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Black Mass Process

Isothermal Reaction Calorimetry and Carius Tube Screening

Client	ICoNiChem Widnes Ltd
Client location	Widnes, UK
Contact	Jenny Edwards
Report issue date	21st April 2020
Report number	J4028005382R1/2020, DRAFT 3






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1. PROJECT DETAILS AND TEST WORK APPROVAL STATEMENT

Quotation Numbers	3016006699 and 3016007320
Job Numbers	4028005382 and 4028005638
DEKRA Process Safety Facility	DEKRA Process Safety, Phi House, Southampton Science Park, Southampton, Hampshire, SO16 7NS, UK
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Reviewer	Mr Gordon Amery, Process Safety Specialist
Peer Reviewer	Mr Paul Carter, Safety Testing Specialist
Study Initiation date*	20/02/2020
Start Date of Experimental Work	03/03/2020
Completion Date of Experimental Work	To be added

* Sample, purchase order or last information receipt date, whichever is the latter.

This report has been issued in digital format. In order to ensure that the integrity of the data is maintained, the signed hard copy (in the DEKRA Process Safety archive) will be considered the source document and digital versions will be considered copies. All original test records are kept in a locked archive for a minimum of 10 years after the date of this report. Any remaining material(s) will be stored for a minimum of 1 month after the issue date of this report. This report was prepared by Ingrid Gledhill.

2. INTRODUCTION

This report contains test data for ICoNiChem Widnes Ltd relating to the black mass process which involves the reaction of non-pyrolysed and pyrolysed black mass (battery material) with nitric or sulphuric acid and hydrogen peroxide. In this assessment isothermal reaction calorimeter tests were conducted in order to determine the thermodynamics and kinetics of the reactions. Additionally, the nature of any gas generated during the tests was determined using mass spectrometry.

A Carius tube screening test was also conducted in order to determine the thermal stability of the reaction mixture after completion of the hydrogen peroxide addition. The non-pyrolysed black mass, nitric acid and hydrogen peroxide mixture was selected for this test.

This work is in response to quotation numbers 3016006699 and 3016007320. A formal hazard assessment of the process / plant has not been conducted by DEKRA Process Safety and the consequences of specific process deviations have not been examined[1].

Detailed characterisation of the process tested in this study is provided in Section 3 of this report (with results summarised in Section 6)[2].

The materials used in this assessment were supplied by ICoNiChem Widnes Ltd, with some reagents sourced from laboratory chemical suppliers (see test sections for details of vendors / batch numbers).

[1] Process safety requires that all possible explosion, thermal stability and chemical reaction hazards are evaluated and that a suitable basis for safe operation is determined and implemented. Should the materials or processing conditions change then consideration should be given to re-assessment.
[2] A description of the test procedures together with full test results and information on their interpretation is given in the test sections of this report. The appendix provides background information on the subject matter. DEKRA Process Safety's Laboratories are GLP (Good Laboratory Practice) compliant and this study was carried out to the principles of GLP.

3. PROCESS INFORMATION

A process description was provided to DEKRA Process Safety by Jenny Edwards (ICoNiChem Widnes Ltd).

Experiment 1 – Non-Pyrolysed dissolved in 98 % Sulphuric Acid and Hydrogen Peroxide;

Water (ml)	41.5
98 % Sulphuric Acid (ml)	21.9
Hydrogen Peroxide 30 % (ml)	36.6
Black Mass (g)	24.44
Total Volume (ml)	100

Experiment 2 – Non-Pyrolysed dissolved in 60 % Nitric Acid and Hydrogen Peroxide;

Water (ml)	26.7
60 % Nitric Acid (ml)	49.6
Hydrogen Peroxide 30 % (ml)	23.7
Black Mass (g)	15.74
Total Volume (ml)	100

Experiment 3 – Pyrolysed dissolved in 60 % Nitric Acid and Hydrogen Peroxide;

Water (ml)	26.7
60 % Nitric Acid (ml)	49.6
Hydrogen Peroxide 30 % (ml)	23.7
Black Mass (g)	15.74
Total Volume (ml)	100

Experiment 4 – New Black Mass dissolved in 60 % Nitric Acid and Hydrogen Peroxide;

Water (ml)	26.7
60 % Nitric Acid (ml)	49.6
Hydrogen Peroxide 30 % (ml)	23.7
Black Mass (g)	15.74
Total Volume (ml)	100

Procedure

1. Add water
2. Add black mass
3. Agitate (no heat required)
4. Add acid over 4 hours
5. Add hydrogen peroxide over 4 hours

4. ISOTHERMAL REACTION CALORIMETRY

Test Objective and Information

Isothermal reaction calorimetry is used to determine the thermodynamics and kinetics of a chemical reaction. The principle is based on measurement of the quantity of heat that flows across the reactor wall when an exothermic or endothermic process takes place. This is proportional to the temperature difference between the reaction mass contents and the reactor jacket. The heat released or absorbed by any reaction occurring in the reactor at any period in time can be directly determined by performing a heat balance across the system.

There are two methods for determining the heat flow associated with a reaction. These are heat flow calorimetry and real time calorimetry (RTCal™).

Heat flow calorimetry

In the heat flow calorimetry method, the heat flow due to the reaction (Q_r) is made up of the measured heat flow across the reactor wall (Q_{flow}), the heat supplied or removed by dosing of reagents (Q_{dos}), the heat accumulated in the reaction mass (Q_{accum}) and the heat lost to the surroundings (Q_{loss}).

$$Q_r = Q_{flow} + Q_{dos} + Q_{accum} + Q_{loss}$$

By measuring Q_{flow}, Q_{dos} and Q_{accum} a figure for the enthalpy occurring in the calorimeter during the reaction can be determined. By performing electrical calibrations both before and after the reaction, the change in heat transfer area and the environmental heat losses (Q_{loss}) can be accounted for.

Real time calorimetry

Real time calorimetry (RTCal™) is based on heat flux sensors located in the jacket of the reactor. Vertically and horizontally positioned sensor bands detect the heat flow across the wall of the reactor online and in real time. Experiments conducted using RTCal™ are independent of the properties of the reaction mass hence calibrations only need to be conducted after exothermic stages to measure the heat capacity (Cp) of the mixture. Theoretically RTCal™ provides more realistic and accurate data, especially for reactions in which the viscosity changes.

If calibrations are performed at the start and end of the reaction, both the standard heat flow method and the RTCal™ method can be used to determine Q_r. For both methods the reaction calorimeter is operated under isothermal conditions (as opposed to isoperibolic conditions - i.e. constant cooling load).

Mettler $RC1_e$™ calorimeter

The Mettler $RC1_e$™ comprises a jacketed and agitated reactor, a thermostatically controlled heat transfer medium which is pumped around the reactor jacket, an electric calibration heater and a temperature monitoring system. Atmospheric pressure and high pressure reactors are available. A pressure transducer can be connected to the high pressure reactor in order to measure the pressure throughout the test. An automated gas burette system and / or a pH probe can also be connected to either reactor in order to measure gas generation and pH throughout the test.

Experimental method

The process under investigation is usually examined in a semi-batch operation. The reaction solvent and starting materials are charged to the reactor, heated to the required temperature and allowed to reach equilibrium with the jacket temperature.

For the heat flow calorimetry method, the calibration heater is activated and a known quantity of electrical energy is input into the system. This will cause the temperature of the reactor contents to rise slightly which in turn triggers the jacket heat transfer fluid temperature to decrease until a dynamic equilibrium is established whereby the rate of heat removal by the heat transfer medium and environmental heat losses will equal the rate of heat supplied by the heater. When the calibration heater is switched off, the jacket temperature will revert to equilibrium with the reaction mass temperature. The integral of the power differential with time in Watt seconds can be expressed directly to the total quantity of electrical energy supplied by the calibration heater. This ratio is directly proportional to the overall heat transfer coefficient (U) and the heat transfer area (A). The value determined here will necessarily incorporate a factor for the total environmental heat loss.

For the real time calorimetry method, calibrations to obtain the overall heat transfer coefficient (U) are not required but quantification of the heat capacity of the reaction mixture (Cp) after each exothermic stage is needed. The Cp can be measured in several ways: by application of temperature ramps, performing a full or RTCal calibration or by using the QuickCal™ method which allows evaluation of the heat transfer characteristics of the reactor (U.A) and heat capacity of the batch (Cp) in a single calibration.

Once calibration is complete and the reaction mass temperature is once again in equilibrium with the jacket, the reaction phase is started. The reactant is added to the reactor at a constant rate, ideally using a diaphragm pump, and the reaction mass temperature and jacket temperature monitored. If, during the reagent addition an exothermic or endothermic process takes place the reaction mass temperature will change. Providing the process is exothermic, the temperature of the oil in the reactor jacket will decrease until a dynamic equilibrium is achieved whereby the rate of heat evolution in the reacting system matches the sum of the rate of heat removal by the jacket and environmental losses (under near isothermal conditions). The converse occurs if the reaction is endothermic. Once the addition is complete the jacket oil temperature is allowed to revert to temperature equilibrium with the sample.

The time taken for temperature equilibrium to re-establish itself is dependent on the rate of reaction. If the reaction rate is fast, or essentially instantaneous, equilibrium with the jacket temperature will be achieved rapidly. However, if the rate of reaction is slow and some unreacted reagent accumulation occurs in the reactor then there will be a considerable “tail-off" period following completion of the addition before temperature equilibrium is re-established. The quantity of any accumulated heat is determined as a percentage of the overall heat release.

Once the reaction is complete a calibration is conducted. Note that the U.A value obtained will be different to the data from the first calibration as the active heat transfer area has changed and the physical properties of the reaction mixture may have changed. By comparing the two electrical calibrations with measured heat release due to the reaction, the heat of reaction can be determined.

The apparatus is shown below (RTCal vessel with sensor bands is shown in the picture on the right) and generic equipment and test information is contained in Table 4.1.



Typical RC1 Apparatus

Table 4.1: Equipment Configuration / Settings for Isothermal Reaction Calorimetry

Parameter	Setting / Configuration
Reactors	AP01 or MP10 (high pressure)
Heat flow measurement technique	Standard heat flow or RTCal™
Minimum sample volume	120 cm^3 (AP01) / 300 cm^3 (MP10)
Maximum sample volume	480 cm^3 (AP01) / 850 cm^3 (MP10)
Test atmosphere	Typically air or nitrogen
Temperature range	-30 – 230°C (162°C for RTCal™ reactors)
Sensitivity	≤ 0.1 $W.l^{-1}$
Thermocouple type	Pt100 sensors
Pressure range	0 – 10 barg
Data acquisition system	iControl 5.3.32

Interpretation of Results

The measured heat flow is integrated across the reaction period to provide an overall heat of reaction. The quantity of accumulated heat is also determined as a percentage of the overall heat release. The heat flow data is used to calculate the potential adiabatic temperature rise for the reaction. This is the temperature rise which would occur in the absence of any heat removal, dissipation or secondary reaction. The Maximum Adiabatic Temperature (MAT) can then be calculated (Note: Maximum Temperature of the Synthesis Reaction (MTSR) is used interchangeably with MAT assuming full accumulation). This is the maximum temperature which could be achieved if the exothermic reaction occurred with no heat loss (for example, in the event of a complete loss of cooling) and is the sum of the normal process temperature and the adiabatic temperature rise. The MAT/MTSR together with information on the boiling point and thermal stability of the reaction mixture can be used to determine the Criticality Class of the reaction.

4.1 Test Results for Non-Pyrolysed Black Mass Dissolved in Sulphuric Acid and Hydrogen Peroxide

Date	03/03/2020
Operator	G. Amery
SOP Reference	SOP 315
Test System	Mettler RC1$_e$™ Reaction Calorimeter
Test Filename	RC4028005638A

Test Objective

To determine the thermodynamics and kinetics of the additions of sulphuric acid and hydrogen peroxide to non-pyrolysed black mass when conducted under isothermal conditions (at 22°C). Additionally, the rate and total quantity of gas generated during the reaction was measured using an automated gas burette system.

Test Materials

Chemical	Mass (g)	Source	Batch Number	DEKRA Reference
Non-pyrolysed black mass	48.9	ICoNiChem	N/A	400019397
Distilled water	83.0	Acros	N/A	400018539
Sulphuric acid 98 % w/w	80.4	Aldrich	MKCK3467	400018866
Hydrogen peroxide 30 % w/w	81.1	Fisher	1920191	400019420

Test Parameters

Parameter	Setting / Configuration
Reactor	AP01 RTC
Reactor volume	500 ml
Stirrer	Glass propeller (without baffle)
Stirrer speed	500 rpm
Test atmosphere	Air
Test pressure	Atmospheric
Test mode	Tr (isothermal at 22°C)
Reflux configuration	No
Addition method	ProMinent pump for sulphuric acid addition Solenoid valve for hydrogen peroxide addition
Dip pipe employed	No
Gas burette employed	Yes
pH probe employed	No

The non-pyrolysed black mass and water were charged to the vessel and equilibrated at 22°C before a calibration was conducted. These calibrations (conducted using the QuickCal™ method) allow evaluation of the heat transfer characteristics of the reactor (U.A) and heat capacity of the batch (Cp). The addition of sulphuric acid was then conducted over 4 hours. On completion of the reaction the hydrogen peroxide addition was conducted over 4 hours. Further calibrations were conducted after each step as necessary.

Test Results

The experimental profile obtained from the test is illustrated in Graphs 4.1.a – 4.1.c. Mass spectrometer spectra are provided in Graphs 4.1.d – 4.1.g.

Sulphuric Acid Addition (Graph 4.1.b)

The addition was found to be exothermic and the total quantity of heat evolved was found to be 62.4 kJ. This equates to a heat of reaction of -77.7 $kJ.mol^{-1}$ (of sulphuric acid) or -1276.9 $kJ.kg^{-1}$ (of non-pyrolysed black mass). The heat capacity of the mixture on completion of the reaction was found to be 2380 $J.kg^{-1}.K^{-1}$. This indicates that the adiabatic temperature rise for the reaction is 123.6 K. No accumulation of unreacted feed was observed.

Gas generation was observed and 1134 ml was generated over the addition period (ca. 44 ml of this was due to displacement of the head space gases by the added volume of material). On completion of the addition no further gas was generated. The maximum rate of gas generation was found to be 17.3 $ml.min^{-1}$. The gas generated was analysed using a mass spectrometer. An example of the spectra obtained is provided in Graph 4.1.d and Graph 4.1.e. Peaks were observed at mass numbers 12, 16 and 44 indicating that the gas generated was carbon dioxide. Very small peaks were observed around mass numbers 60 and 90 indicating that traces of toluene were also present.

On completion of the reaction the mixture was observed to be an opaque black solution.

Hydrogen Peroxide Addition (Graph 4.1.c)

The addition was found to be exothermic and the total quantity of heat evolved was found to be 50.9 kJ. This equates to a heat of reaction of -63.3 $kJ.mol^{-1}$ (of sulphuric acid) or -1040.4 $kJ.kg^{-1}$ (of non-pyrolysed black mass). The heat capacity of the mixture on completion of the reaction was found to be 2761 $J.kg^{-1}.K^{-1}$. This indicates that the adiabatic temperature rise for the reaction is 62.8 K. Minor accumulation of unreacted feed was observed with 1.6 % of the total heat being generated after the addition was complete.

Gas generation was observed and 6842 ml was generated over the addition period (ca. 73 ml of this was due to displacement of the head space gases by the added volume of material). On completion of the addition a further 1263 ml of gas was generated over approximately 13 hours. It should be noted that the mixture was still generating gas when the test was terminated. The maximum rate of gas generation was found to be 63.0 $ml.min^{-1}$. The gas generated was analysed using a mass spectrometer. An example of the spectra obtained is provided in Graph 4.1.f and Graph 4.1.g. Peaks were observed at mass numbers 16 and 32 indicating that the gas generated was oxygen. Very small peaks were observed around mass numbers 60 and 90 indicating that traces of toluene were also present.

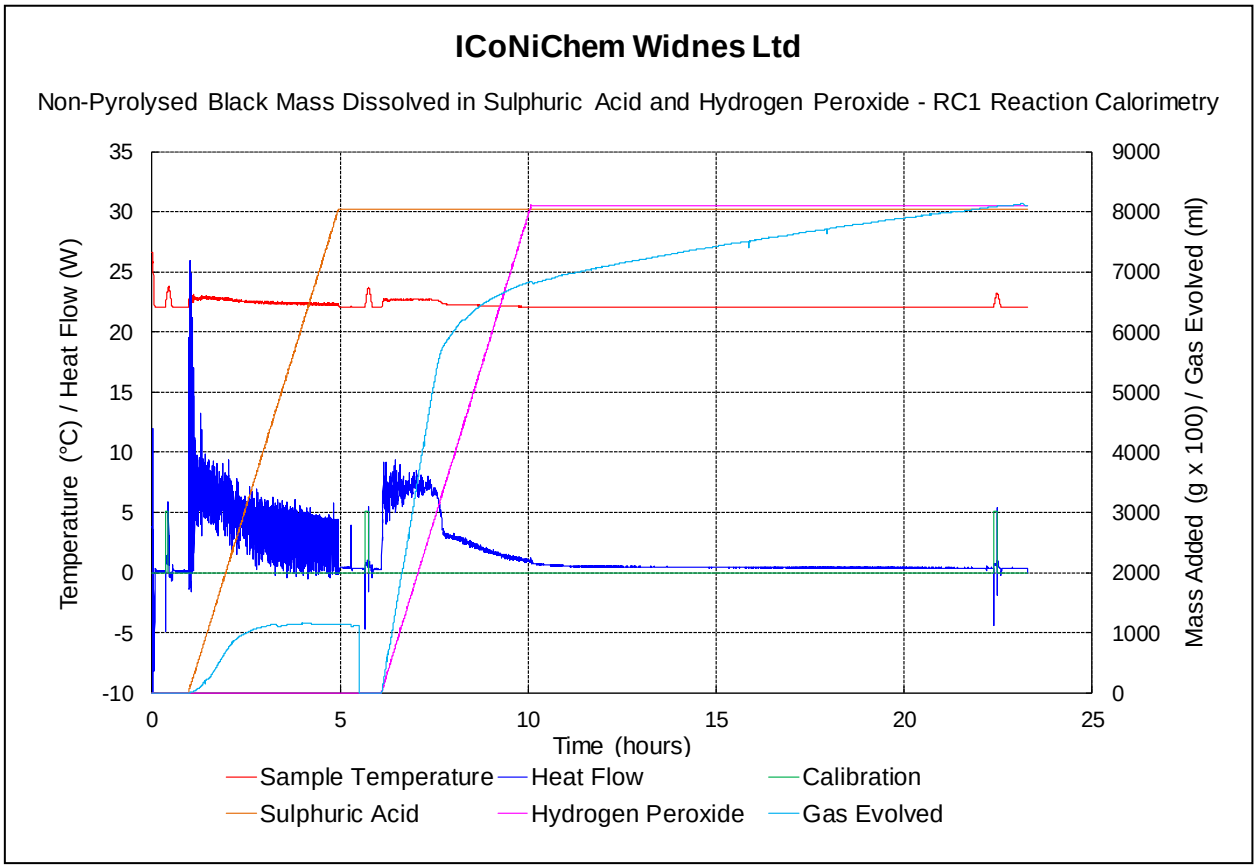
On completion of the reaction the mixture was observed to be a grey slurry with some surface foam.

The following table (Table 4.2 on the following page) summarises the experimental data obtained.

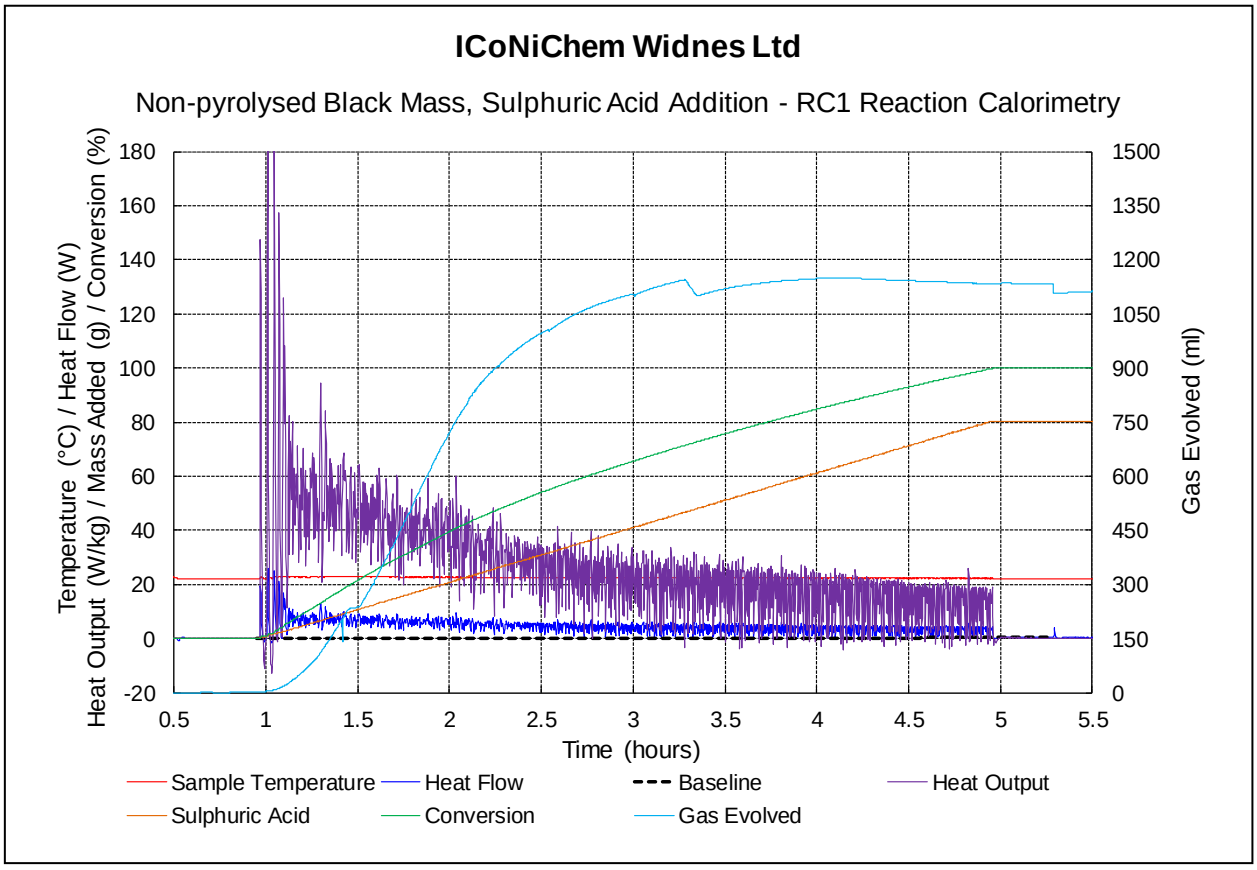
Table 4.2: Summary of RC1 Data

	Sulphuric Acid Addition	Hydrogen Peroxide Addition
Limiting reactant name	Sulphuric acid	Sulphuric acid
Mass used (g)	78.79	78.79
Molecular weight ($g.mol^{-1}$)	98.079	98.079
Moles used (mol)	0.803	0.803
Type of baseline	Proportional to conversion	Proportional to conversion
Qr method	RTC	RTC
Calculated Cp at end of reaction ($J.kg^{-1}.K^{-1}$)	2380	2761
Calculated U value at start of reaction ($W.m^{-2}.K^{-1}$)	201.4	177.7
Calculated U value at end of reaction ($W.m^{-2}.K^{-1}$)	177.7	135.3
Total heat evolved or absorbed (kJ)	62.4	50.9
Total mass of reactants (kg)	0.212	0.293
Calculated heat of reaction ($kJ.mol^{-1}$ of sulphuric acid)	-77.7	-63.3
Calculated heat of reaction ($kJ.kg^{-1}$ of non-pyrolysed black mass)	-1276.9	-1040.4
Total adiabatic temperature rise (K)	123.6	62.8
Heat evolved after addition (kJ)	0	0.80
Extent of accumulation (%)	0	1.6
Adiabatic temperature rise due to accumulation (K)	0	1.0
Peak heat flow ($W.kg^{-1}$ of reaction mixture)	~180	~40
Total quantity of gas generated (ml)	1090	> 8032

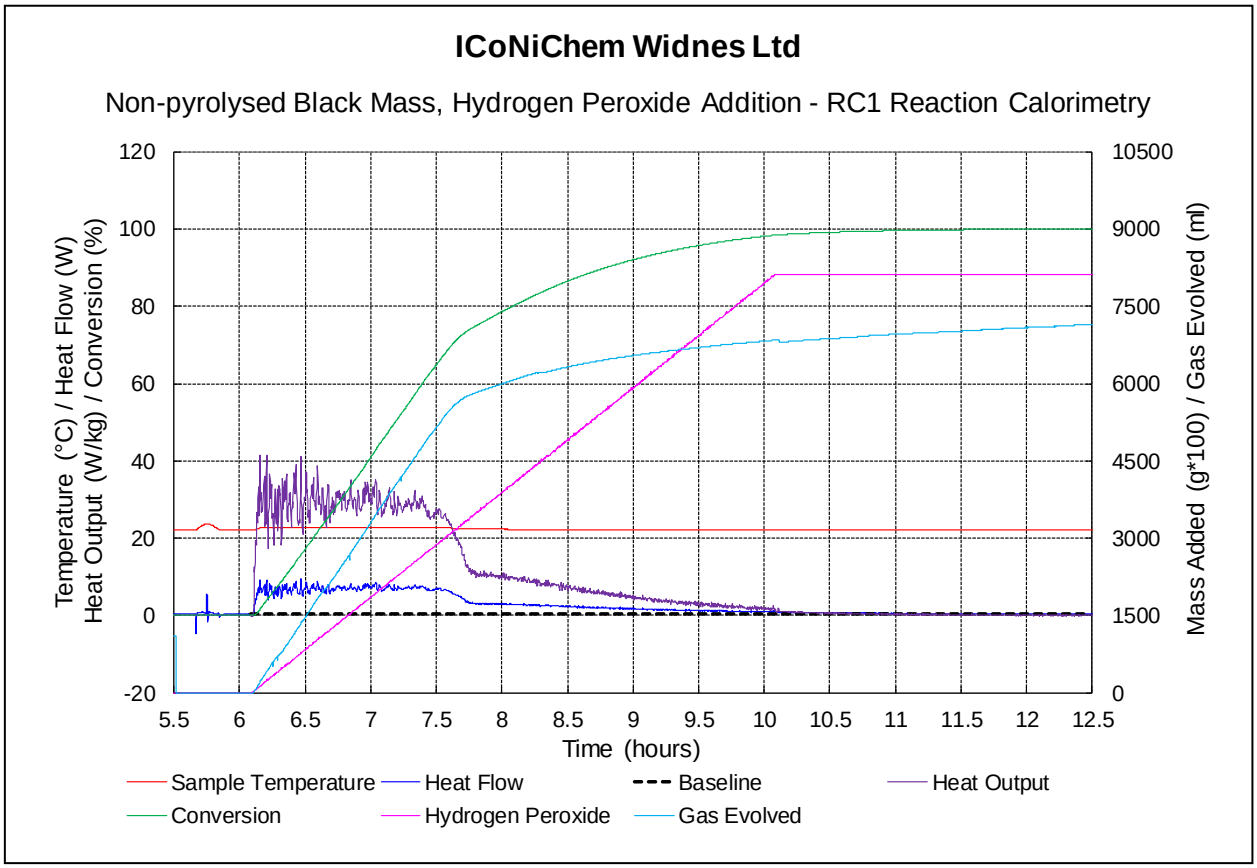
Graph 4.1.a


ICoNiChem Widnes Ltd
Non-Pyrolysed Black Mass Dissolved in Sulphuric Acid and Hydrogen Peroxide - RC1 Reaction Calorimetry
Temperature (°C) / Heat Flow (W)
Mass Added (g x 100) / Gas Evolved (ml)
Time (hours)
35
30
25
20
15
10
5
0
-5
-10
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
5
10
15
20
25
Sample Temperature
Heat Flow
Calibration
Sulphuric Acid
Hydrogen Peroxide
Gas Evolved

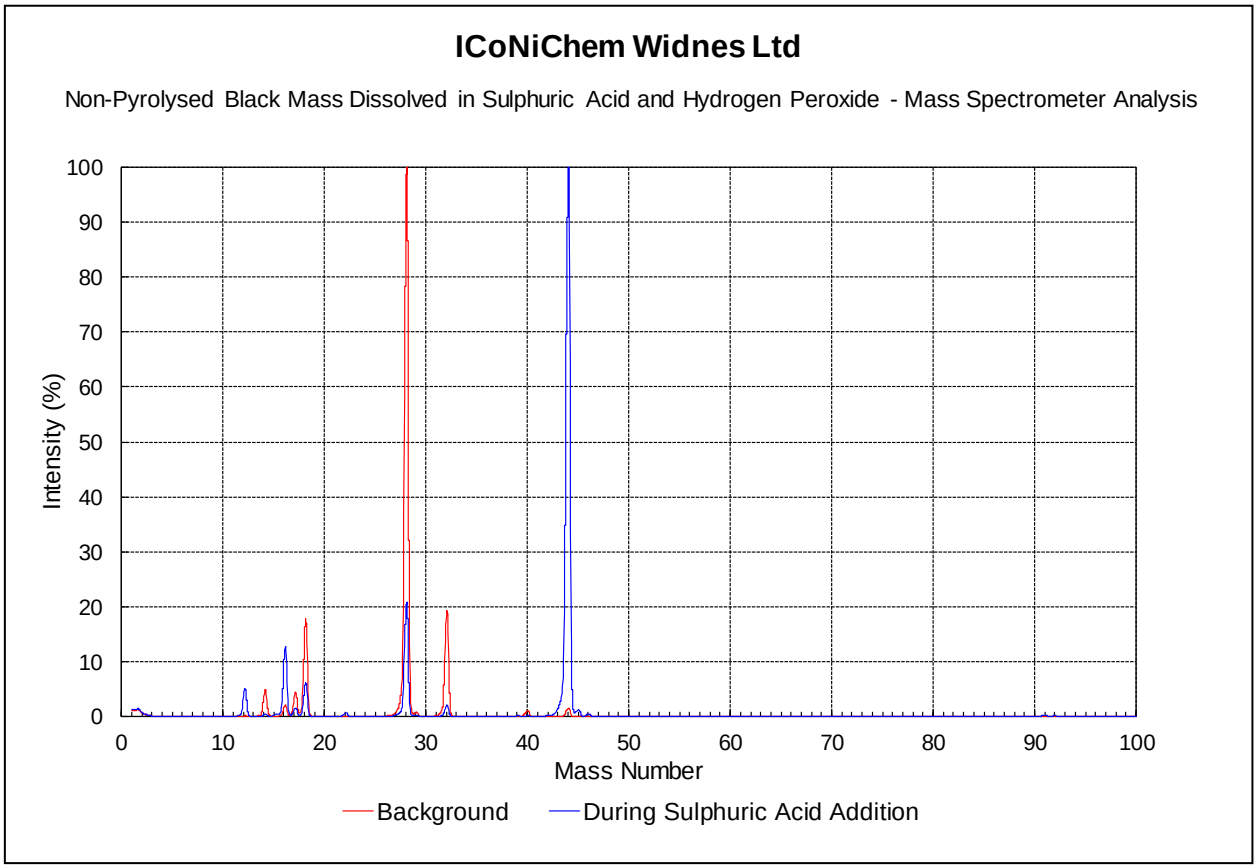
Graph 4.1.b


ICoNiChem Widnes Ltd
Non-pyrolysed Black Mass, Sulphuric Acid Addition - RC1 Reaction Calorimetry
Temperature (°C) / Heat Flow (W)
Heat Output (W/kg) / Mass Added (g) / Conversion (%)
Gas Evolved (ml)
180
160
140
120
100
80
60
40
20
0
-20
1500
1350
1200
1050
900
750
600
450
300
150
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
Time (hours)
Sample Temperature
Heat Flow
Baseline
Heat Output
Sulphuric Acid
Conversion
Gas Evolved

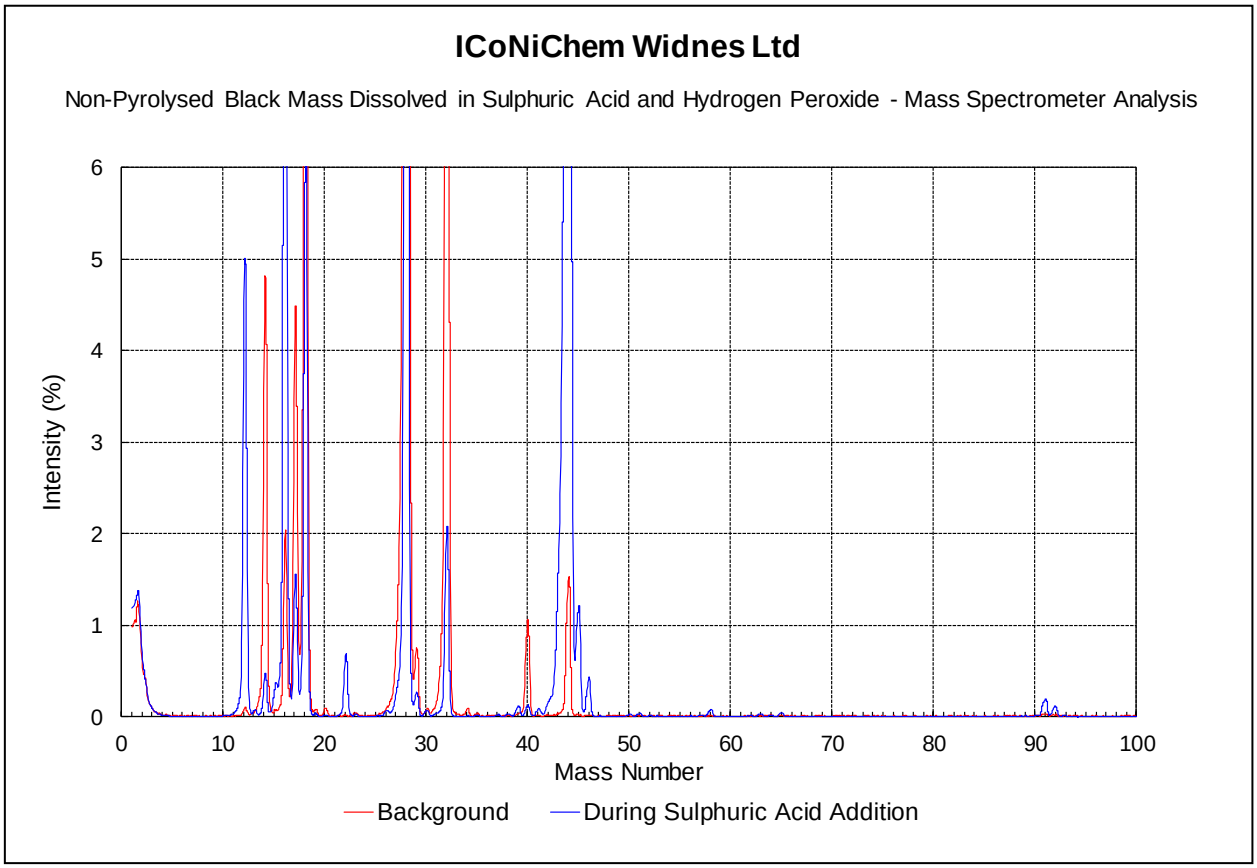
Graph 4.1.c


ICoNiChem Widnes Ltd
Non-pyrolysed Black Mass, Hydrogen Peroxide Addition - RC1 Reaction Calorimetry
Temperature (°C) / Heat Flow (W)
Heat Output (W/kg) / Conversion (%)
Mass Added (g*100) / Gas Evolved (ml)
120
100
80
60
40
20
0
-20
10500
9000
7500
6000
4500
3000
1500
0
5.5
6
6.5
7
7.5
8
8.5
9
9.5
10
10.5
11
11.5
12
12.5
Time (hours)
Sample Temperature
Heat Flow
Baseline
Heat Output
Conversion
Hydrogen Peroxide
Gas Evolved

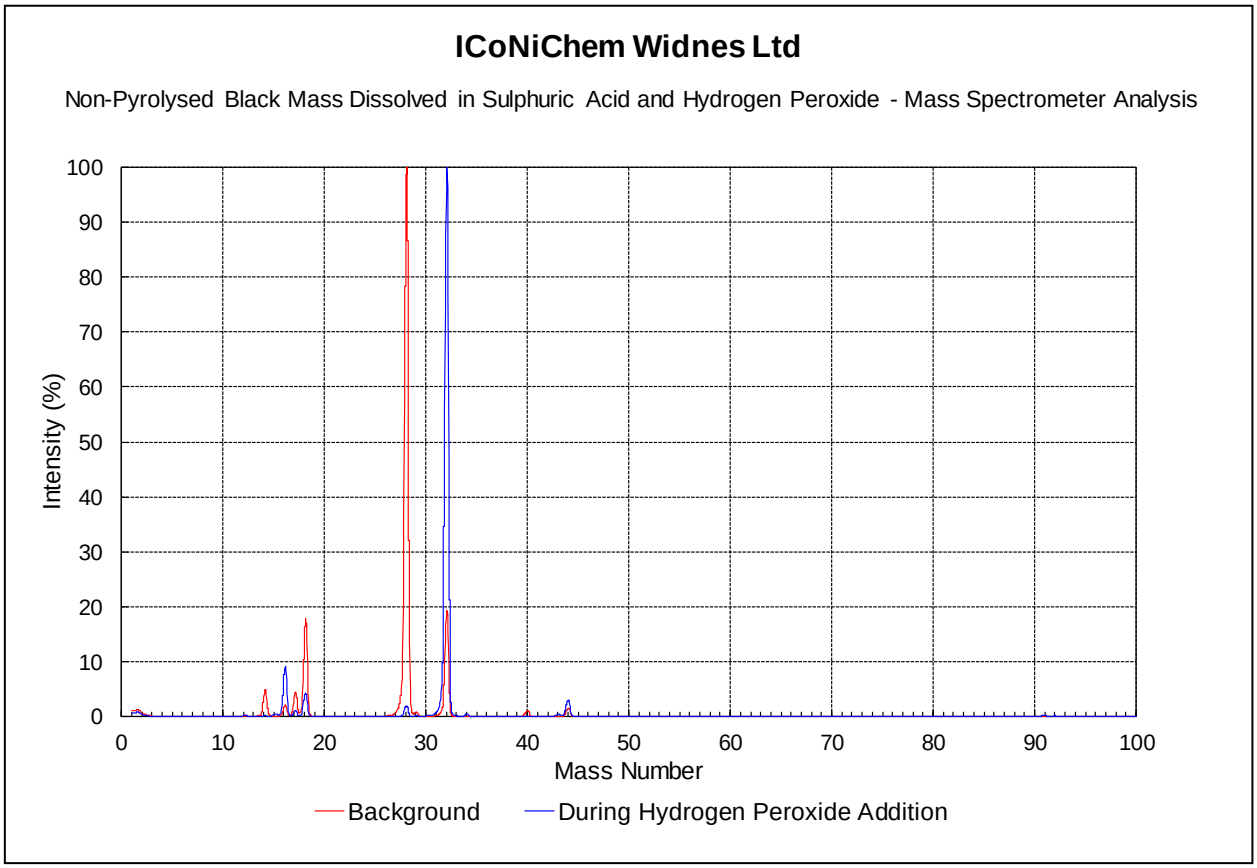
Graph 4.1.d


ICoNiChem Widnes Ltd
Non-Pyrolysed Black Mass Dissolved in Sulphuric Acid and Hydrogen Peroxide - Mass Spectrometer Analysis
Intensity (%)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
Mass Number
Background
During Sulphuric Acid Addition

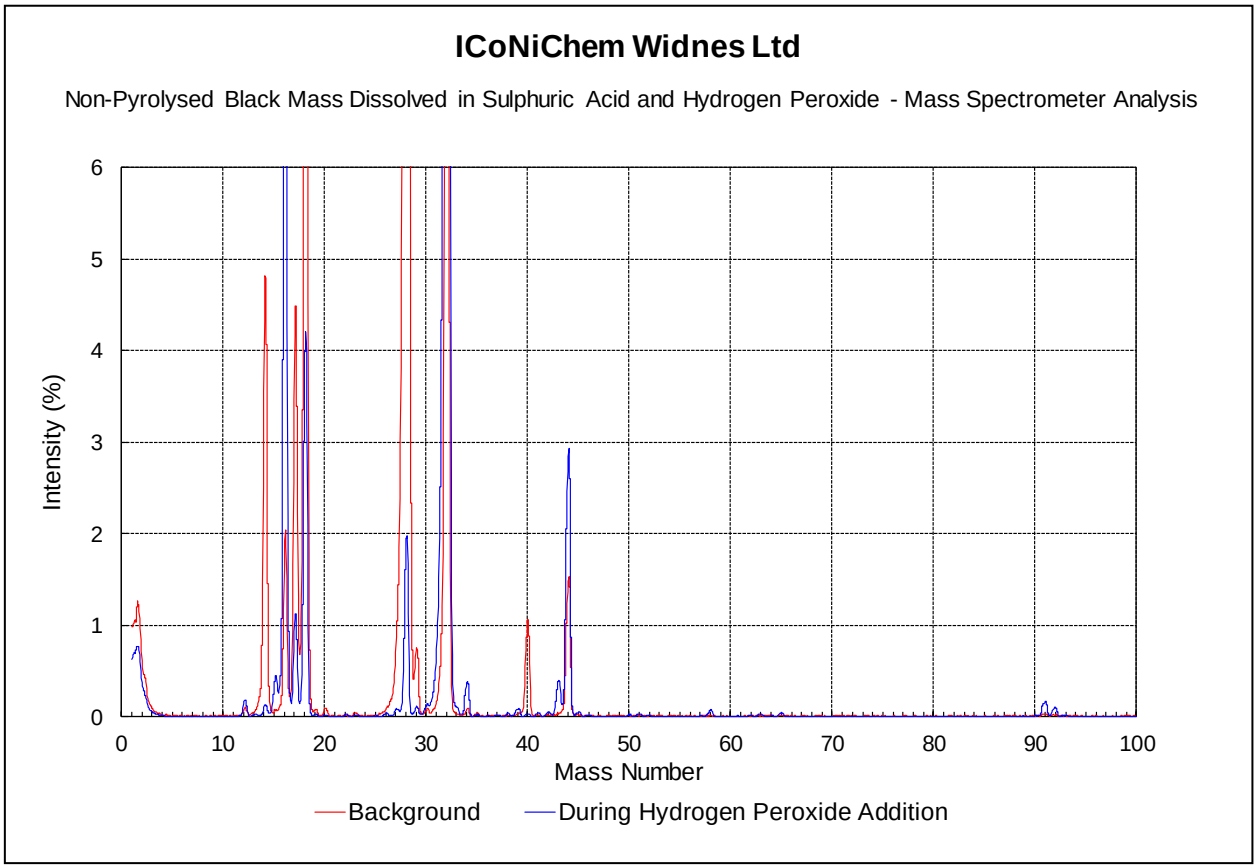
Graph 4.1.e


ICoNiChem Widnes Ltd
Non-Pyrolysed Black Mass Dissolved in Sulphuric Acid and Hydrogen Peroxide - Mass Spectrometer Analysis
Intensity (%)
0
1
2
3
4
5
6
0
10
20
30
40
50
60
70
80
90
100
Mass Number
Background
During Sulphuric Acid Addition

Graph 4.1.f


ICoNiChem Widnes Ltd
Non-Pyrolysed Black Mass Dissolved in Sulphuric Acid and Hydrogen Peroxide - Mass Spectrometer Analysis
Intensity (%)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
Mass Number
Background
During Hydrogen Peroxide Addition

Graph 4.1.g


ICoNiChem Widnes Ltd
Non-Pyrolysed Black Mass Dissolved in Sulphuric Acid and Hydrogen Peroxide - Mass Spectrometer Analysis
Intensity (%)
0
1
2
3
4
5
6
0
10
20
30
40
50
60
70
80
90
100
Mass Number
Background
During Hydrogen Peroxide Addition

4.2 Test Results for Non-Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide

Date	04/03/2020
Operator	G. Amery
SOP Reference	SOP 315
Test System	Mettler RC1$_e$™ Reaction Calorimeter
Test Filename	RC4028005638B

Test Objective

To determine the thermodynamics and kinetics of the additions of nitric acid and hydrogen peroxide to non-pyrolysed black mass when conducted under isothermal conditions (at 22°C). Additionally, the rate and total quantity of gas generated during the reaction was measured using an automated gas burette system.

Test Materials

Chemical	Mass (g)	Source	Batch Number	DEKRA Reference
Non-pyrolysed black mass	47.2	ICoNiChem	N/A	400019397
Distilled water	80.1	Acros	N/A	400018539
Nitric acid 60 % w/w	203.9	Aldrich	STBJ4899	400018570
Hydrogen peroxide 30 % w/w	78.9	Fisher	1920191	400019420

Test Parameters

Parameter	Setting / Configuration
Reactor	AP01 RTC
Reactor volume	500 ml
Stirrer	Glass propeller (without baffle)
Stirrer speed	500 rpm
Test atmosphere	Air
Test pressure	Atmospheric
Test mode	Tr (isothermal at 22°C)
Reflux configuration	No
Addition method	ProMinent pump for nitric acid addition Solenoid valve for hydrogen peroxide addition
Dip pipe employed	No
Gas burette employed	Yes
pH probe employed	No

The non-pyrolysed black mass and water were charged to the vessel and equilibrated at 22°C before a calibration was conducted. These calibrations (conducted using the QuickCal™ method) allow evaluation of the heat transfer characteristics of the reactor (U.A) and heat capacity of the batch (Cp). The addition of nitric acid was then conducted over 4 hours. On completion of the reaction the hydrogen peroxide addition was conducted over 4 hours. Further calibrations were conducted after each step as necessary.

Test Results

The experimental profile obtained from the test is illustrated in Graphs 4.2.a – 4.2.c. Mass spectrometer spectra are provided in Graphs 4.2.d – 4.2.g.

Nitric Acid Addition (Graph 4.2.b)

The addition was found to be exothermic and the total quantity of heat evolved was found to be 24.7 kJ. This equates to a heat of reaction of -12.7 $kJ.mol^{-1}$ (of nitric acid) or -523.5 $kJ.kg^{-1}$ (of non-pyrolysed black mass). The heat capacity of the mixture on completion of the reaction was found to be 2699 $J.kg^{-1}.K^{-1}$. This indicates that the adiabatic temperature rise for the reaction is 27.6 K. No accumulation of unreacted feed was observed.

Gas generation was observed and 1032 ml was generated over the addition period (ca. 149 ml of this was due to displacement of the head space gases by the added volume of material). On completion of the addition no further gas was generated. The maximum rate of gas generation was found to be 25.7 $ml.min^{-1}$. The gas generated was analysed using a mass spectrometer. An example of the spectra obtained is provided in Graph 4.2.d and Graph 4.2.e. Peaks were observed at mass numbers 12, 16 and 44 indicating that the gas generated was carbon dioxide. Very small peaks were observed around mass numbers 60 and 90 indicating that traces of toluene were also present.

On completion of the reaction the mixture was observed to be an opaque black foamy liquid.

Hydrogen Peroxide Addition (Graph 4.2.c)

The addition was found to be exothermic and the total quantity of heat evolved was found to be 43.9 kJ. This equates to a heat of reaction of -22.6 $kJ.mol^{-1}$ (of nitric acid) or -929.4 $kJ.kg^{-1}$ (of non-pyrolysed black mass). The heat capacity of the mixture on completion of the reaction was found to be 2797 $J.kg^{-1}.K^{-1}$. This indicates that the adiabatic temperature rise for the reaction is 38.3 K. Minor accumulation of unreacted feed was observed with 5.0 % of the total heat being generated after the addition was complete.

Gas generation was observed and 6804 ml was generated over the addition period (ca. 71 ml of this was due to displacement of the head space gases by the added volume of material). On completion of the addition a further 386 ml of gas was generated over approximately 13 hours. It should be noted that the mixture was still generating gas when the test was terminated. The maximum rate of gas generation was found to be 63.1 $ml.min^{-1}$. The gas generated was analysed using a mass spectrometer. An example of the spectra obtained is provided in Graph 4.2.f and Graph 4.2.g. Peaks were observed at mass numbers 16 and 32 indicating that the gas generated was oxygen. Very small peaks were observed around mass numbers 60 and 90 indicating that traces of toluene were also present.

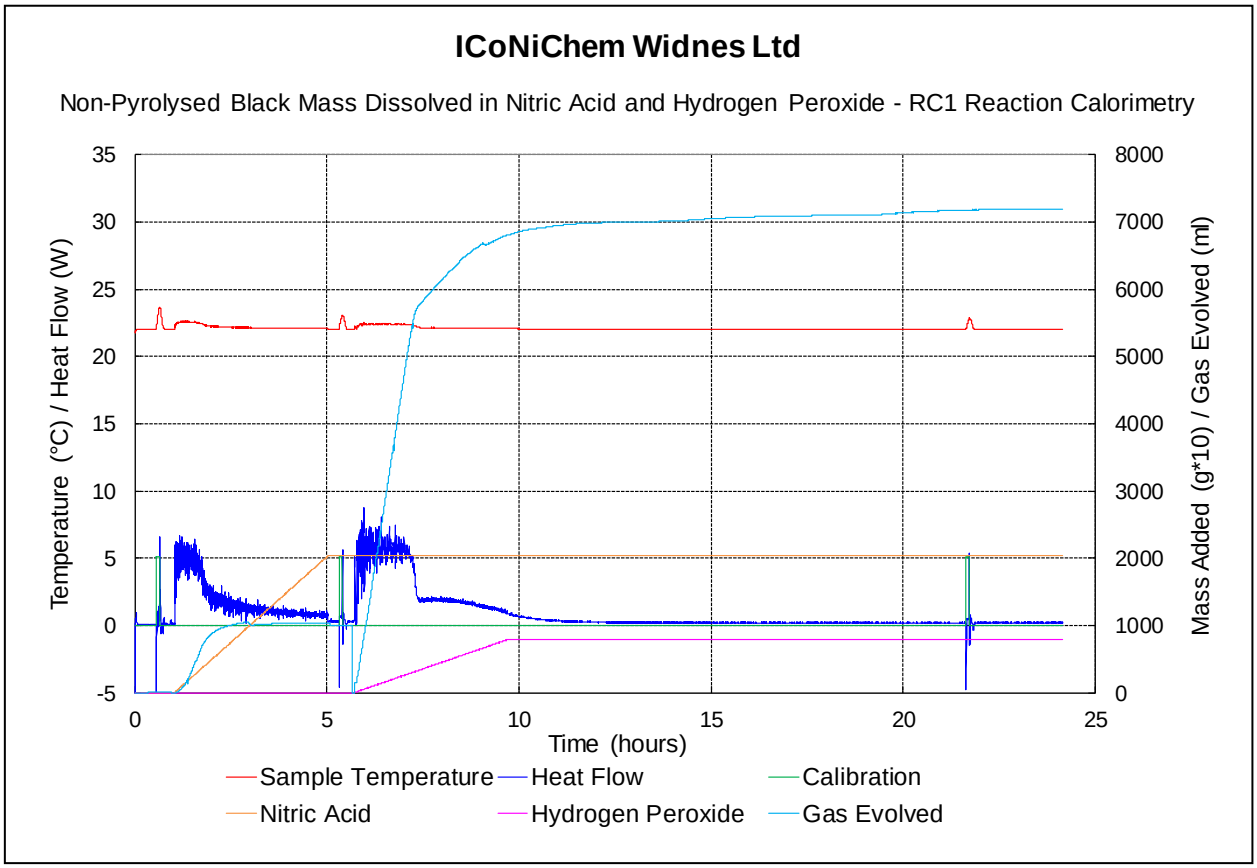
On completion of the reaction the mixture was observed to be a black foamy slurry.

The following table (Table 4.3 on the following page) summarises the experimental data obtained.

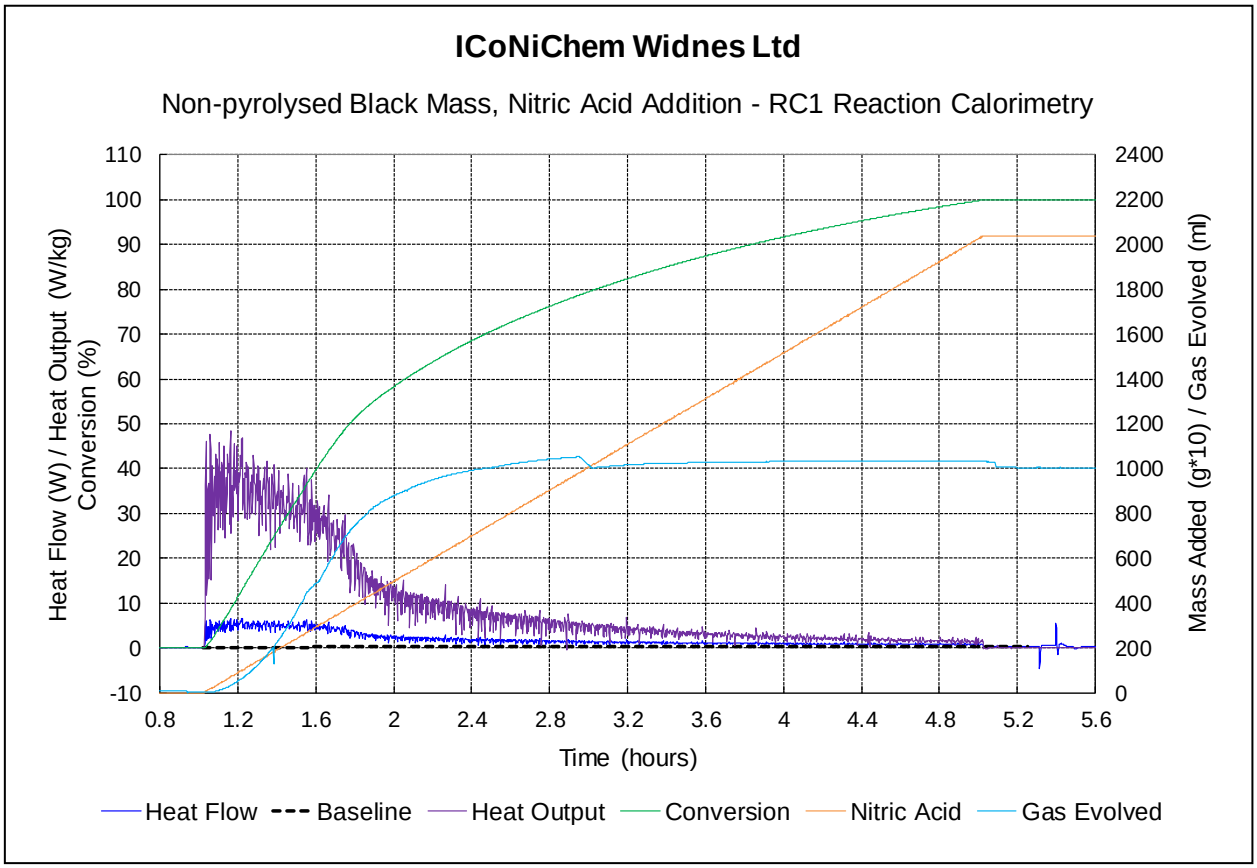
Table 4.3: Summary of RC1 Data

	Nitric Acid Addition	Hydrogen Peroxide Addition
Limiting reactant name	Nitric acid	Nitric acid
Mass used (g)	122.34	122.34
Molecular weight ($g.mol^{-1}$)	63.01	63.01
Moles used (mol)	1.941	1.941
Type of baseline	Proportional to conversion	Proportional to conversion
Qr method	RTC	RTC
Calculated Cp at end of reaction ($J.kg^{-1}.K^{-1}$)	2699	2797
Calculated U value at start of reaction ($W.m^{-2}.K^{-1}$)	197.8	171.9
Calculated U value at end of reaction ($W.m^{-2}.K^{-1}$)	171.9	163.0
Total heat evolved or absorbed (kJ)	24.7	43.9
Total mass of reactants (kg)	0.331	0.410
Calculated heat of reaction ($kJ.mol^{-1}$ of nitric acid)	-12.7	-22.6
Calculated heat of reaction ($kJ.kg^{-1}$ of non-pyrolysed black mass)	-523.5	-929.4
Total adiabatic temperature rise (K)	27.6	38.3
Heat evolved after addition (kJ)	0	2.2
Extent of accumulation (%)	0	5.0
Adiabatic temperature rise due to accumulation (K)	0	1.9
Peak heat flow ($W.kg^{-1}$ of reaction mixture)	~45	~20
Total quantity of gas generated (ml)	883	> 7119

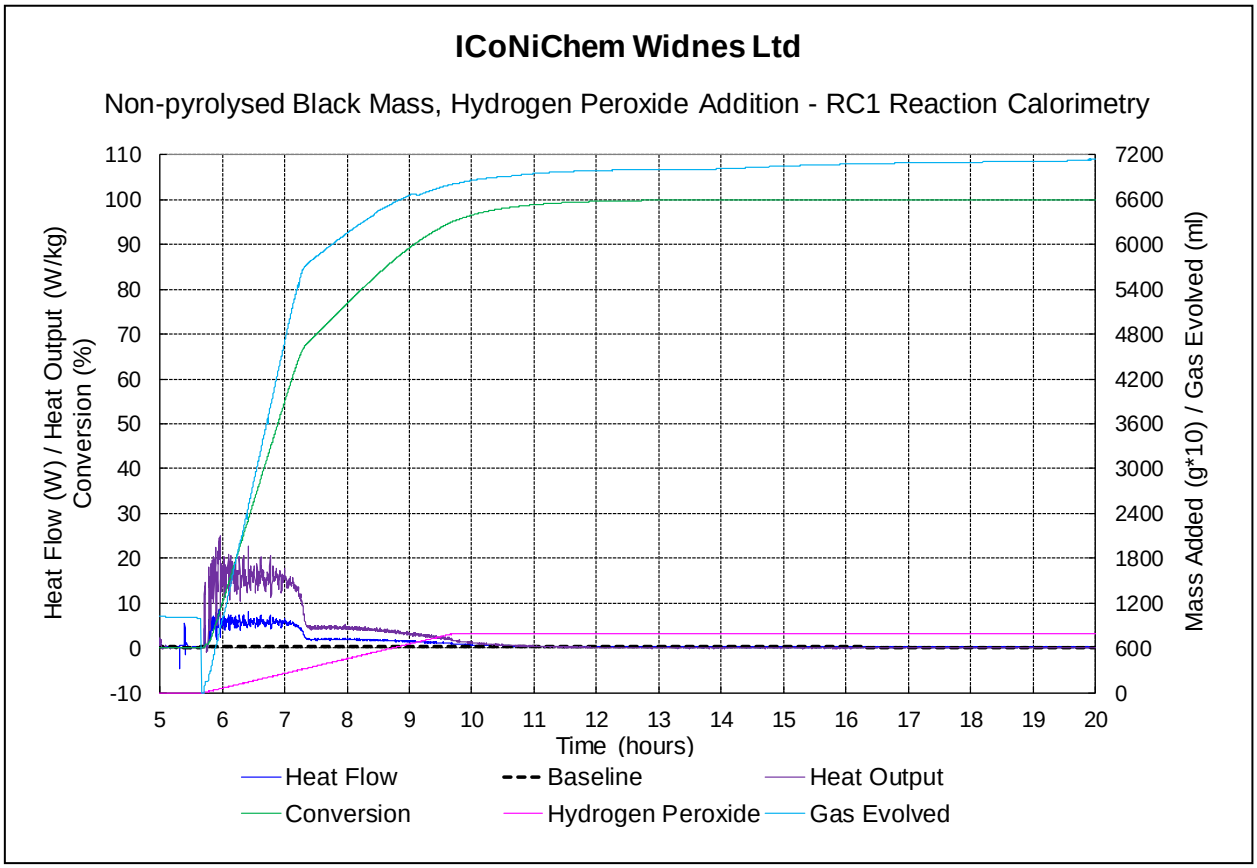
Graph 4.2.a


ICoNiChem Widnes Ltd
Non-Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - RC1 Reaction Calorimetry
Temperature (°C) / Heat Flow (W)
Mass Added (g*10) / Gas Evolved (ml)
Time (hours)
Sample Temperature
Heat Flow
Calibration
Nitric Acid
Hydrogen Peroxide
Gas Evolved

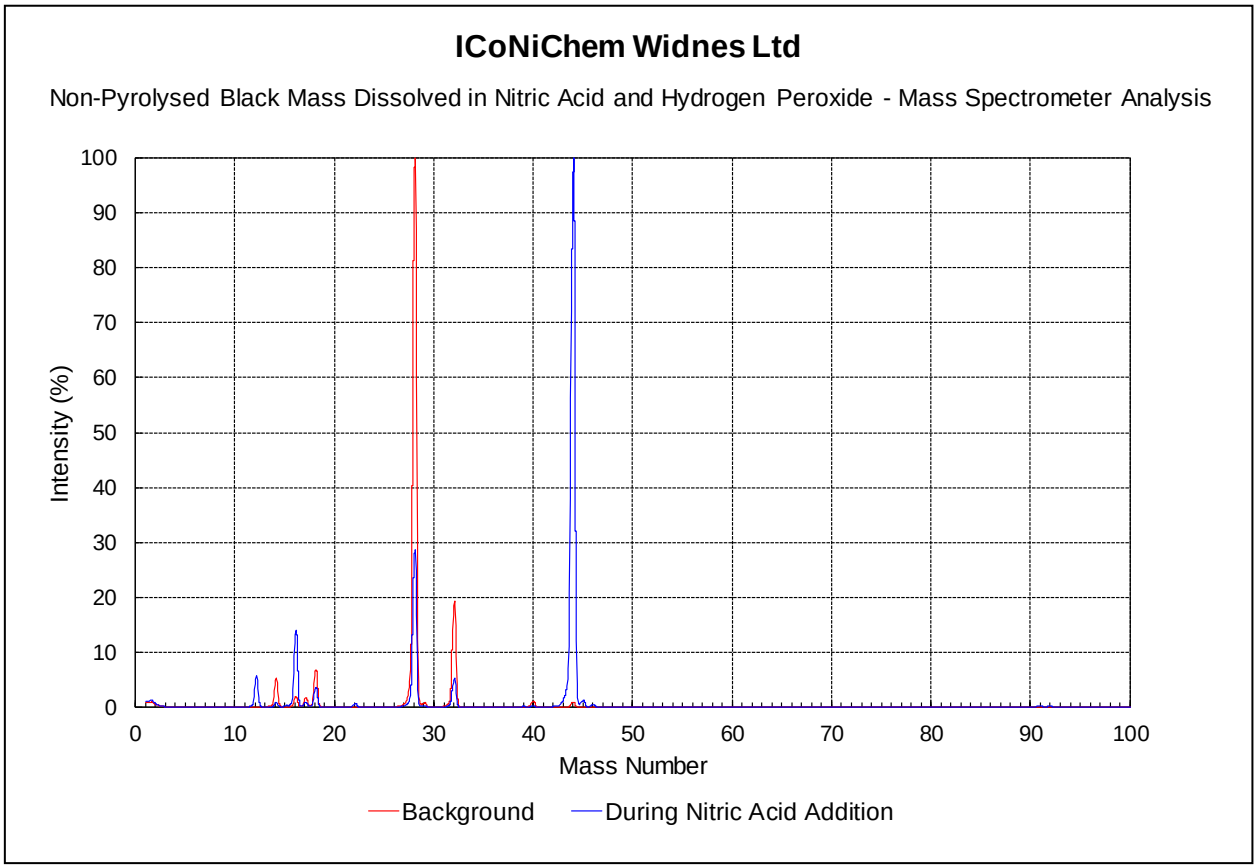
Graph 4.2.b


ICoNiChem Widnes Ltd
Non-pyrolysed Black Mass, Nitric Acid Addition - RC1 Reaction Calorimetry
Heat Flow (W) / Heat Output (W/kg)
Conversion (%)
Mass Added (g*10) / Gas Evolved (ml)
Time (hours)
Heat Flow
Baseline
Heat Output
Conversion
Nitric Acid
Gas Evolved

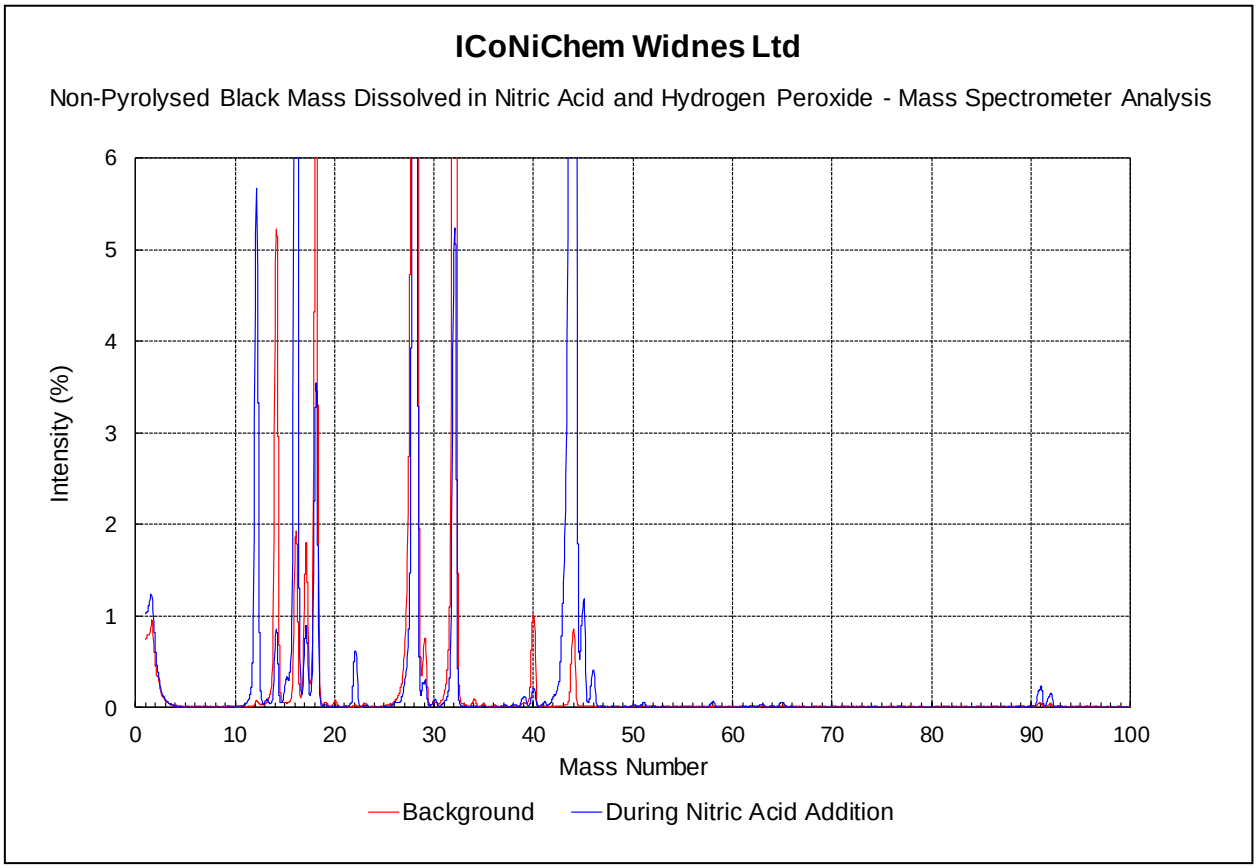
Graph 4.2.c


ICoNiChem Widnes Ltd
Non-pyrolysed Black Mass, Hydrogen Peroxide Addition - RC1 Reaction Calorimetry
Heat Flow (W) / Heat Output (W/kg)
Conversion (%)
Mass Added (g*10) / Gas Evolved (ml)
Time (hours)
Heat Flow
Baseline
Heat Output
Conversion
Hydrogen Peroxide
Gas Evolved

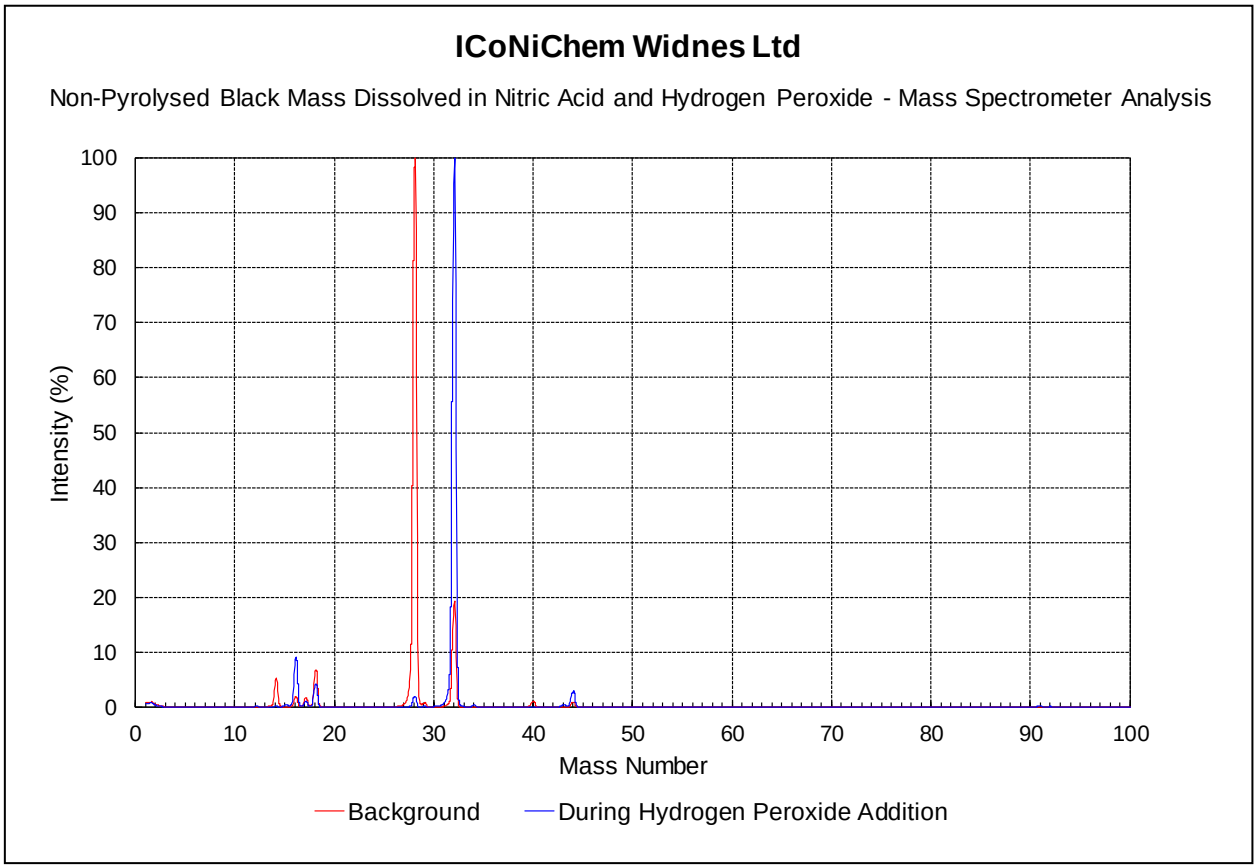
Graph 4.2.d


ICoNiChem Widnes Ltd
Non-Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - Mass Spectrometer Analysis
Intensity (%)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
Mass Number
Background
During Nitric Acid Addition

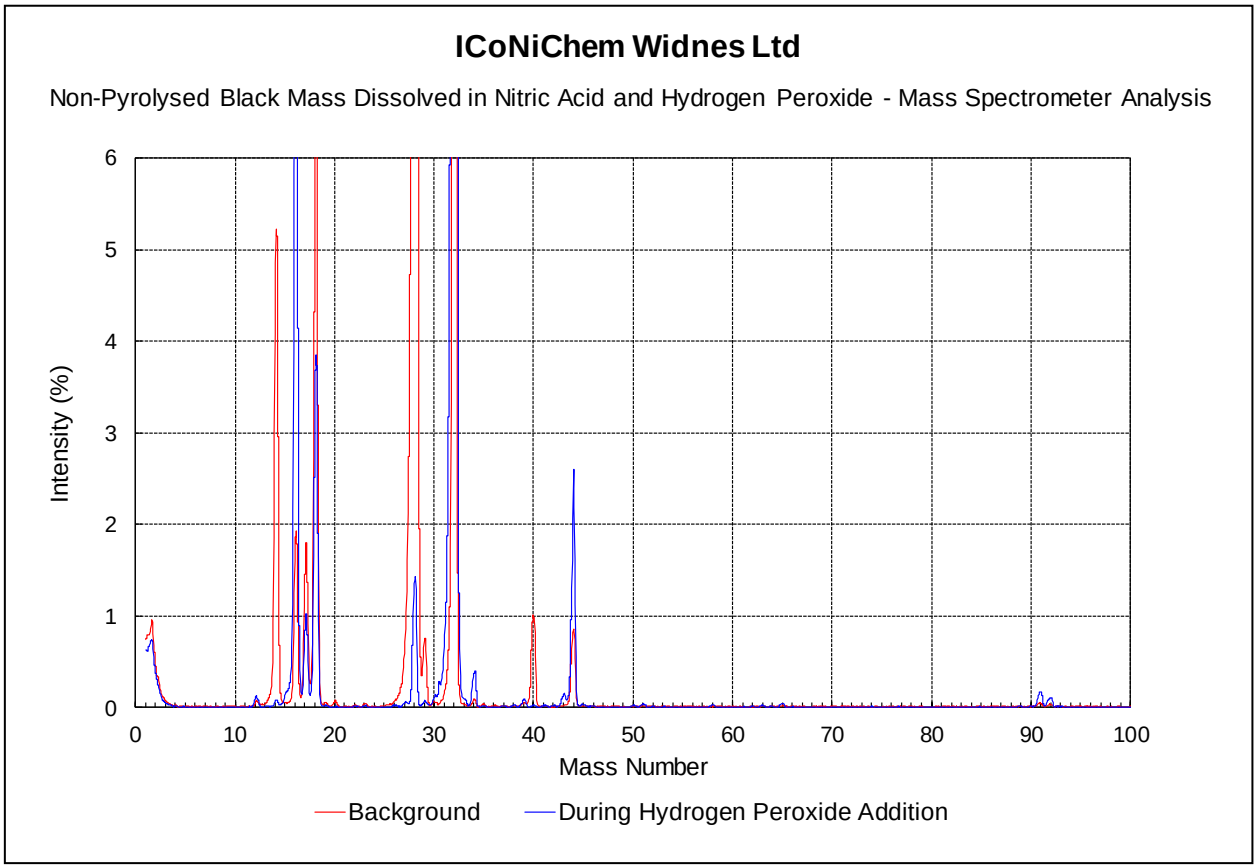
Graph 4.2.e


ICoNiChem Widnes Ltd
Non-Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - Mass Spectrometer Analysis
Intensity (%)
0
1
2
3
4
5
6
0
10
20
30
40
50
60
70
80
90
100
Mass Number
Background
During Nitric Acid Addition

Graph 4.2.f


ICoNiChem Widnes Ltd
Non-Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - Mass Spectrometer Analysis
Intensity (%)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
Mass Number
Background
During Hydrogen Peroxide Addition

Graph 4.2.g


ICoNiChem Widnes Ltd
Non-Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - Mass Spectrometer Analysis
Intensity (%)
0
1
2
3
4
5
6
0
10
20
30
40
50
60
70
80
90
100
Mass Number
Background
During Hydrogen Peroxide Addition

4.3 Test Results for Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide

Date	23/03/2020
Operator	G. Amery / M. D'Lavari
SOP Reference	SOP 315
Test System	Mettler RC1$_e$™ Reaction Calorimeter
Test Filename	RC4028005638C

Test Objective

To determine the thermodynamics and kinetics of the additions of nitric acid and hydrogen peroxide to pyrolysed black mass when conducted under isothermal conditions (at 22°C). Additionally, the rate and total quantity of gas generated during the reaction was measured using an automated gas burette system.

Test Materials

Chemical	Mass (g)	Source	Batch Number	DEKRA Reference
Pyrolysed black mass	47.2	ICoNiChem	N/A	400019396
Distilled water	80.1	Acros	N/A	400018539
Nitric acid 60 % w/w	203.9	Aldrich	STBJ4899	400018570
Hydrogen peroxide 30 % w/w	78.9	Fisher	1920191	400019420

Test Parameters

Parameter	Setting / Configuration
Reactor	AP01 RTC
Reactor volume	500 ml
Stirrer	Glass propeller (without baffle)
Stirrer speed	500 rpm
Test atmosphere	Air
Test pressure	Atmospheric
Test mode	Tr (isothermal at 22°C)
Reflux configuration	No
Addition method	ProMinent pump for nitric acid addition Solenoid valve for hydrogen peroxide addition
Dip pipe employed	No
Gas burette employed	Yes
pH probe employed	No

The pyrolysed black mass and water were charged to the vessel and equilibrated at 22°C before a calibration was conducted. These calibrations (conducted using the QuickCal™ method) allow evaluation of the heat transfer characteristics of the reactor (U.A) and heat capacity of the batch (Cp). The addition of nitric acid was then conducted over 4 hours. On completion of the reaction the hydrogen peroxide addition was conducted over 4 hours. Further calibrations were conducted after each step as necessary.

Test Results

The experimental profile obtained from the test is illustrated in Graphs 4.3.a – 4.3.c. Mass spectrometer spectra are provided in Graph 4.3.d and Graph 4.3.e.

Nitric Acid Addition (Graph 4.3.b)

The addition was found to be exothermic and the total quantity of heat evolved was found to be 29.9 kJ. This equates to a heat of reaction of -15.4 $kJ.mol^{-1}$ (of nitric acid) or -634.0 $kJ.kg^{-1}$ (of pyrolysed black mass). The heat capacity of the mixture on completion of the reaction was found to be 2716 $J.kg^{-1}.K^{-1}$. This indicates that the adiabatic temperature rise for the reaction is 33.2 K. Accumulation of unreacted feed was observed with 13.2 % of the total heat being generated after the addition was complete. No significant gas generation was observed.

On completion of the reaction the mixture was observed to be a black suspension.

Hydrogen Peroxide Addition (Graph 4.3.c)

The addition was found to be exothermic and the total quantity of heat evolved was found to be 59.5 kJ. This equates to a heat of reaction of -30.7 $kJ.mol^{-1}$ (of nitric acid) or -1260.6 $kJ.kg^{-1}$ (of pyrolysed black mass). The heat capacity of the mixture on completion of the reaction was found to be 2794 $J.kg^{-1}.K^{-1}$. This indicates that the adiabatic temperature rise for the reaction is 52.0 K. Accumulation of unreacted feed was observed with 30.0 % of the total heat being generated after the addition was complete.

Gas generation was observed and 6793 ml was generated over the addition period (ca. 71 ml of this was due to displacement of the head space gases by the added volume of material). On completion of the addition a further 3219 ml of gas was generated over approximately 22 hours. It should be noted that the mixture was still generating gas when the test was terminated. The maximum rate of gas generation was found to be 67.1 $ml.min^{-1}$. The gas generated was analysed using a mass spectrometer. An example of the spectra obtained is provided in Graph 4.3.d and Graph 4.3.e. Peaks were observed at mass numbers 16 and 32 indicating that the gas generated was oxygen.

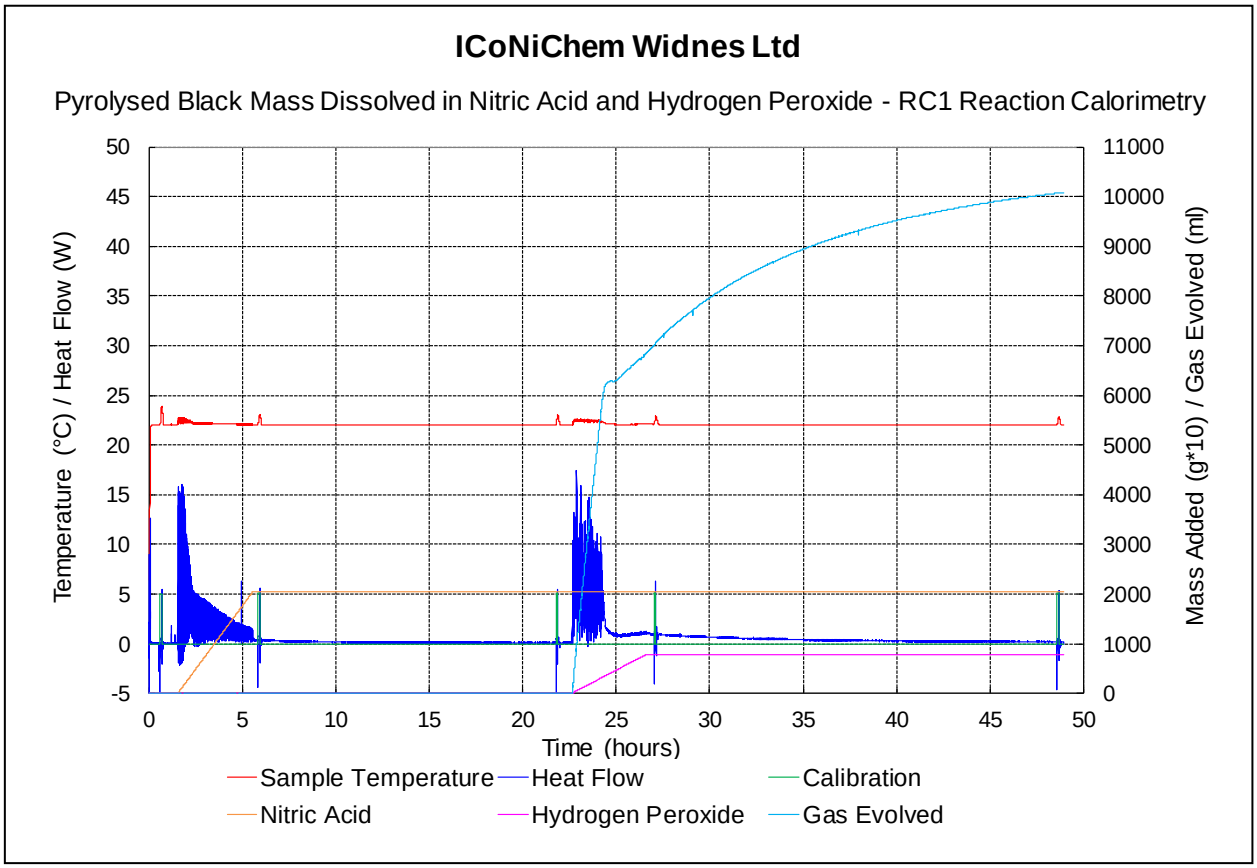
On completion of the reaction the mixture was observed to be a black slurry / suspension.

The following table (Table 4.4 on the following page) summarises the experimental data obtained.

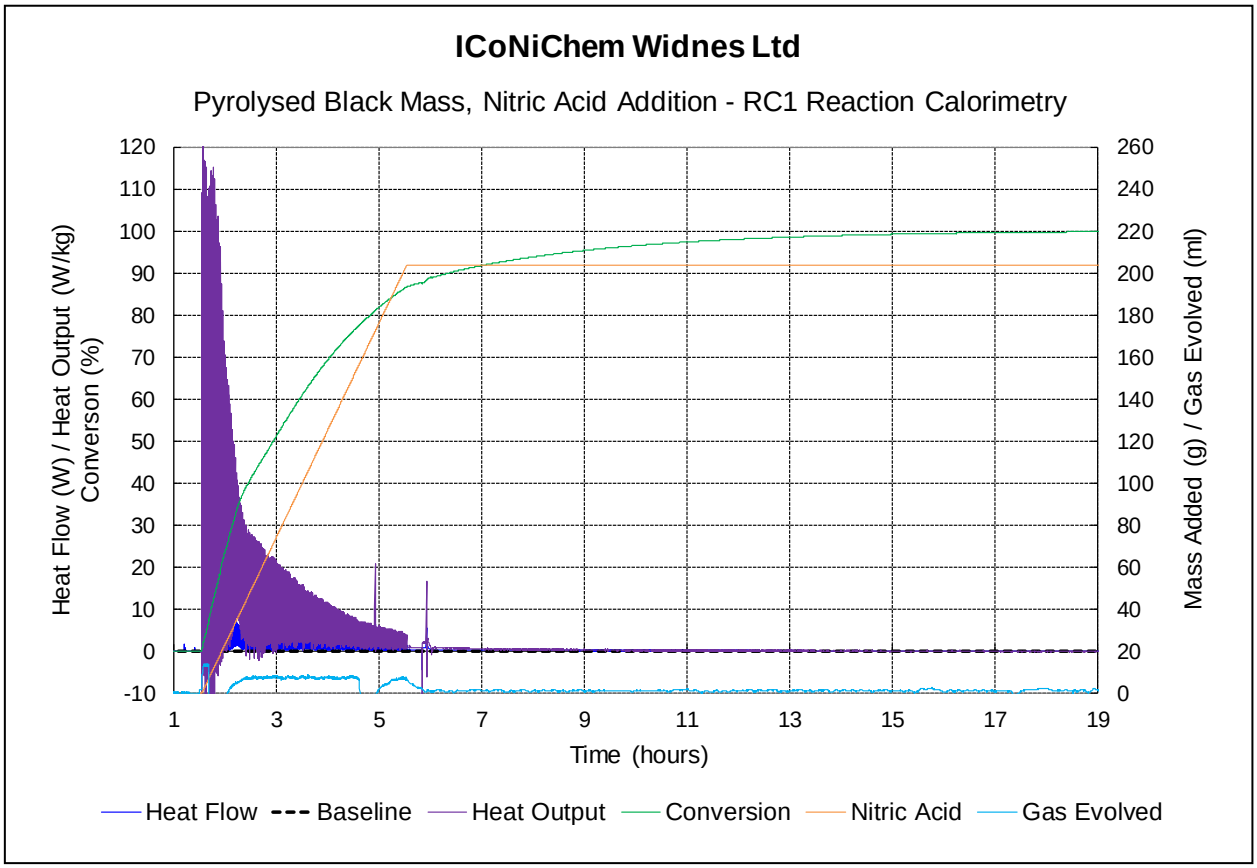
Table 4.4: Summary of RC1 Data

	Nitric Acid Addition	Hydrogen Peroxide Addition
Limiting reactant name	Nitric acid	Nitric acid
Mass used (g)	122.34	122.34
Molecular weight ($g.mol^{-1}$)	63.01	63.01
Moles used (mol)	1.941	1.941
Type of baseline	Proportional to conversion	Proportional to conversion
Qr method	RTC	RTC
Calculated Cp at end of reaction ($J.kg^{-1}.K^{-1}$)	2716	2794
Calculated U value at start of reaction ($W.m^{-2}.K^{-1}$)	185.6	172.7
Calculated U value at end of reaction ($W.m^{-2}.K^{-1}$)	170.1	164.7
Total heat evolved or absorbed (kJ)	29.9	59.5
Total mass of reactants (kg)	0.331	0.410
Calculated heat of reaction ($kJ.mol^{-1}$ of nitric acid)	-15.4	-30.7
Calculated heat of reaction ($kJ.kg^{-1}$ of pyrolysed black mass)	-634.0	-1260.6
Total adiabatic temperature rise (K)	33.2	52.0
Heat evolved after addition (kJ)	4.0	17.8
Extent of accumulation (%)	13.2	30.0
Adiabatic temperature rise due to accumulation (K)	4.4	15.6
Peak heat flow ($W.kg^{-1}$ of reaction mixture)	~120	~50
Total quantity of gas generated (ml)	0	> 9941

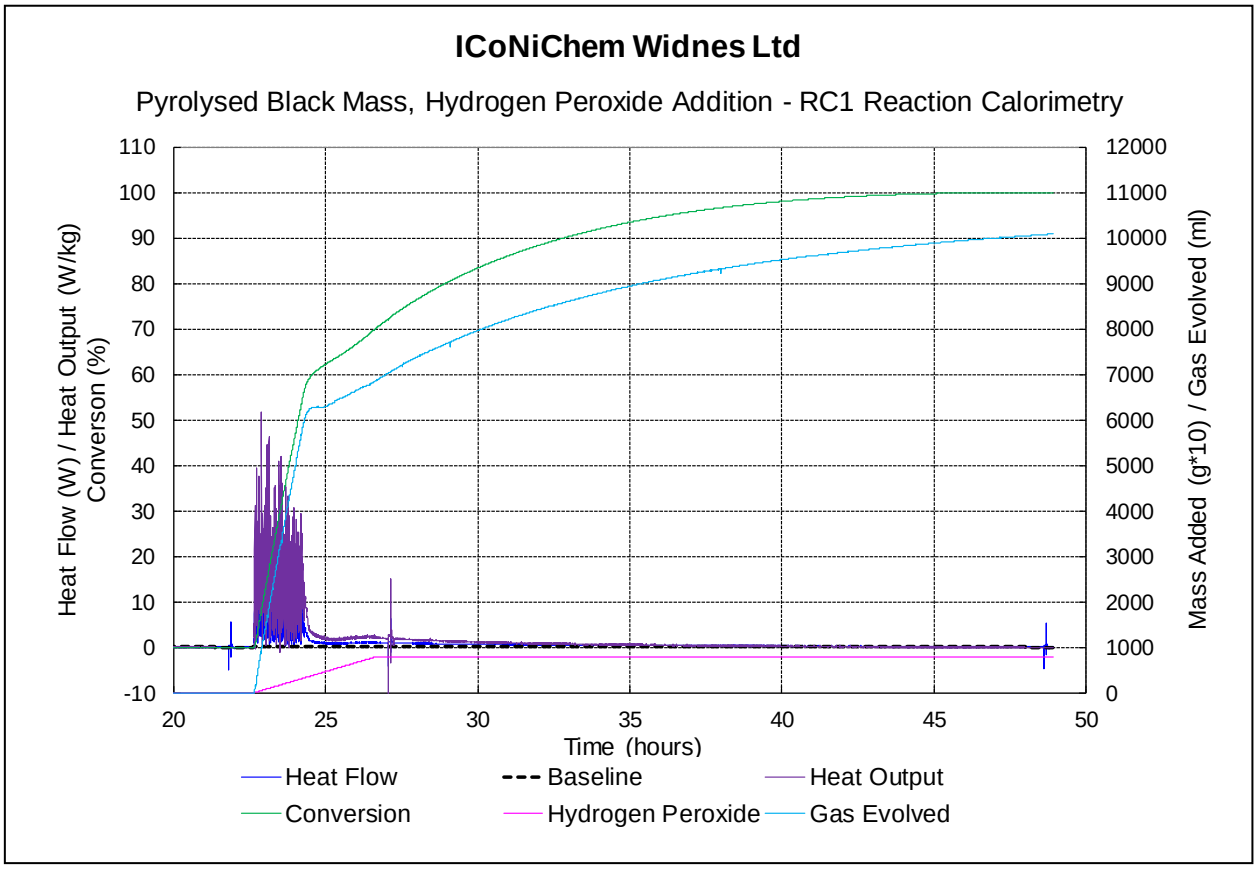
Graph 4.3.a


ICoNiChem Widnes Ltd
Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - RC1 Reaction Calorimetry
Temperature (°C) / Heat Flow (W)
Mass Added (g*10) / Gas Evolved (ml)
Time (hours)
Sample Temperature
Heat Flow
Calibration
Nitric Acid
Hydrogen Peroxide
Gas Evolved

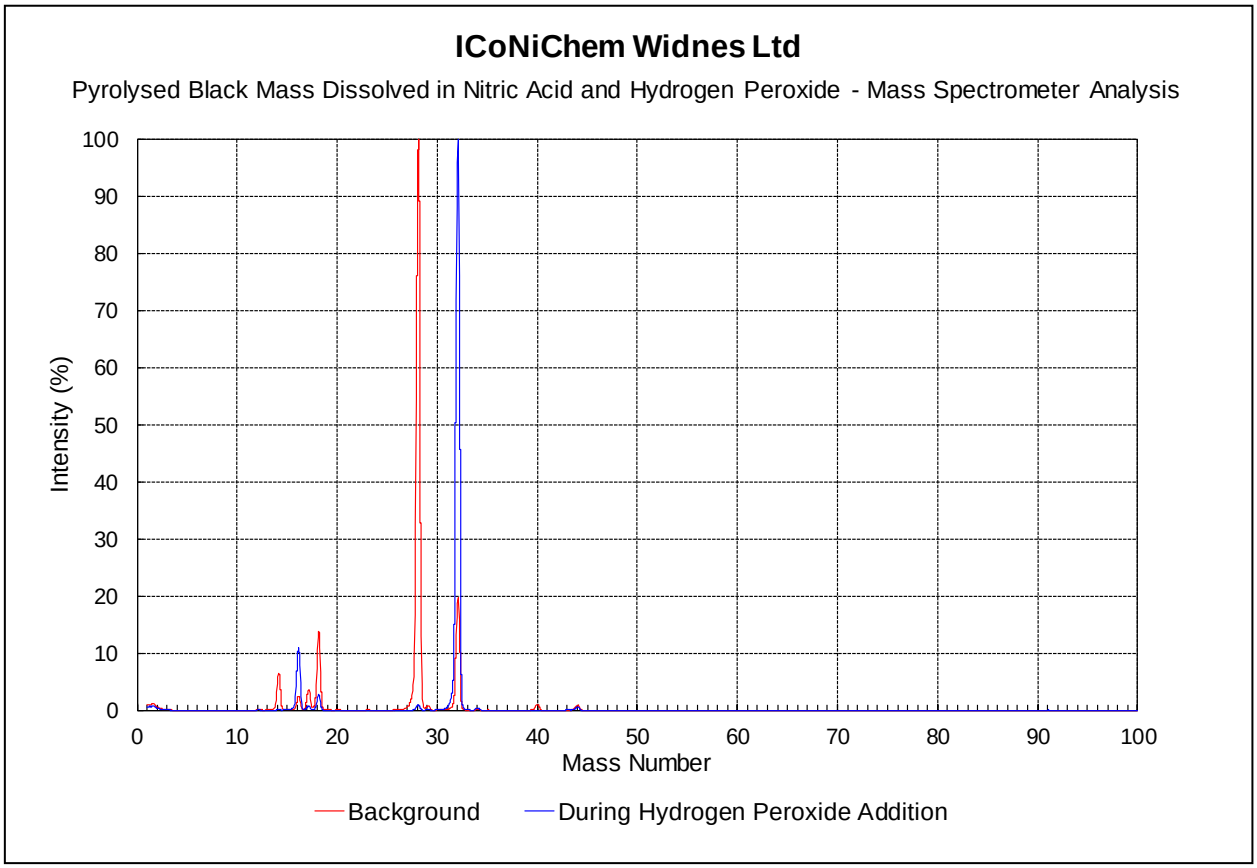
Graph 4.3.b


ICoNiChem Widnes Ltd
Pyrolysed Black Mass, Nitric Acid Addition - RC1 Reaction Calorimetry
Heat Flow (W) / Heat Output (W/kg)
Converson (%)
Mass Added (g) / Gas Evolved (ml)
Time (hours)
Heat Flow
Baseline
Heat Output
Conversion
Nitric Acid
Gas Evolved

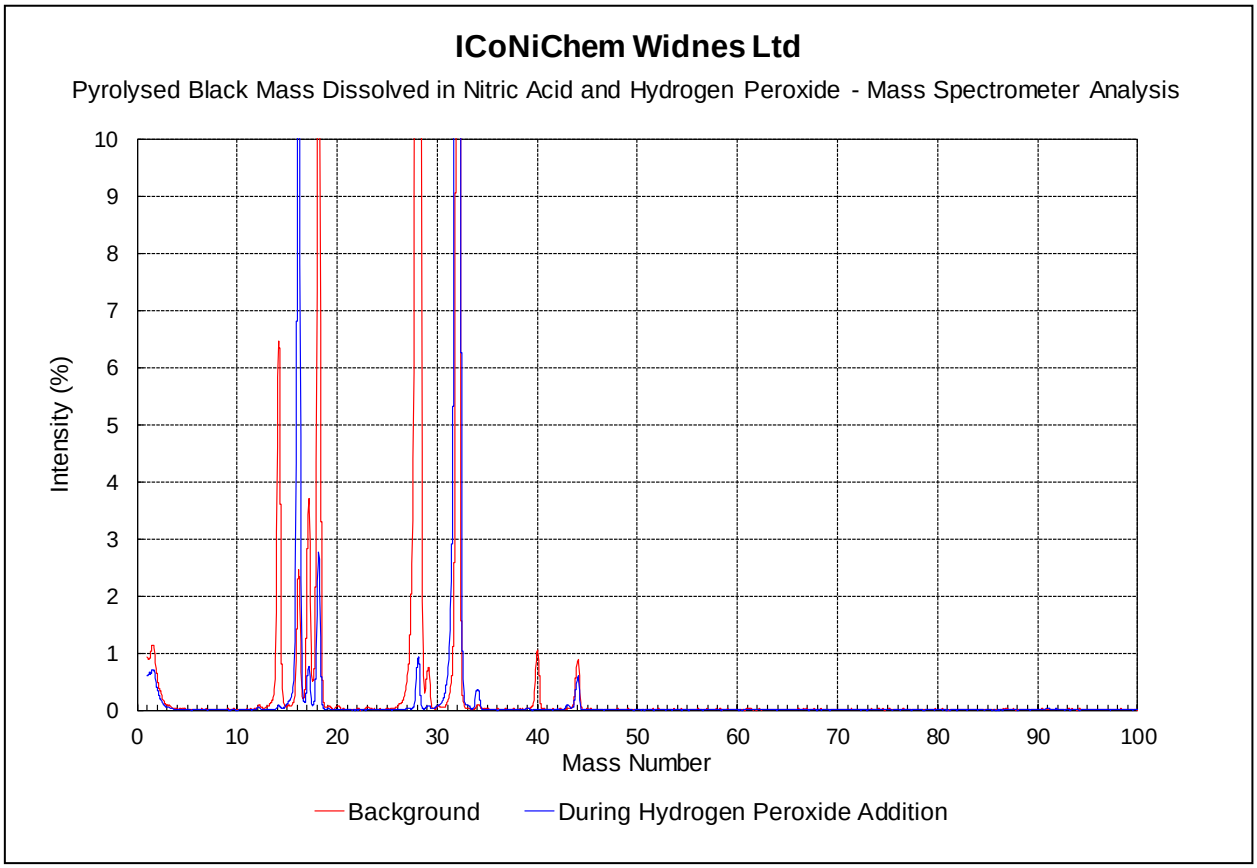
Graph 4.3.c


ICoNiChem Widnes Ltd
Pyrolysed Black Mass, Hydrogen Peroxide Addition - RC1 Reaction Calorimetry
Heat Flow (W) / Heat Output (W/kg)
Conversion (%)
Mass Added (g*10) / Gas Evolved (ml)
Time (hours)
Heat Flow
Baseline
Heat Output
Conversion
Hydrogen Peroxide
Gas Evolved

Graph 4.3.d


ICoNiChem Widnes Ltd
Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - Mass Spectrometer Analysis
Intensity (%)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
Mass Number
Background
During Hydrogen Peroxide Addition

Graph 4.3.e


ICoNiChem Widnes Ltd
Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - Mass Spectrometer Analysis
Intensity (%)
0
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
80
90
100
Mass Number
Background
During Hydrogen Peroxide Addition

4.4 Test Results for New Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide

Date	31/03/2020
Operator	G. Amery / M. D'Lavari
SOP Reference	SOP 315
Test System	Mettler $RC1_e^{TM}$ Reaction Calorimeter
Test Filename	RC4028005638E

Test Objective

To determine the thermodynamics and kinetics of the additions of nitric acid and hydrogen peroxide to new black mass when conducted under isothermal conditions (at 22°C). Additionally, the rate and total quantity of gas generated during the reaction was measured using an automated gas burette system.

Test Materials

Chemical	Mass (g)	Source	Batch Number	DEKRA Reference
New black mass	47.2	ICoNiChem	N/A	400019836
Distilled water	160.2*	Acros	N/A	400018539
Nitric acid 60 % w/w	201.9	Aldrich	STBJ4899	400018570
Hydrogen peroxide 30 % w/w	78.9	Fisher	1920191	400019420

*double the normal quantity of water was added in order to give a suspension which stirred adequately in the vessel

Test Parameters

Parameter	Setting / Configuration
Reactor	AP01 RTC
Reactor volume	500 ml
Stirrer	Glass propeller (without baffle)
Stirrer speed	500 rpm
Test atmosphere	Air
Test pressure	Atmospheric
Test mode	Tr (isothermal at 22°C)
Reflux configuration	No
Addition method	ProMinent pump for nitric acid addition Solenoid valve for hydrogen peroxide addition
Dip pipe employed	No
Gas burette employed	Yes
pH probe employed	No

The new black mass and water were charged to the vessel and equilibrated at 22°C before a calibration was conducted. These calibrations (conducted using the QuickCal™ method) allow evaluation of the heat transfer characteristics of the reactor (U.A) and heat capacity of the batch (Cp). The addition of nitric acid was then conducted over 4 hours. On completion of the reaction the hydrogen peroxide addition was conducted over 4 hours. Further calibrations were conducted after each step as necessary.

Test Results

The experimental profile obtained from the test is illustrated in Graphs 4.4.a – 4.4.c. Mass spectrometer spectra are provided in Graph 4.4.d and Graph 4.4.e.

Nitric Acid Addition (Graph 4.4.b)

The addition was found to be exothermic and the total quantity of heat evolved was found to be 26.2 kJ. This equates to a heat of reaction of -13.5 $kJ.mol^{-1}$ (of nitric acid) or -554.5 $kJ.kg^{-1}$ (of new black mass). The heat capacity of the mixture on completion of the reaction was found to be 3259 $J.kg^{-1}.K^{-1}$. This indicates that the adiabatic temperature rise for the reaction is 19.6 K. No accumulation of unreacted feed was observed. No significant gas generation was observed.

On completion of the reaction the mixture was observed to be a black suspension. The new black mass didn't appear to have been digested or appreciably wetted by the nitric acid addition.

Hydrogen Peroxide Addition (Graph 4.4.c)

The addition was found to be exothermic and the total quantity of heat evolved was found to be 25.9 kJ. This equates to a heat of reaction of -13.4 $kJ.mol^{-1}$ (of nitric acid) or -549.5 $kJ.kg^{-1}$ (of new black mass). The heat capacity of the mixture on completion of the reaction was found to be 3007 $J.kg^{-1}.K^{-1}$. This indicates that the adiabatic temperature rise for the reaction is 17.7 K. Accumulation of unreacted feed was observed with 21.3 % of the total heat being generated after the addition was complete.

Gas generation was observed and 2836 ml was generated over the addition period (ca. 71 ml of this was due to displacement of the head space gases by the added volume of material). On completion of the addition a further 958 ml of gas was generated over approximately 13 hours. The maximum rate of gas generation was found to be 38.4 $ml.min^{-1}$. The gas generated was analysed using a mass spectrometer. An example of the spectra obtained is provided in Graph 4.3.d and Graph 4.3.e. Peaks were observed at mass numbers 16 and 32 indicating that the gas generated was oxygen.

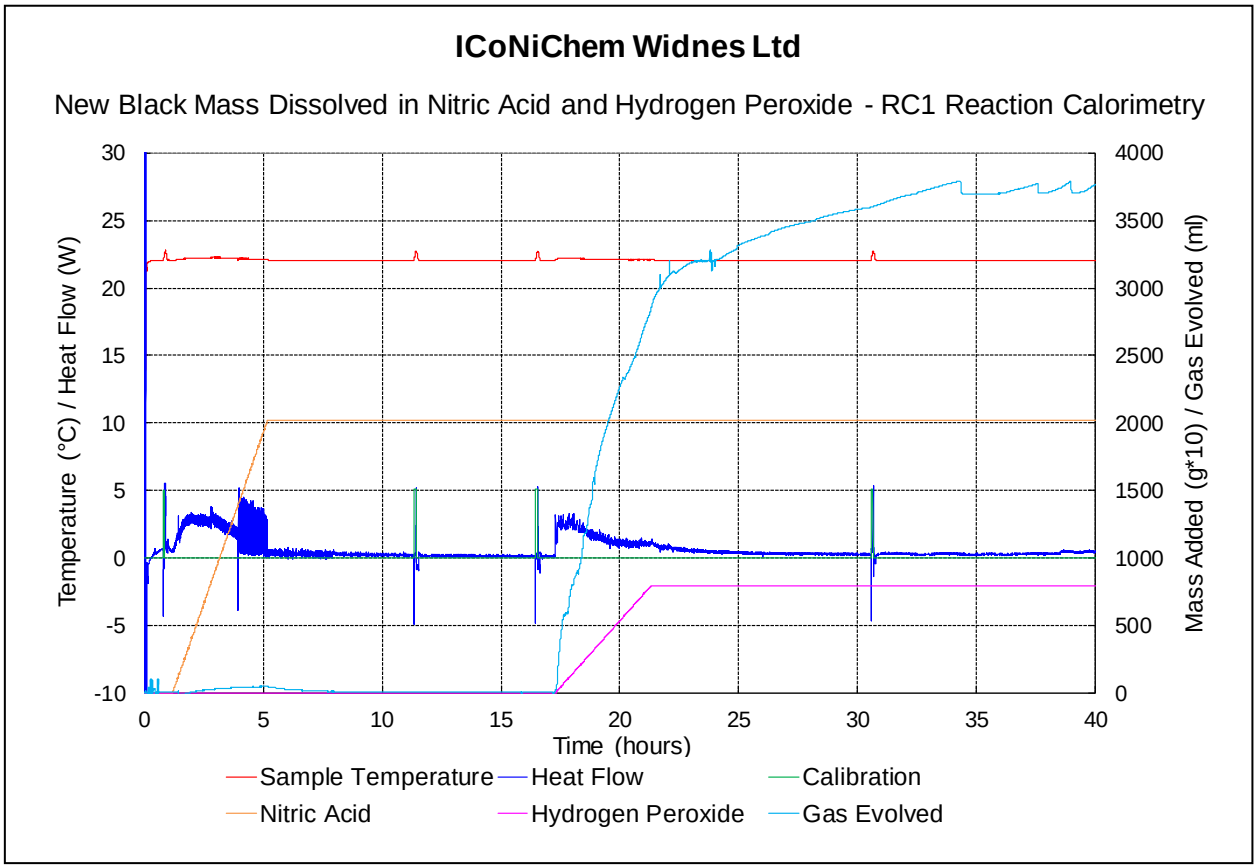
On completion of the reaction the mixture was observed to be a black heavy suspension.

The following table (Table 4.5 on the following page) summarises the experimental data obtained.

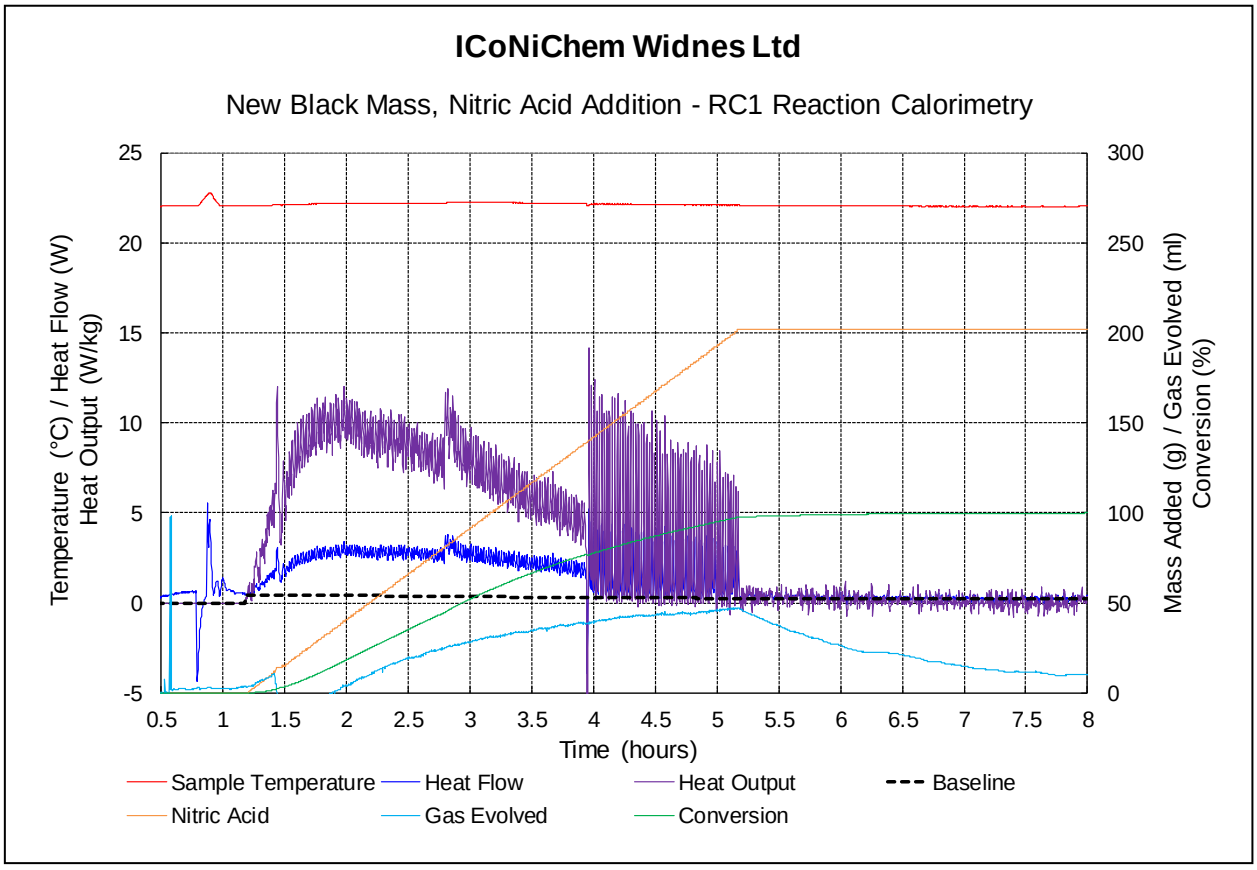
Table 4.5: Summary of RC1 Data

	Nitric Acid Addition	Hydrogen Peroxide Addition
Limiting reactant name	Nitric acid	Nitric acid
Mass used (g)	121.14	121.14
Molecular weight ($g.mol^{-1}$)	63.01	63.01
Moles used (mol)	1.923	1.923
Type of baseline	Proportional to conversion	Proportional to conversion
Qr method	RTC	RTC
Calculated Cp at end of reaction ($J.kg^{-1}.K^{-1}$)	3259	3007
Calculated U value at start of reaction ($W.m^{-2}.K^{-1}$)	248.8	166.0
Calculated U value at end of reaction ($W.m^{-2}.K^{-1}$)	165.2	141.9
Total heat evolved or absorbed (kJ)	26.2	25.9
Total mass of reactants (kg)	0.409	0.488
Calculated heat of reaction ($kJ.mol^{-1}$ of nitric acid)	-13.5	-13.4
Calculated heat of reaction ($kJ.kg^{-1}$ of new black mass)	-554.5	-549.5
Total adiabatic temperature rise (K)	19.6	17.7
Heat evolved after addition (kJ)	0	5.5
Extent of accumulation (%)	0	21.3
Adiabatic temperature rise due to accumulation (K)	0	3.8
Peak heat flow ($W.kg^{-1}$ of reaction mixture)	~11	~7
Total quantity of gas generated (ml)	0	> 3723

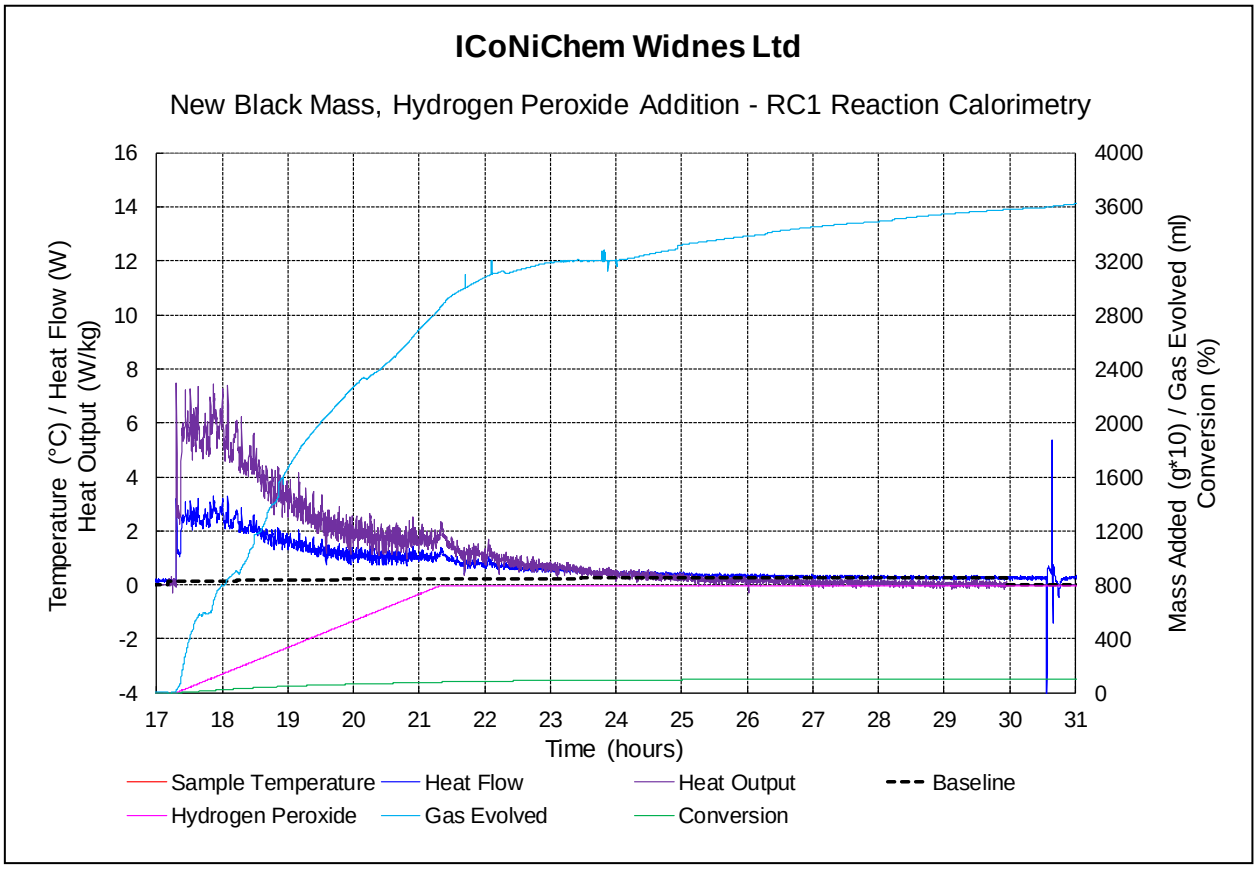
Graph 4.4.a


ICoNiChem Widnes Ltd
New Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - RC1 Reaction Calorimetry
Temperature (°C) / Heat Flow (W)
Mass Added (g*10) / Gas Evolved (ml)
Time (hours)
Sample Temperature
Heat Flow
Calibration
Nitric Acid
Hydrogen Peroxide
Gas Evolved

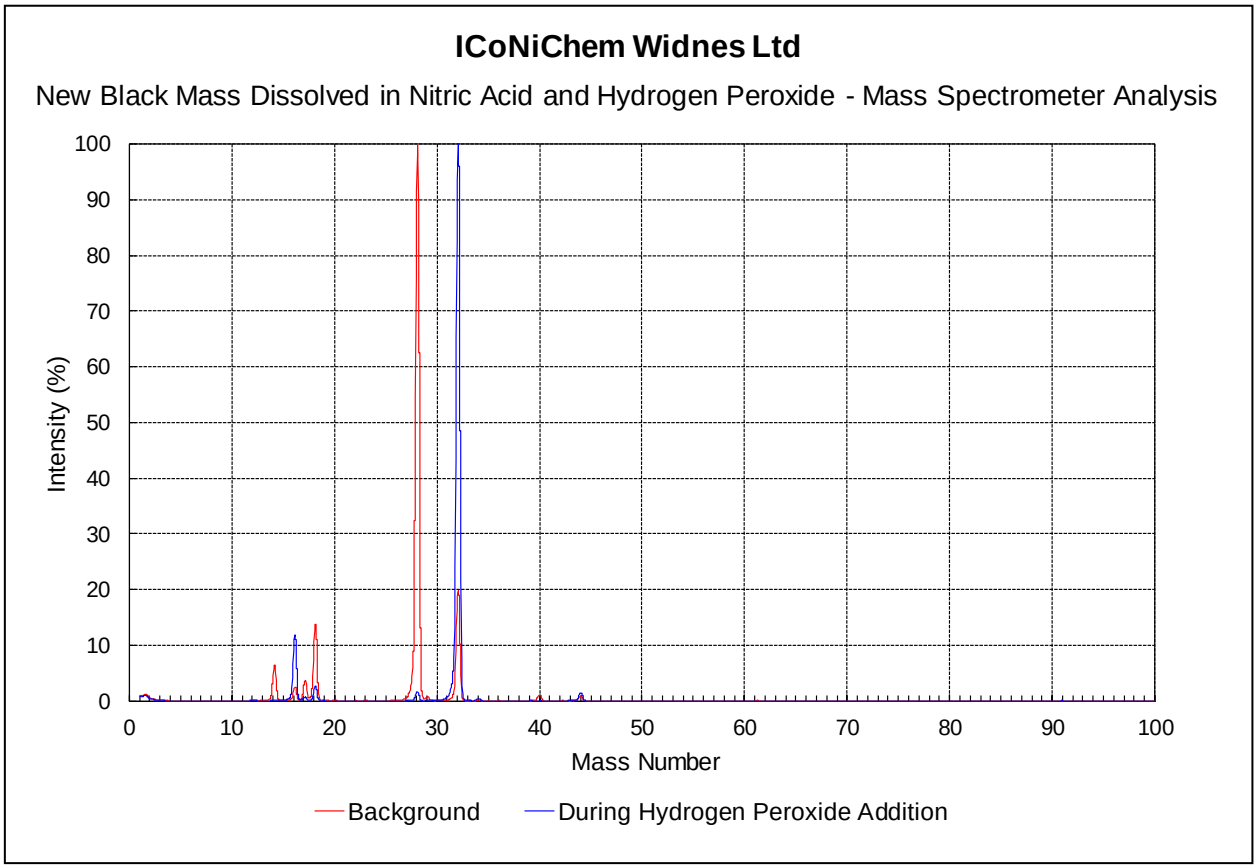
Graph 4.4.b


ICoNiChem Widnes Ltd
New Black Mass, Nitric Acid Addition - RC1 Reaction Calorimetry
Temperature (°C) / Heat Flow (W)
Heat Output (W/kg)
Mass Added (g) / Gas Evolved (ml)
Conversion (%)
Time (hours)
Sample Temperature
Heat Flow
Heat Output
Baseline
Nitric Acid
Gas Evolved
Conversion

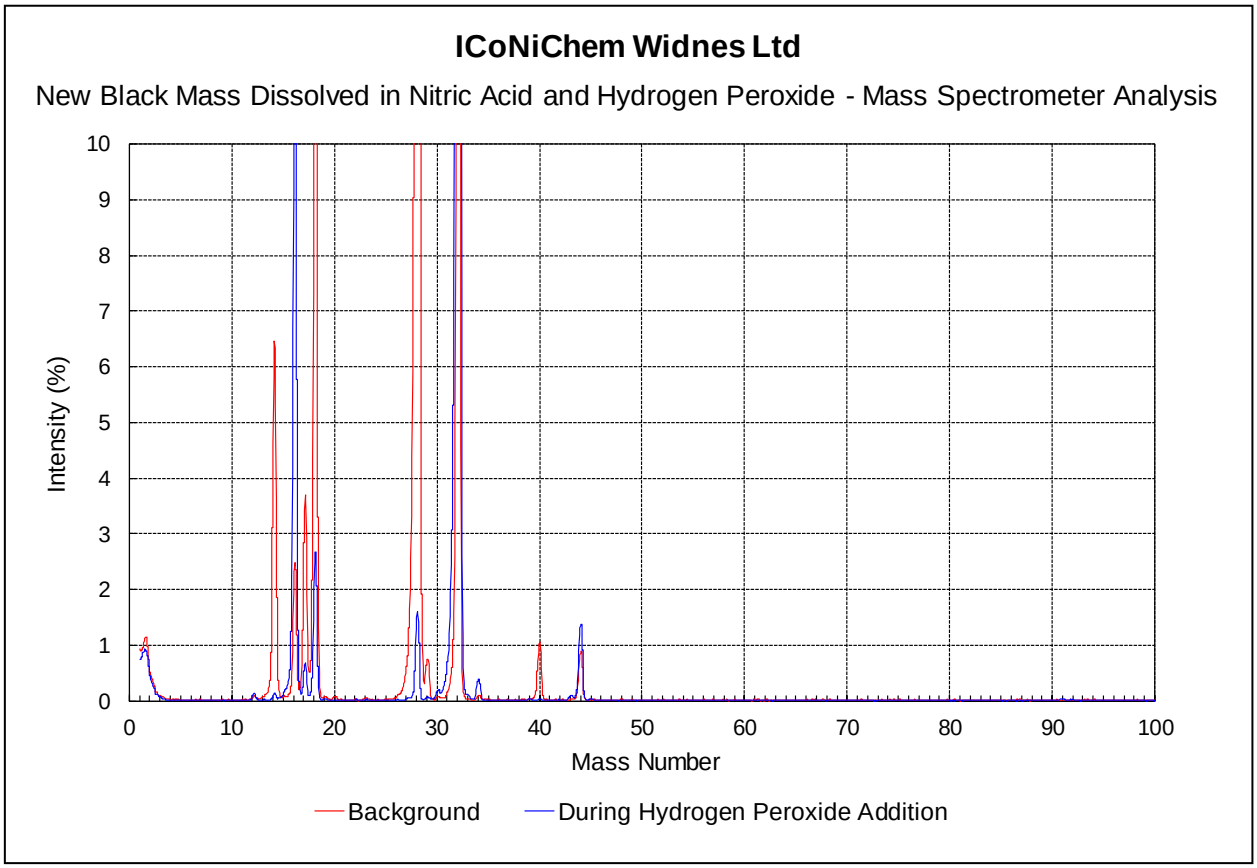
Graph 4.4.c


ICoNiChem Widnes Ltd
New Black Mass, Hydrogen Peroxide Addition - RC1 Reaction Calorimetry
Temperature (°C) / Heat Flow (W)
Heat Output (W/kg)
Mass Added (g*10) / Gas Evolved (ml)
Conversion (%)
Time (hours)
Sample Temperature
Heat Flow
Heat Output
Baseline
Hydrogen Peroxide
Gas Evolved
Conversion

Graph 4.4.d


ICoNiChem Widnes Ltd
New Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - Mass Spectrometer Analysis
Intensity (%)
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
Mass Number
Background
During Hydrogen Peroxide Addition

Graph 4.4.e


ICoNiChem Widnes Ltd
New Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - Mass Spectrometer Analysis
Intensity (%)
0
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
80
90
100
Mass Number
Background
During Hydrogen Peroxide Addition

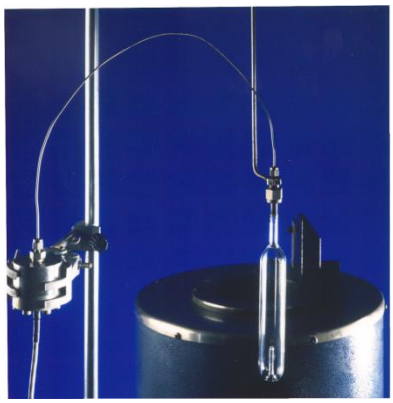
5. CARIUS TUBE SCREENING TEST

Test Objective and Information

The Carius tube test is a differential thermal analysis (DTA) technique to provide preliminary data on thermal stability. It is neither adiabatic nor low phi factor and hence data cannot be scaled up directly to large scale without the application of safety factors. The test is conducted to identify endothermic and exothermic activity in a reagent, reaction intermediate, reaction mass or final product and to provide some guidance as to the onset temperature and magnitude of any such activity. Gas generation and vapour pressure effects are also measured.

The test sample is charged to a high pressure, glass Carius tube which is equipped with a thermocouple pocket and an adapter at the outlet to connect to a pressure transducer or gas flow measurement device. The tube is installed in an oven capable of withstanding rupture of the tube and ignition of the contents. The temperature of the oven is ramped from ambient to 400°C (or until the pressure reaches 55 barg) at a pre-set rate of normally 0.5 $K.min^{-1}$ or set to an isothermal set point. The oven temperature (reference temperature), the temperature at the centre of the sample and the pressure in the tube are recorded throughout the test.

The apparatus is shown below and generic equipment and test information is contained in Table 5.1.



Typical Carius Apparatus

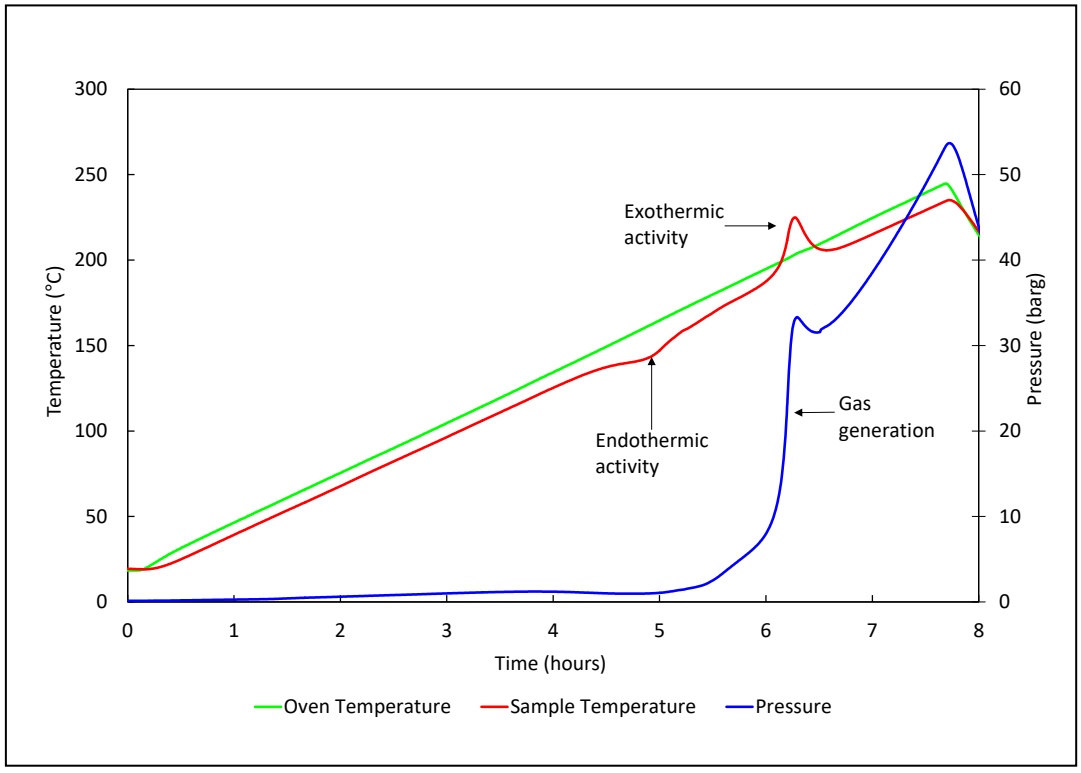
Table 5.1: Equipment Configuration / Settings for Carius Tube Screening Test

Parameter	Setting / Configuration
Oven type	Cylindrical 1 kW, 2 l volume
Carius type	Pyrex, 35 cm^3
Test atmosphere	Air or nitrogen
Sample volume	10 cm^3 (typically 10 – 15 g)
Temperature range	Ambient – 400°C
Sensitivity	5 – 10 $K.hr^{-1}$ (3 – 10 $W.kg^{-1}$)
Thermocouple type	K
Heating rate	Normally 0.5 $K.min^{-1}$ (up to 20 $K.min^{-1}$)
Pressure range	0 – 100 barg
Data acquisition system	DASYLab®

Interpretation of Results

A typical temperature / pressure / time graph showing exothermic activity and gas generation is shown below. The onset temperature is indicated by examining any deviation in the sample temperature from the heating rate, the peak height or area under the curve indicating the magnitude of the exothermic activity. An indication of gas generation is given by the Antoine plot, a plot of the pressure (logarithmic scale) against the reciprocal of the absolute temperature. Vapour pressure effects approximate to a straight line on such a plot, any upward deviation (i.e. a discontinuity in the curve) generally indicating evolution of permanent gas.

It is imperative that safety factors are used when relating screening test data to large scale plant. Typically a safety factor of up to 100°C is used on onset temperature, although this will be very dependent on the scale at which the material is to be handled and stored. A minimum safety factor of 50°C is recommended for small scale storage or handling. If the material is to be stored or handled at a temperature near its thermal threshold (including a safety factor), it is recommended that further tests are conducted under low heat loss conditions (e.g. ARC or VSP) to more accurately quantify a safe maximum exposure temperature. The slow heating rate used in the Carius tube test produces a much more accurate definition of onset temperature than that which would be obtained at higher heating rates. For this reason, the safety factor used on Carius tube data is 50°C in most cases. When data gained at higher heating rates (2 $K.min^{-1}$ or higher) is interpreted, safety factors of up to 100°C are commonly used.



Typical Carius Tube Screening Test Graph

5.1 Test Results for Non-Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide

Date	20/03/2020
Operator	K. Arif
SOP Reference	SOP 301
Test System	Carius System 2
Test Filename	C4028005638A1/A2
Sample Preparation	Lab prepared
Ramp Rate	0.5 $K.min^{-1}$
Trip Conditions	400°C / 55 barg
Test Atmosphere	Air

Test Objective

To screen a sample of the final reaction mixture from the non-pyrolysed black mass, nitric acid and hydrogen peroxide reaction in order to determine the onset temperature and magnitude of any endothermic, exothermic or gas generating events when ramped to elevated temperatures.

Test Material

Chemical	Mass (g)	Source	DEKRA Reference
Reaction mixture	12.32	Lab prepared	From RC4028005638B (test 4.2)

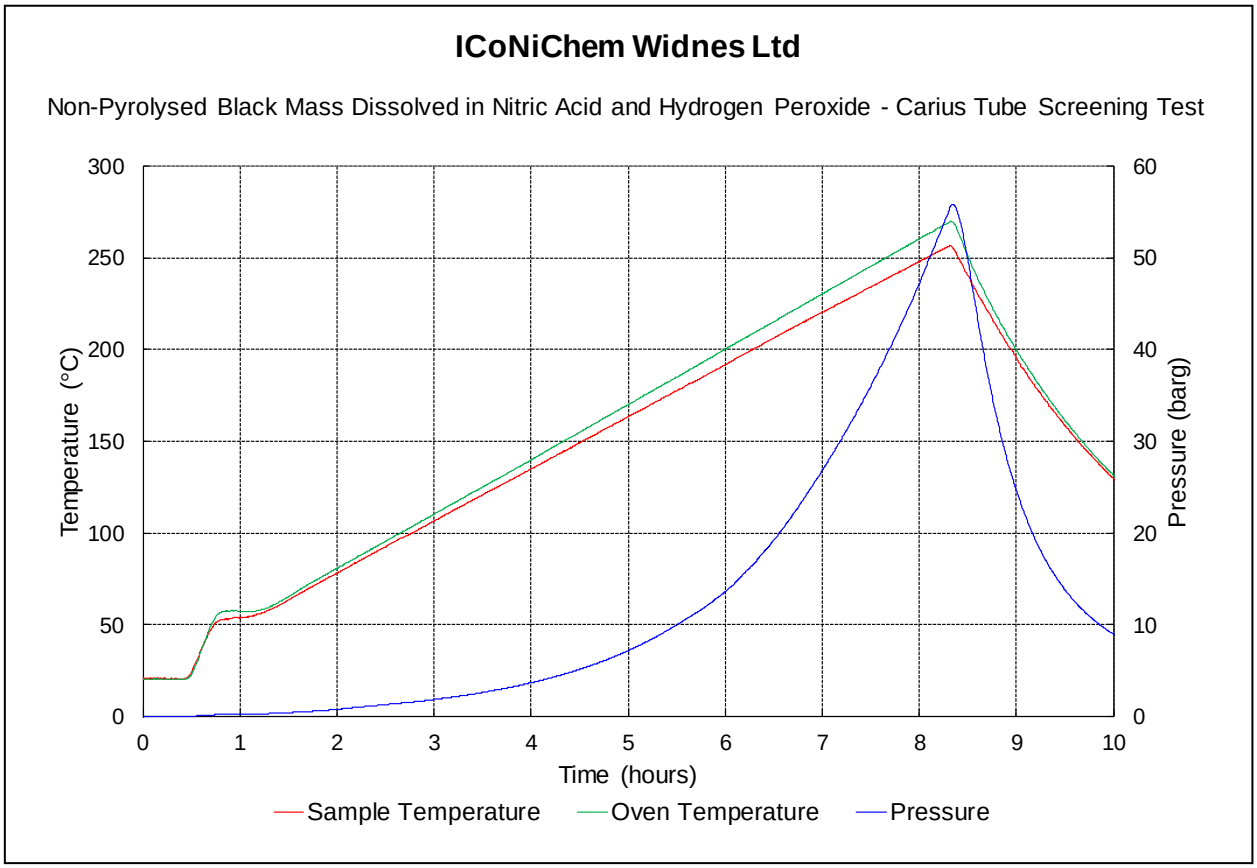
Test Results

Temperature / pressure / time data for the experiment is illustrated in Graph 5.1.a and a plot of differential temperature versus temperature is provided in Graph 5.1.b to clearly illustrate the onset of any endothermic or exothermic activity. The Antoine plot of the pressure (logarithmic scale) against the reciprocal of the absolute temperature is illustrated in Graph 5.1.c.

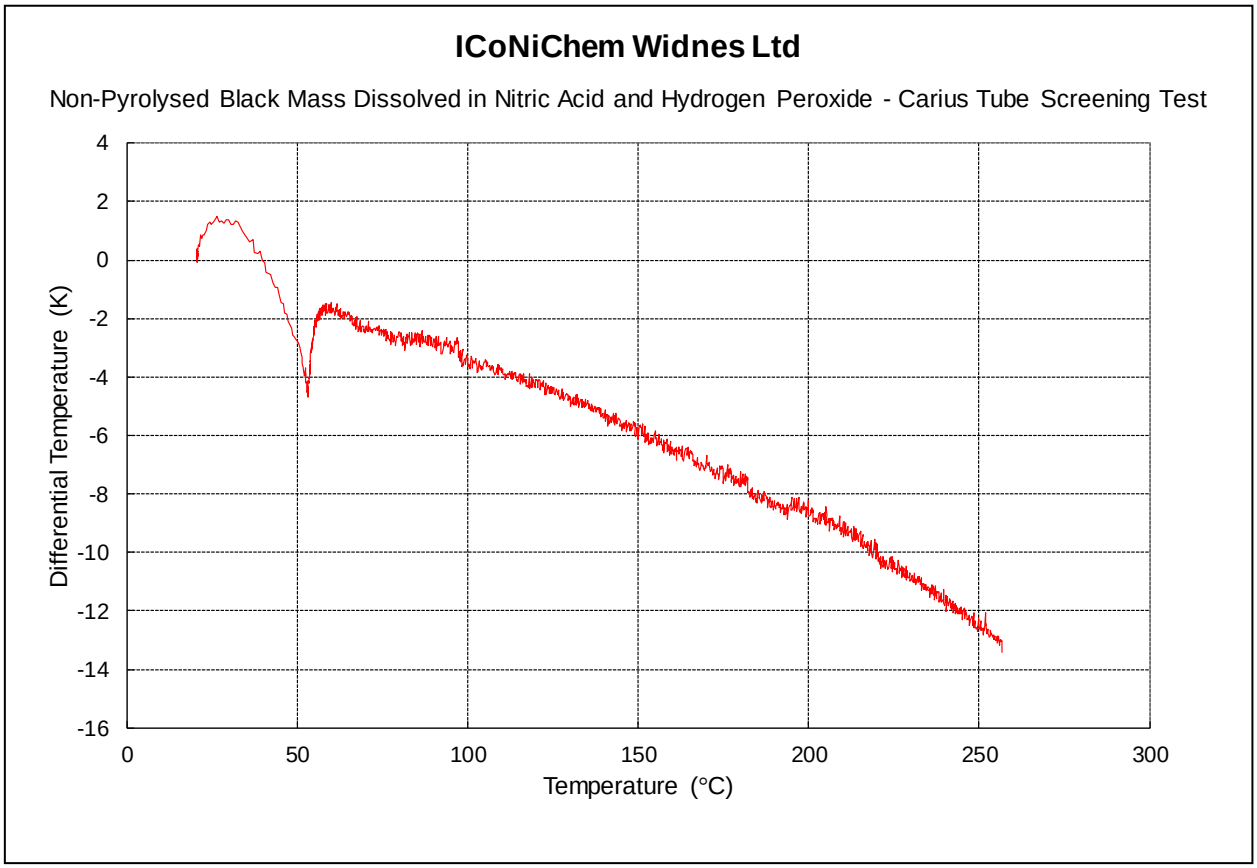
The mixture was not observed to undergo any significant energetic events up to 257°C (at which point the test was terminated due to the pressure limit being attained).

The Antoine plot (Graph 5.1.c) indicates that permanent gases were generated by the mixture from 139.1°C. The residual pressure in the tube at the end of the test (2.4 barg at 20.5°C) confirmed this observation and equated to the formation of 4.5 $cm^3.g^{-1}$ (of mixture) at STP.

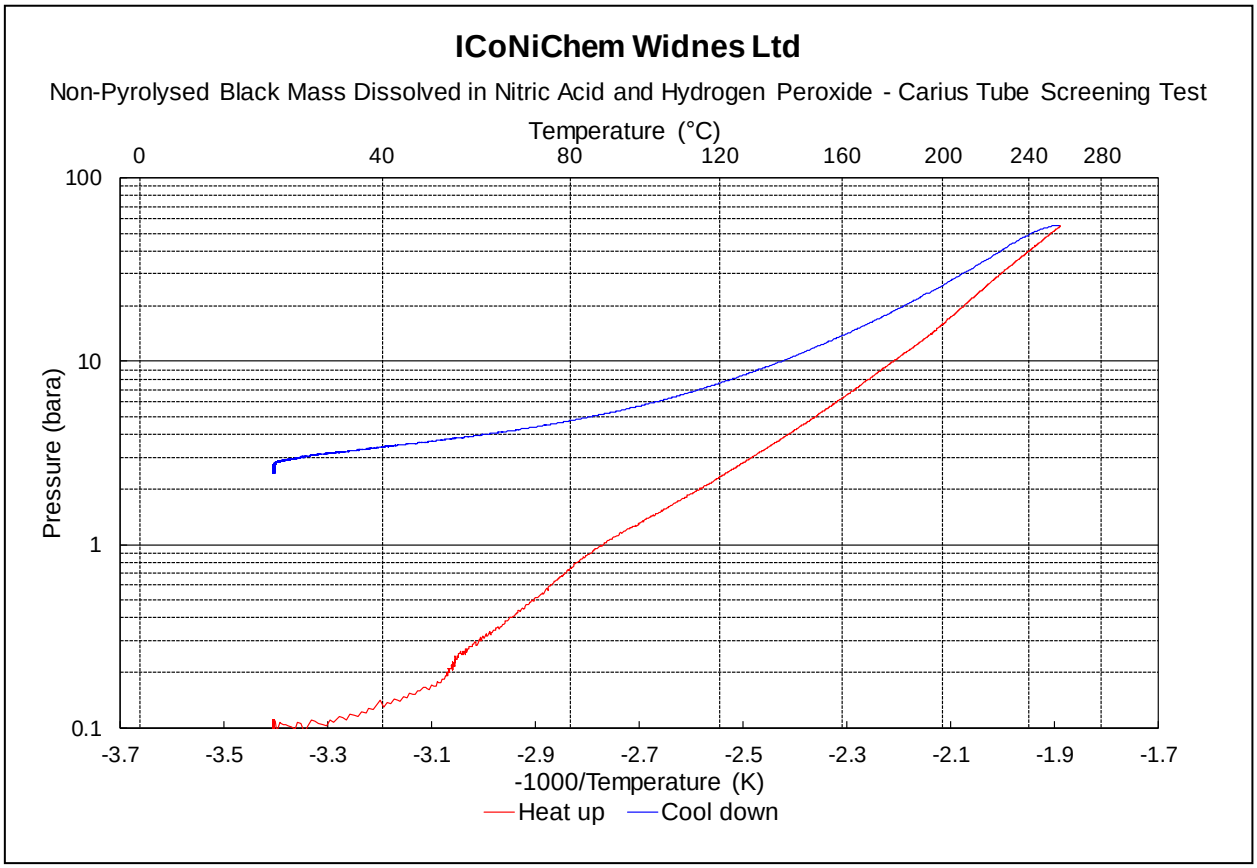
Graph 5.1.a


ICoNiChem Widnes Ltd
Non-Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - Carius Tube Screening Test
Temperature (°C)
Pressure (barg)
Time (hours)
Sample Temperature
Oven Temperature
Pressure

Graph 5.1.b


ICoNiChem Widnes Ltd
Non-Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - Carius Tube Screening Test
Differential Temperature (K)
4
2
0
-2
-4
-6
-8
-10
-12
-14
-16
0
50
100
150
200
250
300
Temperature (°C)

Graph 5.1.c


ICoNiChem Widnes Ltd
Non-Pyrolysed Black Mass Dissolved in Nitric Acid and Hydrogen Peroxide - Carius Tube Screening Test
Temperature (°C)
0
40
80
120
160
200
240
280
100
10
1
0.1
Pressure (bara)
-3.7
-3.5
-3.3
-3.1
-2.9
-2.7
-2.5
-2.3
-2.1
-1.9
-1.7
-1000/Temperature (K)
Heat up
Cool down

6. SUMMARY OF TEST DATA OBTAINED

1. Isothermal reaction calorimeter tests were conducted on the black mass process. The test results are summarised in Table 6.1 and Table 6.2.

Table 6.1: Summary of RC1 Test Results, Non-pyrolysed Black Mass

	Non-pyrolysed Black Mass		Non-pyrolysed Black Mass	
Addition	Sulphuric Acid	Hydrogen Peroxide	Nitric Acid	Hydrogen Peroxide
Reaction temperature (°C)	22	22	22	22
Heat of reaction (kJ.mol^{-1} of acid)	-77.7	-63.3	-12.7	-22.6
Heat of reaction (kJ.kg^{-1} of non-pyrolysed black mass)	-1276.9	-1040.4	-523.5	-929.4
Adiabatic temperature rise (K)	123.6	62.8	27.6	38.3
MTSR (°C)	145.6	84.8	49.6	60.3
Accumulation (%)	0	1.6	0	5.0
Boiling point (°C)*	100	100	100	100
Total quantity of gas generated (ml)	1090	> 8032	883	> 7119

KEY: MTSR = Maximum temperature of the synthesis reaction (i.e. process start temperature plus the adiabatic temperature rise)
*not experimentally determined, based on the boiling point of water

Table 6.2: Summary of RC1 Test Results, Pyrolysed Black Mass and New Black Mass

	Pyrolysed Black Mass		New Black Mass	
Addition	Nitric Acid	Hydrogen Peroxide	Nitric Acid	Hydrogen Peroxide
Reaction temperature (°C)	22	22	22	22
Heat of reaction (kJ.mol^{-1} of acid)	-15.4	-30.7	-13.5	-13.4
Heat of reaction (kJ.kg^{-1} of black mass)	-634.0	-1260.6	-554.5	-549.5
Adiabatic temperature rise (K)	33.2	52.0	19.6	17.7
MTSR (°C)	55.2	74.0	41.6	39.7
Accumulation (%)	13.2	30.0	0	21.3
Boiling point (°C)*	100	100	100	100
Total quantity of gas generated (ml)	0	> 9941	0	> 3723

KEY: MTSR = Maximum temperature of the synthesis reaction (i.e. process start temperature plus the adiabatic temperature rise)
*not experimentally determined, based on the boiling point of water

2. A Carius tube screening test was also conducted on the non-pyrolysed black mass dissolved in nitric acid and hydrogen peroxide. The mixture was not observed to undergo any significant energetic events up to 257°C. Permanent gas generation was observed from 139°C and the residual pressure in the tube equated to the formation of 4.5 cm^3.g^{-1} (of mixture) at STP. The maximum recommended safe handling temperature is therefore 139°C (based on the gas generation onset temperature).

7. APPENDIX

A) Background Information

The identification of the minimum temperature for a runaway reaction depends not only on the kinetics of the reaction but also the rate of heat loss that will occur in the full scale reactor. Natural heat loss from any such processing vessel, be it batch or semi-batch depends on the size of the vessel, the type of agitation and the condition of the vessel jacket (i.e. full, empty, insulated etc.). Normally, in the assessment of chemical reaction hazards, it is assumed that forced plant cooling has failed.

Wright[3] has quantified the heat loss characteristics of a number of process vessels of varying size and insulation thickness. Values range typically from 0.146 $W.l^{-1}.K^{-1}$ for a 0.1 m^3 reactor with 5 cm insulation to 0.027 $W.l^{-1}.K^{-1}$ for a 5.0 m^3 vessel and 0.013 $W.l^{-1}.K^{-1}$ for a 12 m^3 vessel (with 5 cm insulation in each case). The ratio of the combined heat capacity of the sample and container to the heat capacity of the sample alone is called the 'phi factor'. A phi factor of 1.00 denotes a system with zero heat transfer to the vessel walls or surroundings.

When laboratory scale testing is undertaken the natural heat loss characteristics of the test equipment should be taken into consideration before providing data on self heat rate and gas generation rates if that data is to be directly relevant to full scale manufacture.

Experimental techniques to achieve test sensitivities appropriate to these plant heat loss values require accurate, stable temperature control with a high degree of sensor accuracy. Laboratory scale testing at DEKRA Process Safety is normally undertaken on three levels to achieve this degree of sensitivity.

1. Isothermal reaction calorimetry is undertaken to assess the power output and accumulation characteristics of semi-batch processes.
2. Screening tests are conducted that are capable of rapidly monitoring and characterising starting materials, reaction intermediates and reaction mixtures, final products and waste streams. Tests detect any exothermic or endothermic activity, together with any gas generation and vapour pressure effects occurring over the temperature range encountered during processing.
3. Adiabatic (no heat loss) calorimetry is then undertaken to accurately quantify the magnitude of such effects under the low heat loss conditions normally associated with production scale manufacture.

Reaction calorimetry is undertaken using the Mettler RC1 reaction calorimeter. This is a highly sensitive, automated laboratory reactor equipped with calorimetric measuring facilities. Semi-batch processes are generally conducted in either an atmospheric pressure reactor or in a 10 bar pressure vessel. Facilities for pH control, dual additions, reflux operation and measurement exist. The sensitivity of the equipment is exceptional, about 0.2 $W.kg^{-1}$. The equipment provides excellent data on the kinetics of a chemical process (including fully defined accumulation information) under isothermal or isoperibolic conditions (i.e. simulating the conditions employed in large scale chemical processing).

[3] T.K. Wright et al., I.Chem.E. Symp. Series No 102, p 61, 1987

The initial screening is done using the 10 g Carius tube. The apparatus has the ability to clearly identify exothermic activity and provides some guidance as to the magnitude of the exotherm. In addition the equipment is also able to detect the production of non-condensable gas and any vapour pressure effects associated with such phenomena.

It should be emphasised that the screening tests only provide an initial characterisation of the chemical or reaction system. Heat loss from the sample to the surroundings or the sample container itself will introduce significant errors which normally renders the data unacceptable for interpretation on the manufacturing scale. In order to study thermal runaway reactions under conditions normally associated with a low heat loss manufacturing environment, an adiabatic calorimeter is usually employed. The data determined from such laboratory equipment can often be directly interpreted on the plant scale due to its unique low heat loss characteristics (low phi factor).

There are three key areas from which heat losses can occur:

- heating of the vessel itself will remove some energy generated by a reaction
- heat losses to the surroundings will occur
- heat may be removed by the evaporation of volatile components

The Adiabatic Dewar (ADC II) and Vent Sizing Package 2 (VSP2) calorimeters employed by DEKRA Process Safety are able to operate under the highly adiabatic conditions required for such process simulation and consequently are able to examine directly thermal runaways and reaction conditions encountered in large vessels. In addition to the ADC II and VSP2 calorimeters, Accelerating Rate Calorimetry (ARC) can also be conducted on samples presenting a greater exothermic reaction potential. The higher test phi factor is offset by the significantly increased pressure capability of the test equipment (140 bar).

In cases where a plant vessel is very large and well-insulated such that it loses less heat to its surroundings than even the most adiabatic test (i.e. the plant phi factor is lower than that of the test), then the test results are not directly applicable to plant scale. Correction of test data to a lower phi factor, often 1.00 (completely adiabatic), is therefore required. This ‘phi correction’ is performed by DEKRA Process Safety using software tools[4] implementing published methods[5]. It is only possible where the exotherm of interest has completed, and the reaction displays nth order or pseudo-nth order kinetics. More inclusive routines are available.

[4] Cheminform Ltd, 2019. ARKS AC – Processing data of Adiabatic Calorimetry [AC] [software]. Version 1.1.0. Available from: www.cisp.spb.ru

[5] A.A.Kossoy et al. J. Loss Prevention in the Process Industries. 2015, 33, 88-100. doi: 10.1016/j.jlp.2014.11.014