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INVESTIGATING THE INFLUENCE OF REACTIVE PYRITE ON COAL SELF-HEATING

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ABSTRACT: The acceleration of coal self-heating has long been attributed to the presence of reactive pyrite. However, a definitive means of quantifying this effect has been lacking, particularly from the low ambient temperatures experienced at mine sites. A recently developed moist coal adiabatic oven test has been used to investigate the influence of reactive pyrite on self-heating of a high volatile bituminous coal containing sulphur concentrations from 0.62% to 17.95%. A relationship exists between the amount of pyritic sulphur in the coal and the time taken to reach thermal runaway. However, simply measuring the pyritic sulphur concentration of a coal is not sufficient to quantify the accelerated self-heating effect, as it is the form of the pyrite that determines the pyrite reactivity. These findings will be expanded on in the paper as they have a major significance for the risk assessment of coal self-heating.

INTRODUCTION

The presence of pyrite in coal has been recognised as a contributing factor to self-heating for many years, but there has been no standard test developed that quantifies the effect (Miron, *et al.*, 1992). The fundamental reaction for pyrite self-heating is described by Weise, Powell and Fyfe (1987) as:

$$FeS_2 + 8H_2O + 7O_2 \rightarrow FeSO_4.7H_2O + SO_4^{2-} + 2H+$$

This reaction is strongly exothermic and the resultant hydrated sulphate is known as melanterite, which has a well-defined crystal form. It can be seen that the pyrite oxidation reaction is dependent on the presence of both moisture and oxygen. This feature has practical implications for testing.

A number of tests have been developed to rate the propensity of coal for spontaneous combustion (Nelson and Chen, 2007). In the Australian and New Zealand coal industries there is one test that has routinely been used. This is the adiabatic oven R_{70} self-heating rate test (Beamish, *et al.*, 2000, 2001; Beamish and Arisoy, 2008a), which has been used to show the effects on coal self-heating rate of rank (Beamish, 2005), type (Beamish and Clarkson, 2006) and mineral matter (Beamish and Blazak, 2005; Beamish and Sainsbury, 2008; Beamish and Arisoy, 2008b). The R_{70} self-heating rate is a low temperature oxidation spontaneous combustion index parameter that is measured on dried coal from a start temperature of 40°C. The relationship of this parameter to thermal runaway performance of as-mined coal has been interpreted on an inferred basis by comparison with coals that have similar R_{70} values and coal characteristics. As such a reactivity rating scale has been developed for both New South Wales and Queensland conditions using this parameter.

Beamish and Beamish (2010) proposed a new moist coal adiabatic oven test that could be used to benchmark laboratory performance against actual site performance of a range of coals from Australia and overseas that cover the rank spectrum from sub-bituminous to high volatile A bituminous. Since introducing this test to the coal industry a number of additional benchmark coals have been added to the database and tests have been conducted that show this new method is extremely accurate and definitive for assessing the spontaneous combustion risk of coal in a range of environmental situations. In particular, Beamish and Beamish (2011) showed that the new Moist Adiabatic Benchmark (MAB) test was able to quantify the effect of reactive pyrite on the self-heating of a Bowen Basin coal.

This paper presents the results of MAB testing on several samples of a Bowen Basin high volatile bituminous coal with sulphur contents ranging from 0.62% to 17.95% that show the effect of increasing pyrite content on coal self-heating rates.

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ADIABATIC OVEN TESTING

Coal samples

Details of the three samples used in this study are contained in Table 1. The two major benchmark coals are Kideco (Indonesia) and Spring Creek (New Zealand). The Bowen Basin high volatile bituminous coal is from an undeveloped coal deposit, which is not the same as that tested by Beamish and Beamish (2011). All samples were received as fresh cores from exploration boreholes. They were appropriately sealed in gladwrap to prevent oxidation and tightly bound with duck tape to maintain sample integrity as solid cores. Representative splits were taken from each core length for testing. It should be noted that initially only R_{70} testing was conducted on the samples and the MAB testing was conducted some 18 months later. All samples were stored in a freezer between tests. The samples have an ASTM rank of high volatile C bituminous based on the volatile matter and calorific value of the coal.

Table 1 - Coal quality data and test parameters for benchmark and Bowen Basin coal samples

Sample	R_{70} (°C/h)	Volatile matter (%, dmmf)	Calorific value (Btu/lb, mmmf)	ASTM rank	Ash content (%, db)	Sulphur content (%, db)	Moisture content (%)	Start temperature (°C)
Benchmark coals								
Kideco	28.57	51.6	9755	subC	1.8	0.10	24.0	24.4
Spring Creek	5.87	41.3	13749	hvBb	1.2	0.30	11.7	27.0
Bowen Basin high volatile bituminous coal								
BBHVB03	12.33	40.6	11658	hvCb	4.8	0.71	16.6	26.9
BBHVB06	7.20	47.4	12061	hvCb	7.9	4.93	12.7	27.3
BBHVB13	7.11	47.9	12882	hvCb	15.7	8.10	11.7	27.2
BBHVB01	5.52	41.5	11600	hvCb	29.3	19.53	10.3	27.5

Self-heating test procedure

The R_{70} testing procedure essentially involves drying a 150 g sample of <212 μm crushed coal at 110°C under nitrogen for approximately 16 h. Whilst still under nitrogen, the coal is cooled to 40°C before being transferred to an adiabatic oven. Once the coal temperature has equilibrated at 40°C under a nitrogen flow in the adiabatic oven, oxygen is passed through the sample at 50 mL/min. A data logger records the temperature rise due to the self-heating of the coal. The time taken for the coal temperature to reach 70°C is used to calculate the average self-heating rate for the rise in temperature due to adiabatic oxidation. This is known as the R_{70} index, which is in units of °C/h and is a good indicator of the intrinsic coal reactivity towards oxygen.

The major changes from the normal R_{70} method for MAB testing are, testing the coal with its as-received moisture content from the ambient mine start temperature, an increased sample size of approximately 200 g and a decreased oxygen flow rate of 10 mL/min. Increasing the sample size to 200 g provides a greater mass of coal to react that is still manageable without modifying the reaction vessel. Decreasing the oxygen flow rate to 10 mL/min reduces any cooling effect experienced by the coal from moisture evaporation as it self-heats. Effectively, these changes optimise the worst case scenario of developing a heating from as-mined coal.

RESULTS AND DISCUSSION

R_{70} self-heating rate values

The R_{70} self-heating curves for each sample are shown in Figure 1. Their respective R_{70} values are contained in Table 1. It can be seen that the Bowen Basin samples have a very high to ultra high intrinsic spontaneous combustion reactivity rating that is associated with the change in mineral matter content of the coal as indicated by ash content. The highest ash content sample (BBHVB01) has the slowest self-heating rate and the lowest ash content sample (BBHVB03) has the fastest self-heating rate. This is consistent with the heat sink effect of increased mineral matter demonstrated by Beamish and Blazak (2005) and Beamish and Sainsbury (2008).

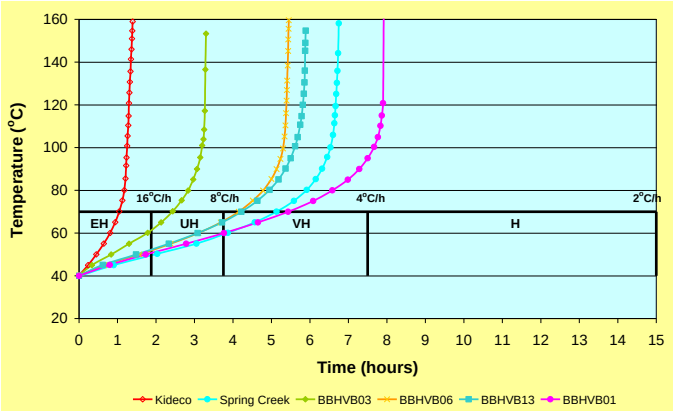

Figure 1 - Adiabatic self-heating curves for samples tested using the normal R_{70} test procedure, showing intrinsic spontaneous combustion reactivity ratings based on Queensland conditions (H = High, VH = Very High, UH = Ultra High, EH = Extremely High)

Table 2 contains the breakdown of the forms of sulphur in each of the Bowen Basin coal samples. It is clear that the sample with the highest total and pyritic sulphur content (BBHVB01) has the lowest R_{70} self-heating rate. However, this appears to be contradictory to the concept of increased self-heating rate due to the presence of pyrite in the coal. The reason for this is that the R_{70} self-heating rate test is performed on a dry basis, after the moisture has been removed from the coal. Therefore, this test does not record any pyrite oxidation reaction as there is no moisture present, and hence the simple heat sink effect of additional mineral matter in the coal controls the self-heating rate under these conditions. It is for this reason that the R_{70} self-heating rate test has not identified coals with possible pyrite self-heating acceleration in the past. Similarly, other spontaneous combustion testing methods where moisture has been completely or partially removed from the coal sample will produce the same erroneous result.

Table 2 - Forms of sulphur for Bowen Basin coal samples (%, air-dried basis)

Sample	Pyritic S	Sulphate S	Organic S	Total S
BBHVB03	0.06	0.09	0.47	0.62
BBHVB06	1.70	0.13	2.55	4.38
BBHVB13	4.61	0.07	2.66	7.34
BBHVB01	10.43	1.02	6.50	17.95

Moist adiabatic benchmark comparison

Results of tests using the new moist adiabatic benchmark method are shown in Figure 2. These results clearly demonstrate the accelerating effect of pyrite oxidation on coal self-heating. As the pyrite content increases, the self-heating rate of the coal also increases. This is shown in Figure 3 where the time taken to reach thermal runaway (100°C) is non-linearly related to the pyrite content of the coal. In a practical sense, the time taken to reach thermal runaway for each sample is indicated in Table 3, based on the results for the two benchmark coals shown in Figure 2. Lower and upper limits are calculated as it is impossible to give a precise projection, due to the many competing variables that affect hot spot development in a bulk coal pile. However, to date these benchmark limits have proven extremely accurate and it is clear that mining and handling of this coal would require a rigid spontaneous combustion management plan that identified the extent of the hazard. Pyritic sulphur removal by washing would be required and the effectiveness of this strategy could be quantified by the MAB test.

The moist adiabatic benchmark test not only shows that the key chemical ingredients for the pyrite oxidation reaction to take place are moisture and oxygen, it also identifies whether the pyrite is present in a form that is readily oxidised. Tests on other coals with high pyritic sulphur contents (often readily identifiable by the presence of visible pyrite grains on cleat or as massive nodules) have shown no reaction using the MAB test. This is because the particle size of the pyrite is too coarse for the oxidation reaction to occur at a rate sufficient to cause accelerated coal self-heating. In the case of the Bowen Basin samples presented in this paper the pyrite occurs as fine layers that are parallel to banding (Figure 4). The thickness of the layers is of the order of microns and thus provides greater surface area access for the oxidation reaction to take place. These layers are presumably composed of submicron pyrite crystals.

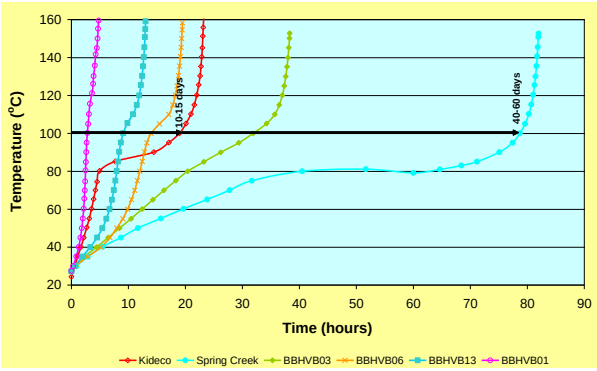

Figure 2 - Moist coal adiabatic self-heating curves for high volatile bituminous coal samples from the Bowen Basin compared with benchmark coals (Note: the case history typical minimum number of days to reach thermal runaway for each of the benchmark coals is shown)

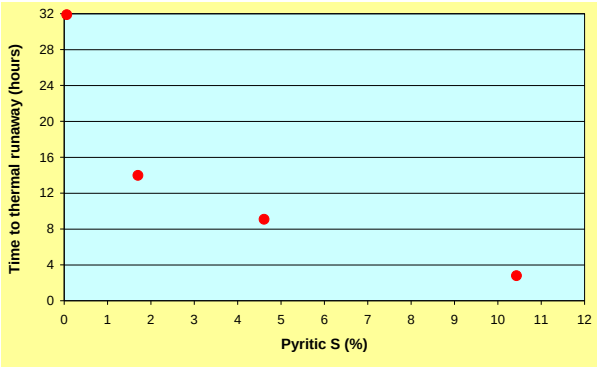

Figure 3 - Relationship between the time taken to reach thermal runaway and pyrite sulphur content of coal

Table 3 - Laboratory measured time to thermal runaway (t_{TR}) and calculated values for mining situations

	Laboratory t_{TR} (h)	Minesite/Stockpile t_{TR} (days)	
Sample		Lower limit	Upper limit
BBHVB03	31.9	16	25
BBHVB06	14.0	7	11
BBHVB13	9.1	5	8
BBHVB01	2.8	2	3

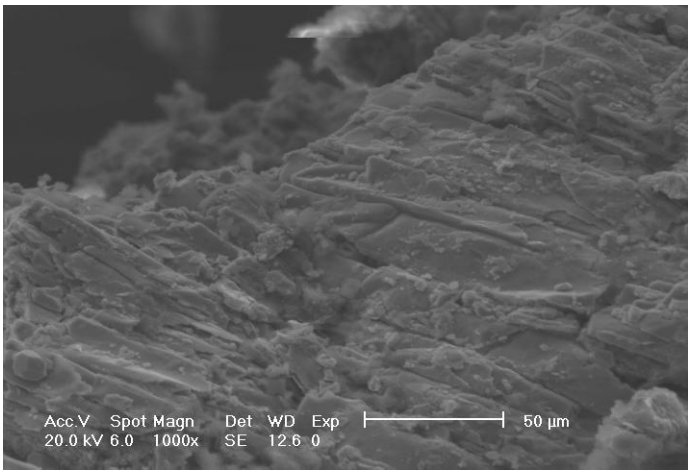

Figure 4 - Scanning electron microscope image of fine pyrite layering in a Bowen Basin high volatile bituminous coal

The resultant products of the pyrite oxidation have been identified by X-ray diffraction and found to be composed of rozenite ($FeSO_4$ $4H_2O$), melanterite ($FeSO_4$ $7H_2O$) and roemerite ($FeFe_2(SO_4)_4$ $14H_2O$). Crystals of these hydrated sulphates can be seen on the exposed coal surfaces in Figure 5. The formation of all these products is highly exothermic. From a practical viewpoint any coal seams that exhibit the growth of these hydrated iron sulphate crystals should be treated with extreme caution in terms of spontaneous combustion management planning. MAB testing of samples will readily quantify the spontaneous combustion propensity of such seams.

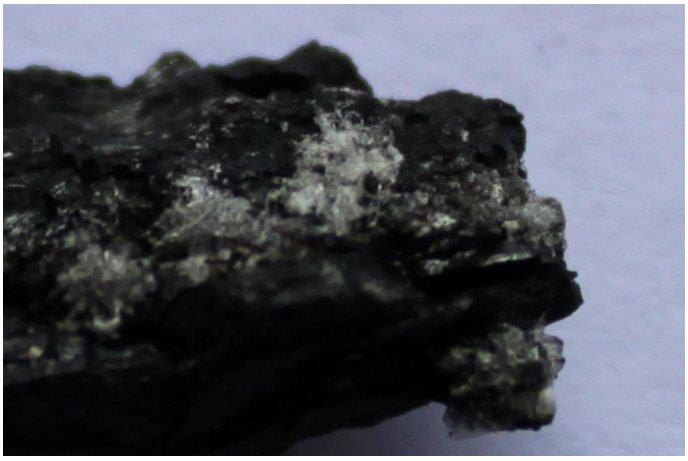

Figure 5 - Bowen Basin high volatile bituminous coal sample showing crystal clusters of hydrated iron sulphates on exposed surfaces

CONCLUSIONS

Adiabatic oven tests of samples from an undeveloped Bowen Basin coal deposit have shown the accelerating effect of pyrite oxidation on coal self-heating. This has only been possible using a new moist adiabatic benchmark test developed by Beamish and Beamish (2010). The older R_{70} self-heating rate test method is unable to quantify the effect as it is performed on a dry basis and one of the key chemical ingredients in the pyrite oxidation reaction is moisture. In fact, the R_{70} test produces a result that is completely erroneous due to the fact that it only measures the reactivity of the coal, which is strongly influenced by heat sink effects from the presence of increasing mineral matter. Hence, the R_{70} value of the coal decreases with increasing pyrite presence (increasing mineral matter).

The form of the pyrite present in the coal is also important in governing the rate of the pyrite reaction. Visible granular or massive nodular pyrite does not react fast enough to cause accelerated coal self-heating. This is readily identified by the new MAB test. The presence of finely disseminated pyrite that readily oxidises can be recognised in the field by the growth of hydrated iron sulphate crystals on exposed coal surfaces.

The MAB test used to quantify the pyrite oxidation effect can also be used to quantify the time taken to reach thermal runaway in mine site situations. A possible management strategy to combat the spontaneous combustion hazard of this coal would be to remove the pyrite by washing. The effectiveness of this strategy can be quantified using the MAB test.

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