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ASSESSING THE REACTIVITY OF PYRITE

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ABSTRACT: The presence of pyrite in coal has often been attributed to being a factor in spontaneous combustion, but quantifying the effect has been problematical from a hazard assessment viewpoint. A simplistic approach of correlating high sulphur content with the presence of reactive pyrite is unreliable and can be misleading. Pyrite needs to be present in an appropriate form (size and morphology) to enhance its oxidation potential. Consequently, it is important to be able to identify and quantify any reactive pyrite contribution to coal mine heatings in a systematic and scientific manner. In 1992, the US Bureau of Mines recognised there was a deficiency in existing testing techniques and recommended that these would need to be changed to assess the effect of pyrite in the self-heating process. Recent advances in adiabatic oven testing have led to development of a new spontaneous combustion Incubation Test that is used to benchmark coal self-heating against the known performance of case history coals. This test is capable of measuring the pyrite oxidation reaction for site-specific conditions and not only quantifies the minimum incubation period for pyrite initiated events to develop, but also shows the manner in which they develop.

INTRODUCTION

The US Bureau of Mines conducted an investigation into the cause of floor self-heatings in an underground coal mine operating in a high rank low volatile bituminous coal seam (Miron, Lazzara and Smith, 1992) and concluded that pyrite oxidation was the primary cause of the heatings due to the form (size and morphology) of the pyrite present in the mine floor horizon. The commonly used self-heating indices for the coal indicated a low spontaneous combustion propensity. Consequently, they concluded that there was a need to amend current spontaneous combustion testing methods to fully assess the effect of pyrite on the self-heating process.

Beamish and Beamish (2011 and 2012) performed adiabatic oven tests on a high volatile bituminous coal, which clearly showed the accelerating effects of reactive pyrite on the coal self-heating process. More recently, Beamish and Theiler (2016) have shown that adiabatic oven incubation testing can also be used to assess the self-heating behaviour of reactive pyrite in black shale waste rock from a metalliferous mine. This paper presents the results of adiabatic oven testing of coal samples that contain high sulphur contents to show the success of incubation testing to distinguish between reactive and non-reactive pyrite and to quantify the effect of reactive pyrite on the self-heating process.

Coal Samples

Analytical details of the high volatile bituminous coal samples used in this study are contained in Table 1. Coals C and D are from the same seam and location at an underground mine with a known history for spontaneous combustion events. Both samples have high total pyritic sulphur contents (Table 2) and X-ray Diffraction Analysis has confirmed that the main mineral constituent in the coal is pyrite. Coal C is a hand-picked part of the seam where pyritic bands parallel to bedding are concentrated. These samples also have high organic sulphur content as shown in Table 2.

Coal E is from another underground coal mine that does not have a history of spontaneous combustion events. The sample location is associated with the presence of a clastic dyke that has intruded into the seam from the roof. In this case X-ray Diffraction Analysis has identified the main

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mineral constituent as marcasite (the orthorhombic form of pyrite). This sample also has an elevated organic sulphur content (Table 2).

Table 1: Coal quality data for high sulphur content coal samples

Sample	Moisture (%, arb)	Ash (%, db)	Volatile Matter (%, dmmf)	Calorific Value (Btu/lb, mmf)	ASTM rank
Coal C	1.1	17.3	43.4	15137	hvAb
Coal D	1.6	8.4	44.8	15372	hvAb
Coal E	2.4	12.2	37.3	14473	hvAb

Table 2: Forms of Sulphur present in high Sulphur coal samples

Sample	Pyritic Sulphur (%, db)	Sulfate Sulphur (%, db)	Organic Sulphur (%, db)	Total Sulphur (%, db)
Coal C	9.70	0.21	3.09	13.00
Coal D	3.32	0.02	2.31	5.65
Coal E	3.23	0.26	1.90	5.39

Spontaneous combustion index parameters

The more commonly used spontaneous combustion index parameters in the Australian Coal Industry are initial self-heating rate (R_{70}), Minimum Self-heating Temperature (SHT), Crossing Point Temperature (CPT) and Relative Ignition Temperature (RIT). The values of these index parameters for each of the high sulphur coal samples are shown in Table 3 and the R_{70} self-heating rate curves for the respective coals are shown in Figure 1. It can be seen that Coals C, D and E all have low spontaneous combustion propensity ratings. The ratings for Coals C and D are completely at odds with the known spontaneous combustion history of the seam.

Table 3: SHT, CPT, RIT and R70 values for the coals used in this studywith their respective spontaneous combustion propensity ratings

Sample	SHT (ºC)	CPT (ºC)	RIT (ºC)	R_{70} (ºC/h)	Propensity Rating
Coal C	114	157	158	0.29	Low
Coal D	116	159	154	0.06	Low
Coal E	104	148	156	0.48	Low

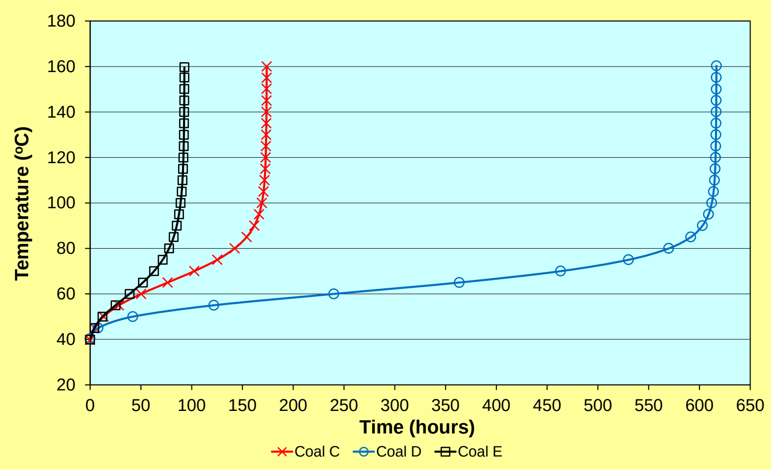

Figure 1: Adiabatic R_{70} self-heating rate curves for coals C, D and E

The R_{70} self-heating rates of all these samples are much lower than normally recorded for their respective rank and ash content. This suppression in reactivity has been observed to correspond with coals that contain high organic sulphur content. It is likely that the organic sulphur may be acting as a natural inhibitor to oxygen reaching reactive sites.

Incubation testing quantification of reactive/unreactive pyrite

The commonly used spontaneous combustion indices only provide a rating of the intrinsic reactivity of the coal. They do not show moisture moderating effects of the self-heating rate at low temperatures, nor do they show the mutual moisture/pyrite effects identified by Arisoy and Beamish (2015a). One of the essential ingredients for pyrite oxidation is water. The R_{70} test (Figure 1), which is conducted on a dry basis, records only the intrinsic coal self-heating and no pyrite self-heating. However, the incubation test of Coal C for example (Figure 2), which starts at a lower temperature and with moisture present, rapidly self-heats and the test is completed in approximately one quarter of the time.

The self-heating rate between 40 and 70 °C in the incubation test is 5.12 °C/h compared to 0.29 °C/h for the R_{70} test. Also, the shape of the self-heating curve is different for the pyritic reaction at low temperature. The non-Arrhenius kinetics that occurs for the coal oxidation reaction (Arisoy and Beamish, 2015b), where the coal self-heating rate decreases before increasing again at higher temperatures due to reactive site availability, is not present for the pyrite oxidation reaction contribution. Therefore, these results clearly show the reactive nature of the pyrite present in this sample and the mutual effects of pyrite and moisture on accelerating the overall coal self-heating rate from the initial start temperature.

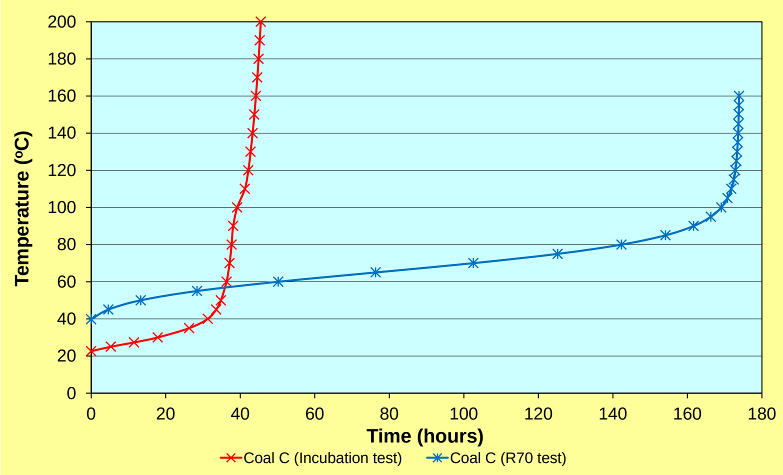

Figure 2: Comparison between incubation test results and R_{70} test results for coal C

Clearly, the moisture available for the pyrite oxidation reaction is a key factor in the overall spontaneous combustion propensity of coals containing reactive pyrite. This is shown in Figure 3 for repeat tests of Coal D at different moisture contents. At low moisture levels there is insufficient water available for the pyrite oxidation to proceed at appreciable rates. At high moisture levels there is too much water available and the self-heating is hindered by the heat loss from moisture evaporation. This is clearly visible in the temperature region of approximately 95 °C where a significant inflection appears in the self-heating curve.

Coal E initially self-heats at a very slow rate (Figure 3), and shows no accelerated self-heating with time, indicating the marcasite that is present in the coal is unreactive. This is at odds with the existing literature, which suggests that marcasite is a more reactive mineral than pyrite under oxidation conditions. These new results would indicate that previous studies have not taken into consideration the influence of the size and morphology of the marcasite on the oxidation reactivity.

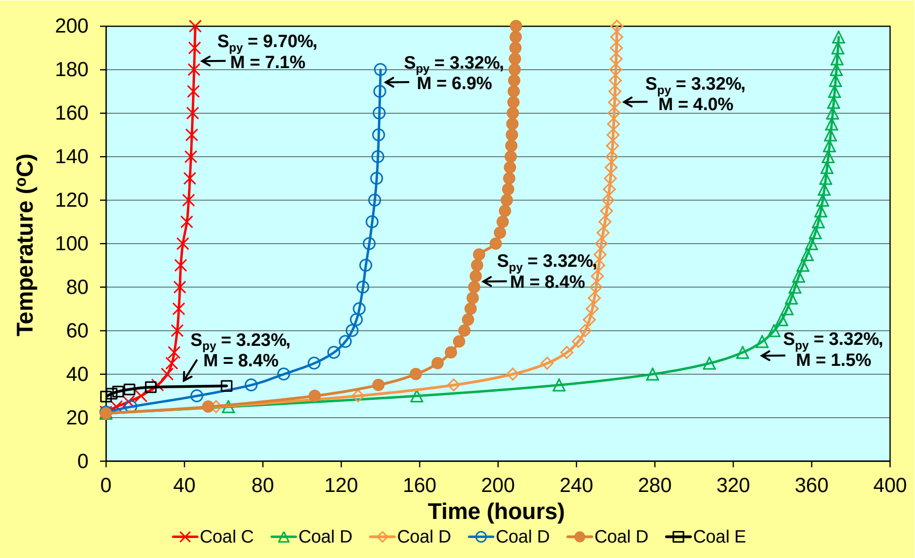

Figure 3: Incubation test results for high sulphur coals showing both reactive and unreactive pyrite self-heating performance, including the effects of moisture availability

CONCLUSION

Identification and quantification of the presence of reactive pyrite in underground coal mines is crucial to developing an appropriate Principal Mining Hazard Management Plan for Spontaneous Combustion. Commonly used index parameters do not provide this information and can be misleading in some instances, particularly for higher rank low reactivity coals and shale units present in immediate roof and floor rocks. Moisture availability plays a major role in the pyrite oxidation reaction and this can be easily demonstrated by using the incubation test method that has recently been developed. The test provides a realistic record of the characteristic self-heating performance of the sample being tested and produces an indication of the minimum incubation period for a spontaneous combustion event to develop. This information is invaluable for safe and effective mining of coal seams where reactive pyrite may be a contributing factor to the spontaneous combustion hazard.

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