_4, acted as promoters, and their minimum SHT's were not determined.

2. CO evolution and O_2 depletion rates from the adiabatic oven tests at the coal-additive mixtures' minimum SHT's can also be used to evaluate the relative

effectiveness of an additive compared to others with the same minimum SHT. However, the correlation does not hold when these rates for coal-additive mixtures with different SHT's are compared.

3. Increasing the concentration of $CaCO_3$ from 5 to 15 to 25 pct had no effect on the minimum SHT of the coal. However, the time required for the coal to reach 150° C increased from 12.6 to 13.4 to 18.5 h, respectively.

4. Increasing the concentration of NaCl from 5 to 15 pct resulted in a decrease in the time for the coal to reach 150° C from 16.3 to 14.1 h. This was attributed to the effect of the ionic strength of the solution on the ability of the coal to adsorb the ionized salt in solution. Increasing the concentration from 15 to 25 pct, however, increased the time to reach thermal runaway from 14.1 to 19.5 h. The large NaCl thermal mass in the 25-pct addition probably masked the ionic strength effect.

5. The relative effectiveness of seven additives was evaluated based on the coal-additive mixtures' times to reach 150° C, and on the times for the exit gas stream concentrations to reach 400 ppm CO and 19 pct O_2 in tests from an initial temperature of 60° C in the adiabatic heating oven. The results did not agree with the relative effectiveness based on the mixtures' minimum SHT's. $NaNO_3$ was the most effective inhibitor under both conditions. However, NaCl and $CaCO_3$ were the least effective additives when compared with others at an initial temperature of 60° C, while NH_4Cl and $NaC_2H_3O_2$ were more effective than any except $NaNO_3$. This indicates that the criteria used to evaluate an additive's effectiveness require careful consideration that takes into account the particular situation.

6. Tests on coal washed with water and with an aqueous solution of nitrilotriacetic acid (NTA), a complexing agent, resulted in delays in the time for the coal to achieve thermal runaway. Analysis of the wash solutions showed that inorganic ions were removed during the washing process, and that the removal of these ions during the sample preparation phase of the additive tests may have contributed to the inhibition of the self-heating of the coal.

7. Differential scanning calorimetry (DSC) tests revealed that reactions occurred between the coal and $NaNO_3$, Na_3PO_4, $NaC_2H_3O_2$, and NaOOCH. However, the reactions occurred at temperatures well above the region of self-heating in the adiabatic oven and therefore did not influence the self-heating process. Reactions also occurred between the coal and $CaCl_2$ and NH_4Cl at lower temperatures, but had no apparent effect on the self-heating process.

8. The additive application process had an inhibiting effect on the self-heating of the coal. A coal-water blank had a minimum SHT 5° C higher than the untreated coal, and when both were tested at an initial temperature of 60° C, the untreated coal reached 150° C in a shorter time. An evaluation of the effectiveness of $CaCO_3$ applied as a slurry and as a dry powder showed that the additive was more effective when added as a slurry, increasing the minimum SHT of the coal 10° C. The increased effectiveness was attributed to a greater penetration of the $CaCO_3$ into the coal pores and better contact with the coal surface, blocking access of oxygen and moisture to the active sites.

9. The mechanism of inhibition is unclear, but it appears that a combination of thermal, chemical, and physical phenomena contribute to the process. No single parameter accounts for the behavior of the additives, although there was a correlation between the heat capacities of the additives and their times to reach 150° C for additives with the same minimum SHT's. The largest effect is probably due to the ability of the coal to swell when wetted by the aqueous solutions, and to the coating of the coal surfaces and sealing of the coal pores by the crystallizing additives during the drying stage of the preparation procedure. This last effect was somewhat dependent on the ionic size of the cations.

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