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The Use of Gel Cast Ceramic Foams as Diesel Particulate Filters

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Abstract

Interest in diesel particulate reduction technologies has been revived over the past few years as a result of the increased popularity in Europe of diesel passenger cars, due to their superior fuel efficiency and advances made in performance, along with new legislation requiring the reduction of exhaust emission products. A number of technologies have been commercialised in this growing market sector including the use of filtration media to clean the exhaust gases. In fact during the course of this work the first diesel particulate filtration (DPF) system to be fitted on a passenger car was introduced by the car manufacturer Peugeot.

One of the many previously studied technologies for the reduction of diesel particulate emissions was through the use of reticulated ceramic foam filters. A more recent alternative approach to the production of porous ceramics is via gel casting. This is now a well studied and commercialised manufacturing process. In addition to being able to successfully filter out diesel particulates from the exhaust, a DPF system also needs to be able to regenerate itself in order to maintain a suitably low back pressure on the engine. The aim of this study was to investigate the suitability of gel cast ceramic foams for use as diesel particulate filtration media and also look at the development of a catalytic regeneration system.

Overall this study has shown that gel casting is a unique process that allows the optimisation of foam permeability and filtration efficiency through careful macro-structural control of the foams’ porosity, cell and window size. This control allows foams to be developed for specific applications and this work has shown that foams with suitably low backpressures and filtration efficiencies >90% can be achieved, making them suitable candidates for use as DPFs.

An active low temperature, <400°C, diesel soot oxidation catalyst, Li/Na/K, has been developed that is tolerant to SO₂ poisoning and is able to operate in the reduced oxygen atmosphere found in a diesel exhaust without any adverse change in catalytic performance. This catalytic system has been successfully applied to the surface of alumina gel cast foams and these Li/Na/K catalysed alumina foams have been shown to effectively promote the catalytic combustion of a model diesel soot with regeneration beginning at temperatures well below 400°C.
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Acronyms

AA – Ammonium acrylate
APS – Ammonium persulphate
CPSI – Cells per square inch
CPSCM – Cells per square centimetre
CMC – Critical micelle concentration
d - Average particle size
d_{cell} – Average window diameter
d_{pore} – Average pore diameter
d_{win} – Average window diameter
DPF – Diesel particulate filter
DSC – Differential scanning calorimetry
EDX – Energy dispersive X-ray analysis
EGR – Exhaust gas re-circulation
%E_E – Percentage filtration efficiency
FBC – Fuel borne catalyst
KE – Kinetic energy
k_1 – Darcian permeability constant
k_2 – non-Darcian permeability constant
L - Length
Li/Na/K – 31.5% Li_2CO_3 – 25% Na_2CO_3 – 43.5% K_2CO_3
P – Pressure
P_i – Inlet pressure
P_o – Outlet pressure
PSD – Particle size distribution
ppi – Pores per inch
ppcm – Pores per centimetre
R_{max} – Maximum rate of combustion
SCR – Selective catalytic reduction
SEM – Scanning electron microscopy
TEM – Transmission electron microscopy
TEMED – N,N,N',N’-tetramethylethylenediamine
T_i – Polymerisation induction time
T_i\text{g} - Ignition temperature
T_{\text{final}} - Complete combustion temperature
T_{\text{max}} - Temperature at the maximum rate of combustion
V_s - Fluid velocity
WFF - Wall flow filter
XRD - X-ray diffraction
\varepsilon - Porosity
\mu - Viscosity
\rho - Density
\Delta P - Backpressure

Equations

\[ \frac{\Delta P}{L} = (P_1 - P_0)/L = (\mu V_s)/k_1 \quad - \text{Equation 1} \]

\[ \frac{\Delta P}{L} = (\mu V_s)/k_1 + (\rho V_s^2)/k_2 \quad - \text{Equation 2} \]

\[ (P_1^2 - P_0^2)/2PL = (\mu V_s)/k_1 + (\rho V_s^2)/k_2 \quad - \text{Equation 3} \]

\[ \frac{(-\Delta P)}{L} = 150 \frac{(1 - \varepsilon)^2 \mu V}{\varepsilon^3 d^2} + 1.75 \frac{(1 - \varepsilon) \rho V^2}{\varepsilon^3 d} \quad - \text{Equation 4} \]

\[ \frac{(-\Delta P)}{L} = 150 \frac{(1 - \varepsilon) \mu V}{\varepsilon^2 d^2} + 6 \frac{(1 - \varepsilon) \rho V^2}{\varepsilon^3 d} \quad - \text{Equation 5} \]
Chapter 1

Introduction

Cars and light trucks with diesel engines are becoming more popular on our roads thanks primarily to increased fuel economy compared to petrol engines and improved engineering allowing a reduction in the engine size and improvements in performance. The diesel engine is also the main power source for the worlds' heavy transport industry in which it is unrivalled. Although it has many benefits, it also has a number of drawbacks, primarily its problematic emissions of nitrogen oxides (NOx) and diesel particulate matter (DPM). As a result worldwide legislation has been introduced in order to force a reduction in diesel exhaust pollutants; achieving these targets is the focus of the current work.

Many techniques have been investigated by car manufacturers that include modifications to the engine and fuel, in trying to meet the stringent future exhaust emission regulations. One well tested and researched route for emissions reduction is through the use of some after-exhaust treatment device, of which a wide variety of technologies exist. One of the main methods employed is to use a diesel particulate filter (DPF) or trap to filter out the DPM from the exhaust stream. A number of different filtration systems have been examined including the use of ceramic foam filters.

In conjunction with any DPF system is the need for filter regeneration due to the build up of trapped soot clogging the filter. Two possible regeneration strategies exist (1) passive - auto-regeneration during regular vehicle operation and (2) active - actively triggering regeneration by raising the temperature of the trap. A number of technologies have been developed around both of these strategies, however due to cost and reliability issues passive systems are the preferred method. One such method currently being investigated is the use of a catalytic coating on a DPF that is active within the temperature window of the diesel exhaust gases, such that a “trapless trap” system can be achieved, i.e. the DPM is destroyed at the
same rate that it is filtered. To date no such system has been successfully developed. Catalyst choice for such a role is very wide and includes transition metal and alkali metal compounds and complex mixed catalyst systems. The use of a catalytic coating is well suited for use in conjunction with a ceramic foam-type filter, due to its deep bed mechanism of filtration facilitating catalyst soot contact. The development of any new filtration system also has to able to have a high filtration efficiency > 80% and maintain a low backpressure in the system to avoid increased fuel consumption.

Chapter 2 of this thesis begins with a brief insight into the diesel engines’ history and operation before discussing in more detail the types and associated problems of the emissions it produces. This is followed by a summary of current European diesel emission regulations and the test methods employed to measure these controlled emissions. A review of DPFs is next concentrating primarily on the use of ceramic foams as filters. Filter regeneration strategies are discussed; firstly the use of active/non-catalytic systems is briefly introduced before passive/catalytic based systems are discussed in more detail, in particular the use of catalytic coatings. Porous ceramic production methods are reviewed, with an emphasis on the gel-casting route. The theory behind the permeability of porous bodies is described and a review of works on the permeability of porous ceramics is presented. Finally a number of the issues regarding materials suitability for use as DPFs is discussed.

Chapter 3 provides a brief description of what is trying to be achieved within the scope of this thesis and how the thesis has been split into three work themes that are continued through in each subsequent chapter.

Chapter 4 presents details of the experimental procedures used in developing a gel cast ceramic foam DPF. Firstly methods of foam production and foam characterisation techniques employed are explained including the procedures for measuring foam permeability and filtration performance. Secondly catalyst material production methods and characterisation techniques are described. This section includes the experimental procedures followed for the selection of just one final catalyst material for use in the third and final stage. The latter stage outlines the methods used in preparing, characterising and evaluating catalytically coated ceramic foams.
Chapter 5 presents the results of experiments performed as outlined in chapter 4. The first of the three sections includes a study on the effect different foaming agents have on the final structure of the foam, relationships between the structural parameters of the foam and tailoring the permeability and filtration performance for use as a DPF. The second section presents the results of the catalyst characterisation and catalyst screening process used in the selection of just one material for use in the third and final stage. In this final section results of different techniques of catalytically coating the foams are given along with the characterisation of the coating and evaluation of the performance of catalytically coated gel cast foams for model diesel soot oxidation.

The results obtained in chapter 5 are discussed next in chapter 6. In the first section the methods to control the foams macroscopic structural parameters are discussed in terms of the physics of foam production and chemistry of the various additives used. The relationship between the foams structural properties, foam permeability and filtration performance is discussed along with the optimisation of these parameters to develop a gel cast foam suitable for use as a DPF. Secondly, the catalyst screening selection process is discussed that begins with the initial comparative TGA study and then moves on to discuss the more end use specific tests such as sulphur dioxide poisoning trials and reduced oxygen concentration atmosphere performance. The development and evaluation of catalysed foams, using the final candidate material chosen from the second section, is then discussed.

In chapter 7 conclusions are drawn from the results and discussions, presented in chapters 5 and 6 respectively, along with suggested ideas on future work to further progress the development of a catalysed gel cast foam DPF. A bibliography of the works referenced in this thesis is presented in the final chapter.
Chapter 2

Literature Review

2.1 The diesel engine

Since the conception of the diesel engine in 1893 by the engineer and inventor Rudolph Diesel [1], from whom its name is taken, it has evolved to become the main power source for the world's heavy transport industry. More recently, through the use of lighter materials and improved engine performance, the diesel engine has been used in passenger cars and offers a number of benefits, primarily improved fuel economy, over its main rival the petrol or Otto engine.

The fundamental difference between the diesel and petrol engine is in the way the reactants of the combustion process, air and fuel, are introduced into the cylinder. In a petrol engine, the air and fuel are mixed prior to being introduced into the cylinder, the mixture is then compressed and ignited by a spark plug. Whereas in a diesel engine only air is compressed in the cylinder. The diesel fuel is injected into the cylinder just before the piston reaches its highest point and since diesel fuel has good self-ignition properties, the fuel droplets ignite spontaneously [2]. The amount of fuel injected into the engine is governed by the load placed on the engine, with the fuel injected over a period of time to avoid excessive pressure in the cylinders.

The above differences in operation lead to differences in both the air-to-fuel ratio ($\lambda$ - the ratio of air available to air required for complete combustion) and the compression ratio (the ratio of the maximum (piston in lowest position) to the minimum (piston in highest position) combustion chamber volume). Table 1 illustrates some typical values of the compression and
air-to-fuel ratios and the effective efficiency for both petrol and diesel engines [2]. It is the combination of diesel engines having larger compression and air-to-fuel ratios and having lower pumping energy losses than the petrol engine that lead to it being more energy efficient, i.e. having better fuel economy than the petrol engine [2].

<table>
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<tr>
<th>Engine Type</th>
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<tr>
<td>Compression ratio</td>
<td>16 – 24</td>
<td>7 - 10</td>
</tr>
<tr>
<td>λ (air-to-fuel ratio)</td>
<td>1.1 – 6</td>
<td>0.9 - 1.1</td>
</tr>
<tr>
<td>Effective efficiency</td>
<td>0.3 – 0.45</td>
<td>0.25 - 0.3</td>
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Table 1. Typical values for compression ratio and efficiency of diesel and petrol engines [2]

2.1.1 Diesel emission products

Diesel engines convert the chemical energy stored in diesel fuel into mechanical power. Theoretically diesel fuel, which is a mixture of hydrocarbons, only produces carbon dioxide (CO₂) and water vapour (H₂O) during fuel combustion, together with the unused portion of air. Typical concentrations of these gases in diesel exhaust are shown below, they vary with engine load and speed [3]:

- CO₂ 2 – 12 %
- H₂O 2-12%
- O₂ 3-17%
- N₂ – balance

However, diesel emissions also include pollutants that either have adverse health effects or have a negative effect on the environment. These pollutants are by-products of the combustion process that originate through a number of non-ideal processes such as; incomplete combustion of the fuel, reactions between the mixture components under high temperature and pressure, combustion of lubricating oil and oil additives, as well as combustion of non-hydrocarbon components of diesel fuel, e.g. sulphur [3].
2.1.2 Regulated harmful emissions

Diesel emissions that are regulated both in Europe, the US and a number of other countries are:

- Carbon monoxide (CO)
- Hydrocarbons (HC), including either the total hydrocarbons (THC) or only the non-methane hydrocarbons (NMHC).
- Nitrogen oxides (NOx)
- Particulate matter (PM), diesel particulate matter (DPM) or total particulate matter (TPM)

Carbon monoxide is an odourless, colourless and toxic gas that is generated through the incomplete combustion of the fuel. CO concentration in diesel exhaust varies between 5-1500 ppm [4].

The HCs found in diesel emissions originate from the diesel fuel and the lubricating oil. They consist of a large number of compounds such as benzene, toluene and naphthalene [5]. A number of hydrocarbons can also be found adsorbed onto the DPM although HC emission regulations refer only to the volatile gas phase HCs. HC concentration in diesel exhaust ranges from approximately 20-300 ppm [5].

NOx emissions including both nitric oxide (NO) and nitrogen dioxide (NO₂), are one of the two major pollutants from diesel exhaust. They are generated from nitrogen and oxygen combining under the high pressure and temperatures in the engines’ cylinders [6]. NOx emissions consist primarily of NO (approximately 95%) and contain only a small percentage of NO₂ [5]. Total NOx concentration in diesel exhaust is typically in the range 50-1000 ppm [5].

Diesel particulate matter (DPM), along with NOx, is the main pollutant from diesel engines and is clearly evident in the plumes of black smoke emitted. DPM is very complex and its’ physical and chemical properties are still not fully known. DPM consists of elemental carbon nuclei, 7.0 nm to 0.04 μm in diameter, which are generated in the cylinder during combustion,
on the surface of this carbon HCs are adsorbed [7]. These carbon nuclei particles aggregate together and form larger agglomerates of carbon particles, sometimes these are referred to as accumulation mode particles. Nucleation of hydrated sulphuric acid in the diesel exhaust leads to the production of sulphate particles that are separate from the carbon particles [8]. Sulphuric acid in the diesel exhaust is derived from the sulphur present in the fuel. This sulphur is converted during combustion to primarily sulphur dioxide (SO$_2$) but a small percentage of sulphur trioxide (SO$_3$) is formed. The following reaction then occurs leading to the formation of sulphuric acid:

$$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$$

These sulphate particles along with the carbon nuclei and adsorbed HCs form DPM. The latter is commonly divided into three fractions, as illustrated in the schematic in figure 1 [7]:

1. Solid fraction (SOL) – elemental carbon nucleus
2. Soluble organic fraction (SOF) – adsorbed HCs
3. Sulphate particulates (SO$_4$) – hydrated sulphuric acid

![Figure 1. Schematic of diesel particulate matter [7]](image)

DPM is, therefore, a complex mixture of organic and inorganic compounds in solid and liquid phases. DPM is defined as being all the compounds that are collected on a pre-conditioned filter in a dilution tunnel at a temperature of 52°C [2]. Therefore the total PM (TPM) emitted is a combination of the SOL + SOF + SO$_4$. The actual composition of DPM depends upon the particular engine, its load and speed, such that “wet” particulates, a great percentage of SOF,
and "dry" particulates, mostly carbon, can be obtained under certain conditions. Typical DPM concentration in exhaust gas is between 20-200 mg m\(^{-3}\).

2.1.3 Unregulated harmful emissions

As previously mentioned, the sulphur present in the diesel fuel leads to the formation of primarily SO\(_2\) in the exhaust gas along with some SO\(_3\). SO\(_2\) can be readily oxidised to SO\(_3\), which in turn leads to the formation of sulphate particles and an overall increase in the TPM emitted. The concentration of SO\(_2\) in the exhaust is directly proportional to the fuel sulphur content as illustrated in figure 2; a 500 ppm S diesel fuel produces exhaust SO\(_2\) levels of around 20 ppm. The effect of lube oil consumption on the emitted SO\(_2\) concentration is also shown since this becomes more important as the level of sulphur in the fuel decreases [5].

![Figure 2. Exhaust SO\(_2\) as a function of fuel sulphur content [5]](image)

Although not included in the regulated NO\(_x\) emissions, nitrous oxide (N\(_2\)O) is emitted from diesel engines in very low concentrations of around 3 ppm. Recent concerns have been raised over its contribution to the greenhouse effect as well as its attack on stratospheric ozone.

Polynuclear aromatic hydrocarbons (PAHs) are aromatic HCs with two or more benzene rings. This type of compound has been found to be present in the gas phase and in the SOF of DPM. Many of these PAHs have been shown to be carcinogens that lead to adverse health effects. The most harmful compounds of four and five rings are found almost exclusively in
the organic fraction (SOF) of DPM with a fraction of the lighter compounds being present in the gaseous phase of diesel exhaust [7].

### 2.1.4 Environmental problems associated with diesel emissions

Of the four regulated emissions of diesel exhaust, NOx emissions are deemed to have the most detrimental effect on the environment and diesel emissions contribute substantially to total NOx emissions. Emissions of NOx are known to contribute to the 'greenhouse effect', which results in the warming of the earth's surface, more commonly referred to as global warming [9]. NOx emissions are the second most important (after CO₂) of the traffic derived contributors to the greenhouse effect [10]. NOx is also a major contributor, along with oxides of sulphur (SOx), to the phenomena of acid rain, which has caused widespread damage to forests and waterways throughout Europe and North America [11]. Although SOx are a major contributor to the acid rain phenomena, SOx emissions from road transport is only a minor constituent [10]. NOx emissions are also linked, along with HC emissions from automotive exhausts, to the formation of photochemical oxidants e.g. ozone and peroxyacetyl nitrate (PAN) that form the basis of 'summertime smog' [9].

CO is rather less of an environmental pollutant in itself, however CO can be oxidised in the atmosphere to CO₂, which is a greenhouse gas. Thus CO acts indirectly as a greenhouse gas in the atmosphere [10]. The main environmental effect of diesel particulates is in their reduction in visibility, i.e. black smoke, and in soiling materials [12]. In California it is estimated that if 20% of the vehicles were diesel powered this would cause a 20-25% reduction in visibility [12].

### 2.1.5 Gaseous emissions

Of the regulated emissions in diesel exhaust CO is in itself the most toxic, as it readily combines with haemoglobin in the blood, more readily than oxygen, and thus reduces the capacity of blood to transport oxygen. This CO poisoning is reversible, simply by exposure to unpolluted air [10].
In NOx emissions only the NO2 portion is considered in itself to pose a toxicity threat. Exposure to high concentrations of NO2 can lead to respiratory infections and reduced lung function [13].

A number of adverse health effects, in particular respiratory problems, have been attributed to high levels of ozone and other photochemical oxidants in the atmosphere, which are seen visually as smog [13]. Photochemical or summertime smog formation is brought about through the action of sunlight on an atmosphere containing reactive HCs and NOx, both of which are present in diesel exhaust. Of the very reactive chemicals formed in photochemical smog, ozone (O3) is the most biologically active. A number of studies have shown O3 exposure causes a range of serious respiratory problems including an increase in mortality [14].

Although the levels of SOx emission from diesel engines is relatively low, it should be noted that diesel emissions add to the problem of sulphurous wintertime smogs, such as those seen in London in 1952 and 1962. These smogs are composed of SO2 and suspended particulate matter that are emitted primarily from industrial sources and domestic burning of coal and oil and, due to calm weather conditions, are unable to be dispersed [9]. These smogs are well documented as causing a large increase in respiratory problems, especially in the elderly and asthmatics [9, 15].

2.1.6 Diesel particulate matter

The term used to quantify airborne particulate pollution is ‘suspended particulate matter’ (SPM) [9, 16]. Due to the small size of diesel particulates, approximately 90% of diesel particulates are within the size range 7.5 nm to 1.0 μm [17], it makes up a portion of the SPM that is designated as PM10 (particles with diameters <10 μm). PM10 is an important fraction since, due to its small size, it is able to penetrate deeply into the respiratory tract and become deposited in the airways and alveoli of the lungs [18]. There have also been a number of concerns raised over even finer particulates, such as PM2.5 (particles with diameters <2.5 μm), of which the transport sector is a major contributor, as they can penetrate even deeper into the lungs [16].
A number of epidemiological studies have now been performed to evaluate the effect of PM$_{10}$ and DPM on human health. Research by Pope et al [19] has shown that there is a correlation between mortality and morbidity and the concentration of PM$_{10}$ in the atmosphere. A review of epidemiological studies has also demonstrated that ‘there is a clear relationship between levels of PM$_{10}$ and exacerbations of asthma and chronic obstructive pulmonary disease (COPD)’ [20]. With respect to actual DPM there is a large body of evidence to suggest that workers, such as truck drivers, railway workers and bus garage workers, exposed for prolonged periods to diesel exhaust may be at an increased risk of lung cancer [21]. A review by Mauderly [22] suggests that there is a 20-50% increase in risk of lung cancer from long term employment in such jobs. A more recent report of a long term study conducted by Pope et al [23] has proven that there is a definite link between lung cancer and the fine particulate pollution emitted from coal fired power stations, factories and diesel vehicles. Aside from lung cancer, there is also weak evidence to suggest a link between exposure to diesel exhaust and bladder cancer [23].

The actual mechanism by which diesel particulates inhaled into the lungs lead to the formation of cancer is not yet fully understood. A particular group of compounds causing great concern are the polyaromatic hydrocarbons (PAHs) that are released in diesel exhaust emissions. There are a number of different PAHs associated with diesel exhaust including benzo(a)pyrene and benzo(e)pyrene [24]. A number of these compounds, particularly those that contain more than 4 rings, are known carcinogens and mutagens [11]. These PAHs are emitted in the vapour phase but more damaging to human health are the adsorbed PAHs that make up a portion of the SOF of DPM and can therefore penetrate deep into the respiratory tract. There is no actual evidence that pinpoints the development of lung cancer in humans to the PAHs themselves, studies performed involving rats showed that the PAHs do not play a role in tumour development [22]. However, it is the general consensus that the PAHs found in diesel emissions may cause cancer in humans [65]. More recently a number of concerns have also been raised over the solid carbon core of DPM, suggesting that it is probably essential for tumour formation [22, 27].

DPM is therefore a very problematic emission that appears to aggrieve or cause a large number of cancerous and non-cancerous respiratory diseases, although there is still a large amount of research needed to fully quantify its effect on human health. It is these issues over
public health that have prompted many governments worldwide to adopt tough legislation governing emissions of diesel particulates.

2.1.7 Diesel emissions regulations in Europe

It was not until 1982 that the first legislation governing the gaseous emissions from heavy-duty (> 3.5 tonnes) diesel vehicles was introduced [28] and a further 10 years until limits on particulate emissions were specified [29].

The European regulations for heavy-duty diesel engines are more commonly referred to as the Euro I to Euro V regulations [30]. Table 2 below sets out these regulations, they show the emission limits set for the regulated components of diesel exhaust when performed on varying test cycles [31].

<table>
<thead>
<tr>
<th>Standard</th>
<th>Test cycle</th>
<th>CO / g kW⁻¹h⁻¹</th>
<th>HC / g kW⁻¹h⁻¹</th>
<th>NOx / g kW⁻¹h⁻¹</th>
<th>PM / g kW⁻¹h⁻¹</th>
<th>Smoke / m⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Euro I (1992) &gt; 85kW</td>
<td>ECE R49</td>
<td>4.5</td>
<td>1.1</td>
<td>8.0</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td>Euro II (1998)</td>
<td>ECE R49</td>
<td>4.0</td>
<td>1.1</td>
<td>7.0</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>Euro III (2000)</td>
<td>ESC/ELR</td>
<td>2.1</td>
<td>0.66</td>
<td>5.0</td>
<td>0.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Euro IV (2005)</td>
<td>ETC</td>
<td>5.45</td>
<td>-</td>
<td>5.0</td>
<td>0.16</td>
<td>-</td>
</tr>
<tr>
<td>Euro V (2008)</td>
<td>ESC/ELR</td>
<td>1.5</td>
<td>0.46</td>
<td>3.5</td>
<td>0.02</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>ETC</td>
<td>4.0</td>
<td>-</td>
<td>3.5</td>
<td>0.03</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard</th>
<th>Test cycle</th>
<th>CO / g kW⁻¹h⁻¹</th>
<th>HC / g kW⁻¹h⁻¹</th>
<th>NOx / g kW⁻¹h⁻¹</th>
<th>PM / g kW⁻¹h⁻¹</th>
<th>Smoke / m⁻¹</th>
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<td>Euro V (2008)</td>
<td>ESC/ELR</td>
<td>1.5</td>
<td>0.46</td>
<td>2.0</td>
<td>0.02</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>ETC</td>
<td>4.0</td>
<td>-</td>
<td>2.0</td>
<td>0.03</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. Euro emission standards for heavy duty-diesel vehicles [31]

Due to increasing environmental concerns there have been severe reductions in these emission limits since their introduction. This has led to the rapid development of new technologies to meet these demands, as will be discussed later.
Emissions are measured over an engine or vehicle test cycle that is supposed to simulate actual driving conditions. Up until Euro III, emissions testing was performed on a 13-mode steady-state cycle. Test cycle R49, as it is called, is performed on an engine dynamometer that measures emissions at 13 speed and load conditions with the final result being a weighted average of them all [32].

The Euro III regulation saw the replacement of R49 with two new test cycles: a stationary cycle ESC (European stationary cycle) and a transient cycle ETC (European transient cycle). Smoke opacity is measured on the ELR (European load response) test [33]. The ESC test cycle involves testing the engine on an engine dynamometer over a sequence of steady state modes, see appendix 1 [34], while the ETC test cycle is based on research performed at the FIGE Institute, Aachen Germany, on real road cycle measurements. The cycle is split into three parts:

- City driving conditions, maximum speed of 50 km/h, with frequent starts, stops and idling.
- Rural driving, starts with a sharp acceleration and an average speed of 72 km/h.
- Motorway driving, an average speed of 88 km/h.

The duration of the entire cycle is 1800 s with the duration of each segment being 600 s [35].

With Euro III regulations manufacturers requiring type approval of their engine have the choice between either the ESC/ELR or the ETC test. The more stringent Euro IV & V regulations, however, need emissions to be determined on both ETC and ESC/ELR tests [31].
Chapter 2. Literature Review

2.2 Diesel emissions reduction techniques

As previously outlined a reduction in both NOx and particulates from diesel engines is needed from an environmental and public health point of view. Legislation is now in place in order to reduce these pollutants from diesel exhaust. This legislation has forced a number of new technologies to be developed to ensure engines can comply with the legislation. There are three main areas being targeted in an attempt to reduce diesel emissions:

1. Engine design and modifications
2. Use of modified or alternative fuels
3. After-treatment technology

For simplicity and in line with the scope of this work only diesel exhaust after-treatment technology will be discussed further.

Exhaust after-treatment eliminates the pollutants after they have been formed, i.e. post combustion. In more recent years there has been a huge focus on the development of this type of technology in order to meet future emission legislation. The vast majority of after-treatment technologies focus on reducing either NOx or particulates and in some cases both simultaneously. CO and HC emissions from diesel engines are usually low enough. For both of these reduction technologies catalysis plays a major role in most systems.

The topic of diesel exhaust after-treatment for both NOx and particulates is very extensive and although both PM and NOx reduction after-treatment technologies are equally as important, the emphasis here is purely on PM after-treatment technology.

2.2.1 DPM exhaust after-treatment technology

A number of different ideas have been developed to remove particulates from diesel engine exhaust. By far the most common method is the use of some kind of filtration system, of which many types have been examined. These types of filter are commonly referred to as diesel particulate filters (DPFs) or traps. The following is a brief overview of the types of filter materials tested with a more in-depth look at the use of ceramic foams as DPFs. A
number of other after-exhaust technologies that exist for PM reduction will also be described. Finally, since almost all DPFs require the accumulated DPM to be removed in what is commonly termed filter regeneration the different methods of filter regeneration will be discussed.

2.2.2 Diesel particulate filter operating requirements

DPFs have to satisfy a number of specific requirements, the three most important are:

- The filter has to withstand the moderate but long term temperatures of the exhaust gases (up to approximately 500 to 650°C in heavy duty applications) and also the high but short term temperatures reached during the highly exothermic soot oxidation reaction that can be up to 1100°C or more [36].
- A high as possible particle filtration efficiency is required.
- In spite of the high exhaust gas flow rates the pressure drop across the filter must be kept to a minimum since increased backpressures increase the engines pumping losses that cause a reduction in the fuel efficiency. The maximum allowable backpressure is primarily dependent upon the engine size and different manufacturers’ requirements. Typical maximum allowable backpressures for a clean filter at full power are in the range 7-10 kPa and up to 20 kPa for a soot laden filter [37].

2.2.3 Diesel particulate filtration mechanisms

The mechanism of particulate separation from an air stream or liquid flow depends upon the type of filter medium used. There are two types of filtration mechanism encountered in the use of DPFs, (1) deep bed filter and (2) surface filter, illustrated in figures 3 and 5 respectively.
Exhaust gases with particulate

Open pore ceramic foams

Collected particulate
(deep filtration)

Figure 3. Deep bed mechanism of filtration as seen in foam filters [136]

In this kind of filter the collected particulate size is considerably smaller than the mean pore size of the filter media, so that the particles are deposited throughout the body. This particulate deposition onto the filter surface is dependent upon three different mechanisms, as illustrated in the schematic in figure 4:

Figure 4. Particle collection mechanisms [136]
1. **Interception** “may occur when a fluid streamline passes within one particle radius of the collecting body. Then, a particle travelling along the streamline will touch the body and may be collected without the influence of Brownian diffusion or inertia.” [38].

2. **Inertial impaction** becomes more important with increasing particle size. “On approaching the collecting body, particles carried along by the gas stream tend to follow the stream but may strike the obstruction because of their inertia.” [38].

3. **Diffusion** deposition “depends on the Brownian movement exhibited by smaller particulates, particularly those <0.3 μm in diameter. Those particulates do not move uniformly along the gas streamlines. Rather, they diffuse from the gas to the surface of the collecting body and are collected.” [38].

![Diagram of filtration process](image)

**Figure 5.** Surface mechanism of filtration as seen in WFFs

The pore diameter of surface filters is less than that of the particulates it is collecting, such that the particles are deposited on the surface of the filter. The layer or “cake” of collected particulates acts as a filter in itself.
2.2.4 Diesel particulate filters (DPFs)

The main types of filter encountered in the literature are:

**Wall flow filters (WFFs)** are by far the most widely studied and applied filters to diesel engines. WFFs were initially developed from ceramic monoliths designed for use as catalyst supports in the automobile industry by Corning Glass Works [39]. These ceramic monoliths are produced through an extrusion process [39]. The filtering concept involves blocking alternate cell channel openings on the monolith face and similarly blocking the exit channels of the open cells at the face [40]. The filtration process occurs as the particle laden exhaust stream passes through the open channels and is forced through the filter walls due to the plugged end design, as shown in figure 6 [40], dimensions of a typical WFF for DPF application are given in table 3 [41].

![Diagram of gas flow through a WFF](image)

**Figure 6.** Gas flow through a WFF [41]

<table>
<thead>
<tr>
<th>Filter size (d x l) / mm</th>
<th>Volume / litres</th>
<th>Surface area / m²</th>
<th>Max. soot load / g</th>
<th>Cell density / cpsi (cpscm)</th>
<th>Wall thickness / mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>266.7 x 17</td>
<td>11.26</td>
<td>100</td>
<td>100 (15.3)</td>
<td>0.43</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.** Typical dimensions of a WFF used as a heavy duty DPF [41]

The filtration mechanism in ceramic monoliths is initially through a deep bed mechanism as particulates are collected in the pores within the walls through inertial and diffusional deposition. As the load on the filter increases, a filter cake of DPM builds up on the surface of the inlet channels and filtration is now dominated by a surface type mechanism [38].
This cake type filtration mechanism results in the filtration efficiency of WFFs initially being relatively low, depending on the filter properties anywhere in the range 55-80%, however as the filter cake builds up this efficiency is greatly increased to levels >90% [41]. WFFs typically experience large increases in backpressure during the early stages of soot loading, as illustrated in figure 7 [42]. This is a result of partial penetration of the soot into the pores of the filter wall causing a decrease in wall permeability followed by the formation of the filter cake [42].

![Graph](image)

**Figure 7.** Effect of increased soot loading on backpressure (150 mm long , 200 cpsi (31 cpscm) WFF with 0.56 mm wall thickness and d_{pore} of 3.9 μm) [42]

Traditionally, the material of preference for WFF production is cordierite (2MgO 2Al₂O₃ 5SiO₂) since it has a number of useful properties, such as good thermal shock resistance and a low thermal conductivity [40, 41]. The latter property allows thermal regeneration to be more easily sustained. However due to the low melting point of cordierite, 1450°C, problems can occur during uncontrolled thermal regeneration that result in filter failure through melting or cracking and problematic ash sintering to the cordierite filter walls at temperatures as low as 1050°C, which make it very difficult to completely clean filters that have exceeded this temperature [41, 42, 43]. This has led to the development of silicon carbide (SiC) WFFs [41, 43, 44].
SiC has a much higher melting point than cordierite at 2400°C [41]. This allows SiC filters to offer a much higher operating temperature limit than cordierite and due to it having a more favourable pore network, it has lower backpressures [41]. Engine tests have shown SiC WFFs also have superior trapping efficiencies at lower back pressures than cordierite filters, allowing smaller filter sizes to be used [36]. The problem of ash sintering is still present in SiC filters at temperatures very similar to that of cordierite [43]. However, due to SiCs higher thermal conductivity and heat capacity even at high levels of soot loading the maximum temperatures experienced by the filter during uncontrolled regeneration never reaches dangerous levels as illustrated in figure 8 [41].

![Temperature limited maximum soot loading](image)

**Figure 8.** Temperature limited maximum soot loading [41]

However even SiC is not ideal due to poor thermal shock resistance and also greater cost resulting from more expensive starting materials and higher processing temperatures. Efforts are being made to improve the thermal shock resistance of SiC WFFs through the development of Si-SiC composite materials [45].

**Ceramic fibres.** Ceramic fibre wound filters for use as DPFs were initially investigated by Daimler-Benz [46]. This type of filter consists of a perforated stainless steel tube round which a ceramic fibre is wound. One end of this cartridge is closed in order force the exhaust gas through the filter media, as illustrated in figure 9 [47].
Figure 9. Fibre wound cartridge [47]

As opposed to WFFs, fibrous based systems operate via a deep bed filtration mechanism. This type of filtration technology has recently been investigated by 3M using their Nextel, Al₂O₃·SiO₂·B₂O₃, fibre technology [47, 48]. In comparison to WFFs fibrous based systems are generally more resistant to damage by thermal or mechanical stresses [48]. However, they have a number of drawbacks such as poor compatibility with catalyst materials, the fibres are easily damaged by ash deposits which bond them together and can result in voids in the bed and gas leakage. In general fibre type filters tend to be much larger in size and have a lower filtration efficiency whilst the cost of such systems in comparison to WFFs is an issue [48]. Another ceramic fibre based technology that has been investigated for DPF manufacture is knitted fibre filters [49] though to date this technology has not been commercialised.

Wire mesh filters constructed out of stainless steel wires have also been investigated [50], although very little is now reported on their use. Their initial attraction was their compatibility with a number of regeneration strategies including alumina-based wash-coating and electrical regeneration [38]. Porous metal filters have also been investigated as a replacement for ceramics due to them having better thermal conductivities and thermal shock resistance. Problems of corrosion and poor trapping performance are usually associated with this kind of filter, although some work to improve these filters has been done [51, 52].
2.2.5 Ceramic foam DPFs

The use of ceramic foams as DPFs has been investigated by a number of people since the mid 80's. Initial studies determined a number of simple relationships between the properties of the foam and its dimensions to its trapping efficiency and resulting back pressure [53, 54]. It was found that trapping efficiency is most dependent on filter length and foam fineness, the cross sectional area also has an effect, but is less prominent. However the back pressure also increases with increasing foam fineness and filter length whilst increasing cross sectional area causes a large decrease in back pressure [53]. The latter is also increased by an increase in the gas velocity through the filter [54]. As can be seen in figure 10, the trapping efficiency increases with filter length up to a point at which no great increase in trapping efficiency is made by increasing the filter length and filtration efficiency begins to level off. This suggests an optimum length exists beyond which filtration efficiency is not improved, just an undesirable gain in back pressure [51].

![Figure 10. Comparison of trapping efficiency and length for a 60 ppi (23.6 ppcm) foam [51]](image)

The mechanism of DPM deposition in foam filters is best described by a deep bed filtration mechanism [54] in which inertial deposition plays an important part [38]. Due to the primary soot particles being much smaller than the pore size in these filters filtration will occur throughout the foam volume. However as time increases DPM concentrates itself on the inlet face of the filter, which results in an exponential decrease of retained soot along the filter length, as illustrated by figure 11 [54].
A benefit of such a filtration mechanism is that there is a gradual increase in back pressure over a long period of time during filter operation. This is much better than with WFFs that are characterised by very sharp increases in back pressure after much shorter periods of time than the foam filter, as seen in figure 12 [54].

Another benefit reported with the use of foams instead of WFFs is that the DPM ignition temperature is much lower, even on uncatalysed foams [56], as shown in figure 13 [54]. This is believed to be due to differences in the two structures, since the open pore isotropic structure allows for easier propagation of the flame ignition front through the foam [54].
However the main shortcoming of foam filters is in their poor trapping efficiency of the DPM when compared to WFFs. Typical foam filter trapping efficiencies vary between 50-70% whereas the more popular WFF has trapping efficiencies of >85%, this difference is clearly shown in figure 14 [54]. These low figures for the foam necessitate the need for much larger filter volumes compared to WFFs.

A number of studies have investigated the effect of altering the geometry to try to improve this trapping efficiency and lower back pressures. A number of designs have been proposed including stacks [57], V-shaped filters [58], a top hat style and rings [54]. The most interesting designs developed were those termed ‘Z-flow’ filters [59]. These filters
incorporated a series of channels in their structure in various configurations as illustrated in figure 15 [59].

![Various Z-flow filter types](image1)

**Figure 15.** Various Z-flow filter types [59]

These designs allowed for a more homogeneous distribution of DPM throughout the filter volume, especially in the case when tapered channels (denoted by a T, after Z, M or D) were used, and higher trapping efficiencies [59]. The back pressure could also be manipulated by using different channel configurations and by altering the size of the entrance channel at the face (denoted by a letter S), as illustrated in figure 16 and 17 [59].

![Entrance faces of T-type and S-type filters](image2)

**Figure 16.** Entrance faces of T-type and S-type filters [59]
More recently the use of ceramic foams as supports for DPM oxidation catalysts have been investigated [60, 61, 62, 63], these catalyst systems will be discussed in more depth in section 2.3.2.2. These studies once again use reticulated foams, i.e. produced via the replication of a polymeric sponge; a process discussed in more detail in section 2.4, with porosity of 80% and pores in the size range 50 - 65 ppi (19.7 - 25.6 ppcm). Laboratory based pilot plant results measuring the backpressure and filtration efficiency of such systems are given in figures 18 and 19 respectively [62].

**Figure 17.** Backpressure reduction using DTS versus DT, and MTS versus MT filters [59]

**Figure 18.** Backpressure results for a series of 50 mm diameter 17 mm deep zirconia toughened alumina (ZTA) and mullite reticulated foams with 80% porosity and 50 ppi (19.7 ppcm) [62]
**Chapter 2. Literature Review**

**Figure 19.** Gravimetric particulate filtration efficiency for a series of 50 mm diameter 34 mm deep zirconia toughened alumina (ZTA) and mullite reticulated foams with 80% porosity and 50 ppi (19.7 ppcm) [62]

The plot of backpressure in figure 18 shows these foams to have acceptable backpressures over the range of air velocities typically experienced in practice by DPFs. The filtration efficiencies shown in figure 19 appear much higher, >80%, than those previously quoted in the literature for such foams. A possible reason for these differences might be the experimental methods used, since the results in figure 14 were obtained using an actual diesel engine test rig whilst those in figure 19 used a model diesel soot, carbon black. As is to be expected the capture of soot particles within the foam structure results in an increase in the backpressure, as illustrated in figure 20 [62].

**Figure 20.** Effect of trapping, 2 different, carbon particle sizes in the foam on its' backpressure at various air velocities [62]
2.2.6 Non-filter based particulate collection systems

One non-filter based PM collection system makes use of the electric charge on the surface of diesel particulates, through the use of an electrostatic agglomerator, to collect the PM [64]. The collected particles undergo surface agglomeration and grow from ~0.1 μm to over 10 μm at which size they are capable of being collected by mechanical means, i.e. in an inertial impactor or cyclone [65]. Another more recent technique being investigated is the use of a cooling system to encourage particulate growth so that cyclonic separation can be used to collect the particulates [66].

2.2.7 Flow through oxidation catalysts

Flow through oxidation catalyst technology was developed during the early 90’s to meet looming PM emission regulation deadlines in Europe and the US as a quick fix alternative to DPFs, whose technology wasn’t suitably developed for production. This type of system consists of a ceramic monolith, without any plugs as in the DPF, onto whose surface a washcoat containing an oxidation catalyst has been applied [67]. The exhaust gases pass through the monolith and the oxidation catalyst is used to oxidise primarily the SOF portion of the DPM and also any CO and other HCs present [67]. In order to meet PM emission levels and prevent the solid carbon of DPM clogging the filter, the SOF present can be maximised by engine modifications [68]. In general at low engine loading there is a high percentage of SOF present and the reverse is true for high engine loading. This type of technology is very effective at reducing the SOF portion of DPM (up to 80% reduction of the SOF) whilst it has little or no effect on the solid carbon portion [69].

Initially Pt or Pd catalysts with an Al₂O₃ washcoat were applied, since both the metals have high activities for oxidising HCs [67]. However they are also very active in oxidising the SO₂ portion of the diesel exhaust to SO₃, Pt more so than Pd [67]. This leads to the formation of sulphate particles and adds to the TPM output of the engine especially at higher temperatures (>400°C) [69]. A number of studies have investigated this problem and have improved the low temperature selectivity for HC oxidation by addition of V₂O₅ to the catalyst [70]. Sulphate formation can also be suppressed through the use of low sulphur fuels and by placing the system further away from the engine where it is cooler [69]. There is a trade off between
sulphate formation and the light off temperature, which is defined as being the temperature at which 50% conversion is achieved, of the HCs that is dictated by the placement of such systems [69]. Improvements on the Al₂O₃ carrier material have also been made, since catalyst deactivation can occur through the formation of Al₂(SO₄)₂ by using TiO₂, ZrO₂ or SiO₂ carriers that are less prone to sulphation [67].

Problems of more long-term catalyst deactivation are caused by the accumulation of zinc, phosphorous and calcium on or within the catalyst that originate from lubrication oil additives [71]. A more positive benefit of using such catalyst technology is that it also reduces emissions of some non-regulated compounds, such as aldehydes and PAHs.

The reduction of PM emissions through the use of oxidation catalysts has led to their widespread use throughout the world. Heavy-duty diesel engine tests on the US federal test procedure (FTP) have shown that this technology can reduce particulate emissions down to 0.064 g/kW-hr with 368 ppm sulphur fuel, 0.056 g/kW-hr with 54 ppm sulphur fuel and 0.051 g/kW-hr with zero sulphur fuel [72]. However, this kind of technology for PM reduction is limited since it only removes the SOF portion of the soot and has no effect on the solid carbon core and the problem of sulphate formation at higher temperatures increasing the TPM output is still a concern [73]. The limited ability of this technology has prompted a switch back to improving existing DPF technology in order to satisfy the more stringent future PM emission levels.
2.3 Filter regeneration

The use of an effective DPF results in an accumulation of DPM in the filter that leads to an increase in the back pressure on the system and eventually filter clogging. Therefore it is necessary to remove the trapped particulates from the filter in order to maintain a satisfactory air flow and prevent engine damage or increased fuel consumption. This process is often referred to as ‘regeneration’. There are a number of different regeneration strategies available for this purpose. The majority of systems rely on a method of oxidising the collected DPM. This can be achieved through either active or passive means. Active regeneration usually involves the application of some external energy source to initiate combustion, whereas passive systems utilise a catalyst to lower the combustion temperature of the soot so that combustion can occur through the heat of the exhaust gases. Active systems are unfavourable since they are complex, expensive and do not guarantee durability or reliability.

2.3.1 Active/non-catalytic DPF regeneration

An early method suggested for DPF regeneration was through the use a burner to periodically raise the temperature of the exhaust gases in order to oxidise the accumulated DPM [74, 75]. Such burner type systems primarily use diesel as their fuel in combination with either air or the exhaust gas [76, 77]. Burner systems have a number of problems: (1) they cause an increase in fuel consumption [78], (2) unreliability in the burner ignition system can lead to trap overload and subsequent regeneration of such a large accumulation gives rise to a very exothermic reaction that can damage the trap [56] and (3) systems tend to be complex and expensive [79].

Under normal load conditions the exhaust gas temperatures achieved are insufficient to promote combustion of collected DPM on a filter. The exhaust gas temperatures can be raised by some 200°C simply through intake air throttling in order to allow filter regeneration [80]. A reduction in the airflow to the engine causes a reduction in the air-to-fuel ratio that results in higher combustion temperatures and subsequently increased exhaust gas temperatures [74]. Throttling results in a negative effect on both emissions (HC, CO and PM emissions are increased) and fuel consumption (due to the fuel rich combustion, higher heat losses and negative pumping work) [74]. Intake air throttling has proved to be successful at regenerating
DPFs only at high engine speeds and loads, a speed >55 mph was reported as being required for throttling to be successfully applied [74].

As for burner systems, electric heaters placed upstream or in front of the DPF can be used to ignite the DPM trapped in the filter [81]. A particular disadvantage with this type of system is its' large power consumption required for filter regeneration. Systems that draw the power from the electrical supply of the vehicle itself cause a decrease in the fuel economy greater than that seen with a burner type system [82]. Recent innovations to reduce the power consumption have been made using a SiC WFF with a low pressure drop and optimised thermal and gas flow dynamic efficiencies, in conjunction with an improved heater driver [83]. Electric heater type systems have yet to prove their durability and reliability for trap regeneration during driving conditions [84].

During the mid 90’s a number of trials were performed using reverse air flow regeneration [85]. This concept is simply the use of the compressed air from the braking system to blow the collected DPM from one filter into a combustion/collection system [86]. A twin filter system is required to enable continual filtration and regeneration. This method however proved to be rather ineffective at totally cleaning the filter [85].

A more recent novel approach has been the development of the self-heating type filter [87]. These filters are produced out of SiC that as well as having very good high temperature properties, making it suitable for use as a DPF, also has a very low electrical resistance [88]. This last property allows the material to be heated up simply by applying an electric current to it. This type of system has given encouraging results that show regeneration of a DPF is possible using a 24 volt control system and has a wide temperature window of operation [88].

The use of microwave heating to regenerate DPFs has also received attention recently as a potential non-catalytic regeneration method [89, 90]. Due to the carbonaceous nature of DPM it readily adsorbs microwaves and is easily heated up by a microwave source. Some ceramic materials like cordierite on the other hand are more transparent to the microwaves and do not get heated. The result is the selective heating of only the DPM. A number of studies have been performed and have shown that through the optimisation of the microwave technology and the DPF itself, microwaves are capable of regenerating current WFF and foam DPFs [91]. Ceramic foams offer a better filter medium than WFFs for use with microwaves due to them
being more flexible in design and having isotropic thermal expansion and soot combustion properties [91]. A SiC fibre paper filter has recently been proposed for use as a DPF that is particularly suited to microwave regeneration due to each SiC fibre also being heated along with the DPM, leading to good regeneration characteristics [92, 93]. The use of microwave technology for DPF regeneration is still being developed, it does however appear to be an attractive possibility.

2.3.2 Passive/catalytic regeneration

There are primarily two different methods utilised for catalytic DPF regeneration, (1) the addition of a catalyst as a fuel additive and (2) the use of a catalytic coating on the DPF. The following is a discussion on the types of catalysts used in both these strategies and their performances. Some more novel catalytic systems are mentioned in the literature, these will be discussed briefly towards the end.

2.3.2.1 Fuel borne catalysts (FBCs)

FBCs are organometallic compounds that are soluble in diesel fuel. A number of organometallic compounds such as acetyl acetonates, alcoholates, sulphonates, carbonates and carboxylates have been reported in the literature for use with DPFs [2]. The actual organic portion of these compounds is of little importance with regards to the catalytic combustion of the DPM, since post combustion only metal oxide or sulphate remains. The organic portion of the compound is there to provide improved fuel solubility.

These FBCs are mixed into the fuel prior to combustion and are combusted in the engines' cylinders where the metal oxide or sulphate catalysts are formed in close contact with the DPM, sometimes even incorporated into the DPM. This enables a high level of contact between the catalyst and DPM and a good distribution of the two can be obtained in the DPF. There is a general trend with all FBCs for an increase in the dosage rate to lead to lower DPM ignition temperatures until a maximum catalytic effect is seen.

There have been a large number of different alkali [94], transition [95] and precious [2] organometallic compounds investigated for use as FBCs [2]. Several of these compounds have
been successfully commercialised. The following is a brief discussion on the most commonly encountered and commercially available FBCs.

**Copper** based additives have been investigated extensively by scientists at Lubrizol and have proved to be very effective [96]. Actual on-road testing of a turbocharged bus engine has shown Cu based FBCs and DPFs to be very promising, with a 59% reduction in PM emissions whilst maintaining an acceptable backpressure over 30,000 km using low level dosing of 50-70 ppm [97]. The effect of a Cu FBC on regenerating a DPF is shown by the plot of back pressure increase versus time in figure 21 [97].

![Figure 21. Pressure drop profiles for a copper based FBC with a SiC DPF system [97]](image)

Other tests using Cu-octate mixed with an n-heptane carrier have shown it to lower the regeneration of a DPF down to around 288°C [98]. A number of Cu and Cu-Mn based FBCs have been successfully commercialised by Lubrizol.

Some problems associated with Cu containing FBCs are that they tend to form combustion chamber deposits and they strongly catalyse the oxidation of the fuel, the latter can cause the diesel to thicken and become like tar in the fuel tank [99]. More important are concerns raised over possible health problems associated with increased levels of airborne copper, although the projected level of Cu increase expected is believed to cause no risk to human health [100]. Concerns over increases in the level of unregulated compounds, e.g. PAHs, have also been raised [100].
Cerium is another popular kind of FBC that has been studied extensively in conjunction with various DPFs. A particular advantage of cerium over copper based FBCs is that it poses no health hazards due to its biological inertness and non-toxic character. Cerium based FBCs have been commercialised by Rhodia under the brand name Eolys [101] and have been shown to be able to reduce the ignition temperature of DPM down to approximately 300°C [102]. Studies have shown that with the use of such an FBC, at 100 ppm dosage, partial passive filter regeneration of heavily loaded DPFs is possible during city driving conditions [103]. Even without the presence of a DPF, cerium based FBCs are able to reduce PM emissions, a reduction of one third has been reported [103]. However there have been some concerns over the use of FBC without DPFs because of concerns of residue being emitted into the atmosphere. It has been shown that when Eolys is used in conjunction with a DPF this problem can be eliminated [104] and the research has led to a number of European Countries officially recommending its use [104]. Typical dosage rates for cerium-type FBCs are around 50-100 ppm, which is higher than that for other types of FBC. Cerium-platinum type FBCs have recently been reported as being able to regenerate a DPF at temperatures >327°C at levels as low as 5 ppm [105] although this data is based on laboratory results and not engine/road testing. The high activity of this system is believed to be a result of a particular synergy between the platinum and cerium; when copper or iron was used in combination with cerium the effect was significantly smaller [105].

Iron based FBCs have also been studied. This type of catalyst is usually in the form of ferrocene (dicyclopentadienyl iron) [106]. Testing has shown that regeneration temperatures of approximately 300°C are required using a dose of approximately 60 ppm ferrocene, which corresponds to 18 ppm iron [107]. A ferrocene FBC has been commercialised by SAT CHEMIE GmbH under the trade name Satacen.

Other non-ferrocene type iron based FBCs include an iron-strontium catalyst developed by the Octel Company Ltd. This type of catalyst has given some promising results with regeneration temperatures of approximately 200°C [108]. This combination of catalyst was based on earlier work performed on very active sodium-strontium catalysts that lowered the combustion temperature to as little as 160°C [108]. However, the sodium-strontium catalyst attacks cordierite filters thereby reducing their mechanical durability [106].
A number of problems encountered with the use of FBCs are:

- Accumulation of ash deposits (inorganic oxides and salts) on the DPF that in time lead to undesirable increases in the backpressure.
- A high efficiency filter is needed in order to prevent the emission of the metal ashes to the atmosphere.
- Problems of FBCs causing fuel injector fouling need to be addressed.
- Only fuel stable catalysts can be used, since some additives result in deposit formation in the fuel tank.

2.3.2.2 Catalytic coating of DPFs

The second approach to DPF regeneration is the application of the catalyst onto the surface of the DPF, in what is commonly referred to as a catalysed DPF or CDPF. Catalytic coatings are much more suited for use with foam DPFs rather than WFFs due to the differences in trapping mechanism [109]. A WFF, although having high filtration efficiencies, would result in very poor catalyst DPM contact whereas a foam type structure due to its deep bed filtration mechanism allows far better DPM catalyst contact. WFFs are far more suited for use with FBCs, since DPM-catalyst contact has already been achieved.

A wide variety of materials have been investigated in order to determine their catalytic effect on the oxidation of carbonaceous materials (i.e. graphite, DPM, coal chars, etc). Precious metal catalysts have been studied in great detail and have been found to be good catalysts for the oxidation of carbonaceous material. However, the following discussion is confined to non-precious metal-based catalyst systems and the reader should refer to reference [2] and the references therein for more details on precious metal-based catalysts.

The following discussion is primarily based on laboratory studies since very little literature exists on road/engine testing using non-precious metal-based catalysts coated on DPFs. The type of carbonaceous material used varies from study to study, but it allows general trends in catalytic activity to be made that can be applied to all carbonaceous materials i.e. DPM.
Alkali and alkaline earth metal compounds

Alkali metal compounds are well known for their ability to increase the oxidation rate of carbonaceous materials [110]. It is believed that the catalytic activity of the alkali metals is due to the formation of peroxides, which readily react with the carbon. Therefore the degree of activity of alkali metal salts depends strongly upon the type of salt, with carbonates proving most active; K₂CO₃ in particular [110].

In a series of interesting reports, Mochida and Miyazaki et al [111, 112] studied the effect of a number of metal oxide supports for K₂CO₃ and found that a perovskite type oxide, La₀.₈Sr₀.₂Ca₀.₅Mn₀.₄₃Pt₀.₀₃O₃ (LSCMP), improved the activity of K₂CO₃ greatly. They believed that the redox activity of the perovskite support activated the alkali metal salts, thus allowing the sublimation of active species towards the carbon, and also aided in anchoring these active species in the reaction zone by not allowing them to sublime out. The LSCMP support was also shown to enhance the catalytic effect for both alkali metal sulphates and chlorides, although their catalytic activity was less than that of K₂CO₃ [113]. These sulphates and chlorides are interesting due to them being cheaper, however SO₂ and Cl₂ release might cause further environmental problems. With respect to their oxides both Li₂O and Na₂O have some activity, with the reaction for Li₂O commencing in the region 450 to 500°C [114].

The alkaline earth metal oxides have a more modest effect on the catalytic combustion of carbon, certainly much less than the alkali metal oxides, table 4 below outlines the results of a study by McKee [114].

<table>
<thead>
<tr>
<th>Material</th>
<th>T (°C) for 1% burnoff in flowing air (400 ml min⁻¹) (ΔT/Δt = 10 °C min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure graphite powder</td>
<td>763</td>
</tr>
<tr>
<td>graphite + 1% SrO</td>
<td>750</td>
</tr>
<tr>
<td>graphite + 1% MgO</td>
<td>740</td>
</tr>
<tr>
<td>graphite + 1% CaO</td>
<td>728</td>
</tr>
<tr>
<td>graphite + 1% BaO</td>
<td>718</td>
</tr>
<tr>
<td>graphite + 1% Na₂O</td>
<td>608</td>
</tr>
<tr>
<td>graphite + 1% Li₂O</td>
<td>568</td>
</tr>
</tbody>
</table>

Table 4. Effect of alkali and alkaline earth metal oxides on graphite oxidation [114]
Transition metal compounds

The vast majority of studies on carbon oxidation catalysts involve transition metal compounds, of which a number have proven to be very active and have subsequently been developed further for use as DPM oxidation catalysts. The following is a discussion on the most active and widely studied transition metal compounds used for carbonaceous material oxidation.

There are a large number of works in the literature investigating lead (Pb) [115] and its compounds, e.g. PbO [116, 117, 118]. Most of these works are in agreement that PbO is by far the most active transition metal oxide for carbonaceous materials oxidation. In a different report to that of reference [114], McKee showed PbO reduced the $T_{ig}^1$ of graphite powder from 740°C to 382°C [118].

Vanadium pentoxide ($V_2O_5$) is another very active catalyst for the oxidation of carbonaceous material, with most studies highlighting this [117, 118, 119, 120 & 121]. McKee showed that it reduced the $T_{ig}$ of graphite powder from 740°C to 490°C [118]. A number of studies have suggested that the high activity of vanadium is related to its mobility, which is expressed by it having a low melting point and low Tamman temperature. Many have shown molybdenum oxide ($MoO_3$) to possess a high catalytic activity similar to that of $V_2O_5$ [117 & 118].

Cobalt oxide ($Co_3O_4$) has been shown to promote diesel soot combustion when supported on MgO and CeO$_2$ [123]. Work has shown that by the impregnation of MgO with Co oxides and Co,K (K in the form of KOH was used) its catalytic activity for diesel soot combustion is greatly enhanced with Co,K/MgO > Co/MgO > K/MgO = MgO. They have shown that Co/MgO can effectively oxidise diesel soot beginning at approximately 300°C with a $T_{max}^3$ of 450 to 500°C. Through the addition of KOH this temperature is lowered slightly to approximately 250°C with a $T_{max}$ at 378°C. The researchers have also shown that the activity for soot combustion is directly related with the Co oxide reducibility, i.e. the Co oxides

1 $T_{ig}$ is defined as the temperature at which the combustion of the soot begins
2 The Tamman temperature is the temperature at which the lattice atoms of the compound become mobile. It is roughly half the melting point temperature in K [20].
3 $T_{max}$ is defined as being the temperature at the maximum rate of combustion
introduce the necessary redox properties into the catalyst. The need for this redox property will be discussed later. They suggest that the K plays a number of different roles:

- It increases the catalyst soot contact by configuring surface mobility;
- It preserves the redox capacity of the Co oxides formed when calcined at temperatures >400°C;
- It prevents the sintering of Co3O4; and
- It favours the oxidation of soot by consuming the carbon to form carbonate species during combustion.

They also show that Co,K/MgO is effective in catalysing the conversion of NOx to N2 and N2O. The soot catalyst contact is shown to be an important parameter in maximising the catalytic performance of the catalysts.

A number of other studies have also noticed the activity of Co for carbon combustion [119]. McKee saw a reduction in Tlg for graphite from 740°C to 525°C [118].

Copper oxide (CuO) is another active catalyst for carbon oxidation [114, 124]. McKee found it lowered Tlg from 740°C to 570°C [114]. Neeft et al showed that Cu2O displayed a higher Tmax than CuO, at 524°C and 490°C respectively [117]. Whilst Neri et al also found CuO to have a Tmax of approximately 500°C [121]. Ahlstrom et al [120 & 124] commented on the high activity of CuO, which was best at temperatures below 400°C, and went on to prepare a mixed metal oxide of V2O5 and CuO that had a high activity for diesel soot oxidation.

Iron oxide (Fe2O3) is another metal oxide reported by a number of authors as having a moderate to high catalytic activity for carbon oxidation. McKee showed it lowered the Tlg of graphite from 740°C to 593°C, which is slightly better than that of Pt and NiO at 602°C and 613°C respectively [118]. A number of studies have also reported this high activity when used with diesel soot. Neeft et al [117 & 119] showed that Fe2O3 had a Tmax of approximately 467°C whilst work by Ahlstrom et al agrees with this showing Fe2O3 to have a high activity for diesel soot oxidation [120]. However, results by Neri et al show Fe2O3 as having a rather low activity, less than that of TiO2, with a Tmax of approximately 670°C [121].

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There are very few reports in the literature concerning the use of more commonly encountered ceramic materials such as alumina, titania and zirconia as oxidation catalysts. All work involving these materials have shown them to have very poor, if any, catalytic activity for carbon oxidation [125]. These materials are predominantly used as support materials for more active catalysts.

The proposed reaction mechanism occurring during the catalytic oxidation of soot/carbon is believed to be a reduction/oxidation (redox) type mechanism (Mars and van Krevelen mechanism) [126]. The mobile metal oxide catalyst particles are reduced to a lower oxidation state by reaction with the soot/carbon, as in reaction 1 below, and are subsequently re-oxidised to the original oxidation state with ambient oxygen, reaction 2.

\[
\text{Reaction 1} \quad 2\text{MO}(n) + \text{C} \rightarrow \text{CO}_2 + 2\text{MO}(n-1)
\]

\[
\text{Reaction 2} \quad 2\text{MO}(n-1) + \text{O}_2 \rightarrow 2\text{MO}(n)
\]

Using this accepted redox mechanism it can be said that the most important part of the whole mechanism is the reduction step, reaction 1, as without it the catalyst is inactive for soot/carbon oxidation The rate at which the carbon reacts with active catalyst sites is “strongly dependent on the effectiveness of the contact of solid phases” [127].

An interesting study by Neeft et al [119] compares the catalytic activity of a number of transition metal oxides for diesel soot oxidation as a function of the soot-catalyst contact, as shown in figure 22 below.

![Figure 22. Effect of metal oxide catalysts in tight and loose contact on the combustion temperature of model soot [119]](image-url)
The result shows the difference that is achieved simply by altering the way in which the samples are prepared. A “tight” intimate contact, obtained by mechanically forcing the components together, between the soot and catalyst yields much lower $T_{\text{max}}$ values than for the more realistic loose contact, where no force is used to increase the contact. The catalysts that show good loose catalytic activity are generally those that are more mobile due to high volatility and low melting point.

Neeft et al [119] also performed a test whereby a segment of a wall flow filter (WFF) was impregnated with $\text{Co}_2\text{O}_4$ and CuO and diesel soot particulates were deposited on it in a realistic manner. The results showed that although these catalysts had high catalytic activities when tested in the laboratory under tight contact conditions, they had little catalytic activity in the above test. They conclude by saying that the contact between soot and catalyst is of prime importance when determining the reactivity for catalytic soot oxidation. In order for a catalyst to be appreciably active for soot oxidation under practical conditions it needs to have some degree of mobility of the active species.

**Mixed metal composite catalysts**

The above work has led the way for the development of more active catalysts specifically designed to aid the catalytic combustion of DPM. Work during the early 1990’s on the effect of combining two or more active carbon oxidation catalysts compounds together proved fruitful. Investigations showed that the activity of the very active $\text{V}_2\text{O}_5$ catalyst was improved through the addition of Cu salts [124], further work showed that the activity could be improved further by potassium additions [128]. In a Cu-K-V catalyst, in the ratio of 2:2:1, it has been shown to lower the ignition temperature of a flame soot down to 382°C from 616°C [129]. Subsequent studies on these Cu-K-V type catalysts have shown that their high activity is due to the formation of eutectic liquid phases that give the catalyst increased mobility [130]. This liquid phase allows good contact between the active vanadium and copper species and the carbon to be made that allows combustion to progress through a redox type mechanism as outlined previously. Other workers have developed similarly active Cu-K-Mo catalysts whose' high activity is believed to be due to the formation of active liquid and vapour phase copper and chlorine containing compounds that enable “wetting” of the DPM and thus good contact [131].
Unfortunately, these very active and promising catalysts proved to be unfeasible for use as oxidation catalyst in mobile diesel sources due to concerns over health risks. An inherent problem of both systems was the release of toxic CuCl₂, which has also been shown to catalyse the formation of oxychlorinated compounds, such as dioxins, in diesel exhaust [130].

**Eutectic liquid forming systems**

The natural progression on from the above catalyst systems was to try to develop catalysts that posed no health threats but were able to form a eutectic liquid at low temperature and that contained the necessary active species for carbon oxidation.

This ability of eutectic liquids to catalyse the combustion of carbonaceous material by facilitating improved contact between the catalyst and carbon is not a new concept, and was demonstrated on coal chars and graphite in the mid 1980’s [132, 133]. Recent work on the development of this type of catalyst for DPM oxidation has been carried out by workers at Torino University, Italy, under a Brite Euram programme.

The researchers initially began by preparing catalysts that form eutectic liquid phases between halides and vanadates e.g. RbCl + KVO₃. The results showed the most promising to be CsCl + KVO₃, although it was not as active as a Cu-K-V type catalyst there was only a 20°C difference between their T_max values [134, 135]. The benefit of such a catalyst is that poses significantly less health concerns. A KCl + KVO₃ catalyst developed also appears attractive due to its low cost, although it has a much lower activity. These KCl and mixed metal metavanadates have more recently been evaluated to determine their applicability at regenerating a ceramic foam DPF. The result in figure 23 [136] clearly shows that the more active CsVO₃ + KCl catalyst was able to reach a steady state that suggests continual filter regeneration [136]. More recently pyrovanadate based catalysts have been developed, e.g. Cs₄V₂O₇ and K₄V₂O₇, that have shown increased activities over the previously tested metavanadate chloride catalysts, as illustrated in figure 24 [137, 138]. The high activity of the pyrovanadates is not due to the formation of a liquid phase, rather it is believed to be the effect V-O bonds have on C-C bonds in promoting the formation of C-O bonds, although this has yet to be confirmed [137].
Another group of workers at Delft University is also investigating the use of different composition eutectic liquid forming catalysts for DPM oxidation. Their work has focused on the following three mixtures [139, 140] \( \text{Cs}_2\text{MoO}_4 - \text{V}_2\text{O}_5 \), \( \text{CsVO}_3 - \text{MoO}_3 \) and \( \text{Cs}_2\text{SO}_4 - \text{V}_2\text{O}_5 \). All three mixtures form liquid eutectics at around 327-362°C, allowing the catalyst to wet the DPM and DPM oxidation to begin.

They have also shown that ceramic foams would make ideal supports for such catalyst systems, although silicon carbide and silica foams were found to be unsuitable [60]. This was due to the catalyst being unable to adhere to such materials and also promoting the oxidation.
of the SiC. The catalyst was shown to spread and redistribute itself over the foam surface, although this could be reduced by using a foam with a roughened surface [60]. Although no regeneration testing of foams coated with these catalysts has been reported, their oxidation rates at 377°C are said to be comparable with the most effective fuel additives [141].

**Perovskite and spinel type oxides**

In the early 1970s, cobaltate perovskites were investigated and found to be interesting substitutes for noble metals in automotive catalysis, especially for CO oxidation and NO reduction. More recently work has focused on their use as oxidation catalysts for carbon/diesel soot, NO reducing capabilities and combinations of the two.

Work done by Sri Rahayu et al has focused on the use of perovskites with the general formula $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x-y}\text{B'}_x\text{Fe}_y\text{O}_3$ ($\text{B'} = \text{Pt, Ru or Pd, } x < 0.01, y < 0.09$ and $\Phi$ represents a deficiency in the B site) and for DPM combustion [142]. They showed that perovskites of this type were highly active in the catalytic combustion of diesel soot at temperatures >320°C. The two best systems developed were $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.999}\text{Pd}_{0.001}\text{O}_3$ with a $T_{\text{max}}$ of 450°C and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.91}\text{Pd}_{0.09}\text{O}_3$ that had a $T_{\text{max}}$ of 460°C compared to uncatalysed soot at 670°C.

A more recent report in the literature on these materials is by Seong-soo Hong et al [143]. They have investigated the effect of alkali metal substitution into the perovskite structure. Their results showed that the partial substitution of alkali metals into A sites enhanced the catalytic activity and the activity decreased in the following order Cs>K>Na. They suggest that the substitution of Cs gives rise to easy reduction of oxides and forms oxide ion vacancies on the surface and then increases the adsorption rate of active oxygen on the catalyst surface. The best perovskite system developed here is $\text{La}_{0.6}\text{Ce}_{0.2}\text{Cs}_{0.2}\text{CoO}_3$, which has a $T_{\text{ig}}$ of 243°C and a $T_{\text{max}}$ of 315°C.

A number of interesting studies have shown that perovskite and spinel type oxides are able to catalyse the oxidation of DPM and catalyst the reduction of NOx to N₂ simultaneously [144].

Teraoka et al investigated a series of perovskites and K₂NiF₄ type oxides [144, 145 & 146]. Their work showed that perovskite related oxides were superior to transition metal oxides and
Pt/Al₂O₃ with respect to selectivity to NOx reduction⁴. A decrease in the T_{ig} and an increase
in the selectivity was seen with the appropriate substitution of K for La at the A sites. For the
perovskite type oxides, La₀.₉₉K₀.₁FeO₃ and La₀.₉₉K₀.₁Mn₀.₈Cu₀.₂O₃ were the most promising,
lowering T_{ig} to 276°C and 270°C with selectivity for NOx reduction of 5.1% and 4.5%
respectively. Spinel type oxides with the general formula AB₂O₄, were shown to be more
selective to NOx reduction, although they had higher T_{ig} values. La₁.₉₉K₀.₁Cu₀.₉₅V₀.₀₅O₄ and
La₁.₉₉K₀.₀₅Cu₀.₉₅V₀.₀₅O₄ were the best having T_{ig}'s of 295°C and 300°C with selectivities for
NOx reduction of 5.9 and 5.7% respectively.

The formation of CO₂ due to DPM oxidation and N₂ formation occur within the same
temperature range and both NOx conversion and CO₂ conversion versus temperature curves
have the same shape with very close peaks. This suggests that the reactions are occurring
simultaneously. Teraoka et al [144] suggest that the simultaneous removal of NOx and DPM
takes place at the so called “Triple contact point”, where the solid catalyst, the solid portion of
DPM and the gases meet.

Shangguan et al [147, 148] have performed further work on the use of spinel type oxides for
the simultaneous removal of particulates and NOx. Their comparison of spinels to simple
metal oxides and mechanical mixtures of these oxides showed the superiority of the spinels
for the selectivity of NOx to N₂ formation, in agreement with the work of Teraoka et al [144,
145 & 146]. Their results showed that CuFe₂O₄ was by far the most selective catalyst for
NOx reduction with a T_{ig} of approximately 285°C. This performance is comparable to the
best perovskite type oxide they studied. They have shown that the choice of metal cation in
the structure is most important. For both spinels and perovskites CO and Mn based oxides are
the most active and less selective whilst Fe and Cu based oxides are the least active but the
most selective.

Further research by this group investigated, like so many others, the effect of substitution of K
into the CuFe₂O₄ structure. They found that doping with K to yield the catalyst
Cu₀.₉₅K₀.₀₅Fe₂O₄ gave the best result with a lower T_{ig} at 266°C and a higher selectivity for N₂
formation compared to CuFe₂O₄. This promotional effect was not observed for the other
alkali metals and V or Pt.

⁴ Selectivity to NOx reduction is defined here as the molar ratio of the N₂ formed to the charged soot assumed to
be carbon. This is based on the reaction: C+(2-2X)NO+XO₂→CO₂+(1-X)N₂
Saracco et al [149] have investigated the simultaneous removal of diesel soot and NOx over La-K-Cu-V perovskite type catalysts. Their work found that the introduction of K into the lattice of La$_2$CuO$_4$ has the effect of lowering the $T_{\text{max}}$ from 553°C to 543°C whilst little effect on NOx reduction ability was seen. By the introduction of V into the B site of the structure a further lowering of the $T_{\text{max}}$ was seen to 532°C. But, more importantly, a twofold increase of the NOx reduction activity was observed. The only drawback with this La$_{1.9}$K$_{0.1}$Cu$_{0.95}$V$_{0.05}$O$_4$ catalyst was its poor thermal stability that resulted in the loss of V and K such that after six days at 800°C the material had returned to the more stable La$_2$CuO$_4$ and the catalytic activity reflected this change.

**Gaseous phase catalysts**

In the late 1980’s scientists working for Johnson Matthey discovered that DPM oxidation occurred at much lower temperatures in the presence of NO$_2$ [150]. The NO$_2$ was generated from the substantial amount of NO present in the exhaust gases by passing it through a Pt based oxidation catalyst. In fact this technique has been patented and successfully commercialised by Johnson Matthey in the continuously regenerating trap (CRT) technology.

Since then a number of workers have reported that the presence of NOx (NO & NO$_2$) enhances the catalytic combustion of DPM with a variety of catalyst materials including Cu-V-K/Ti [151], Cs$_2$SO$_4$-V$_2$O$_5$ (liquid phase type) [152] and a number of transition metal oxides [153]. In addition to the direct catalytic oxidation of DPM by the metal based catalyst, the presence of NO$_2$ is believed to contribute to the DPM oxidation through the following reactions:

\[
2\text{NO}_2 + \text{C} \rightarrow 2\text{NO} + \text{CO}_2 \\
\text{NO}_2 + \text{C} \rightarrow \text{NO} + \text{CO} \\
\text{NO}_2 + (\text{C-O}) \rightarrow \text{NO} + \text{CO}_2 \quad \text{(C-O is a carbon oxygen surface complex)}
\]

More recently ozone (O$_3$) and ionised air (containing O, NO$_2$, NO and O$_3$), generated by means of a plasma arc have been shown to effectively catalyse the oxidation of DPM at temperatures $<350^\circ$C [154].
2.3.3 Diesel exhaust after-treatment outlook

Due to the limitations of current engine technology and a number of problems presently associated with developing alternative diesel fuels on a large scale, there has been an increased emphasis on exhaust after-treatment devices to meet future emission regulations. It is the general belief in the industry that some form of after-treatment will be required on all diesel engines, especially heavy-duty types. State of the art after-treatment technology as it stands today will not be able to cope on its own to meet all these emission standards. Such after-treatment devices will have to form part of an overall emissions reduction package that includes advanced engine technology and control systems, i.e. a particulate after-treatment device will have to be combined with EGR, for example, to be able to reduce PM and NOx emissions.

Particulate after-treatment is biased toward passive regeneration strategies as such systems are simpler and generally less expensive than active systems. Due to the large success and commercialisation of WFFs compared other types of filter media, the use of FBCs as a means of aiding regeneration appears the most popular choice. However more and more work on the use of catalysed foam DPFs is being performed and as this technology develops catalysed foam DPFs might become a contender against WFF technology. However, both types of passive regeneration are currently not advanced enough to be able to regenerate a DPF of any kind during the temperatures achieved during all driving conditions. For this reason, passive exhaust treatment is going to be, for the time being, very reliant on combining engine technology that enables exhaust gas temperatures to be periodically raised in order to enable regeneration.

2.3.4 Current exhaust after-treatment devices available

The diesel exhaust after-treatment market is very big business and is expected to grow rapidly from current levels of $2.4 billion to over $6.2 billion by 2010 [155]. As would be expected in such a large market there is a lot of competition, and a large array of different technologies are on offer to reduce primarily the regulated emissions of diesel engines [156]. Only some of the systems currently being produced either commercially or in the final stages of testing will be discussed here, for a more extensive summary of the available technology refer to [156].
2.3.4.1 Johnson Matthey’s CRT & SCRT systems

Johnson Matthey have developed an effective system for PM reduction which they’ve called called a continuously regenerating trap (CRT). The system is based upon the discovery by their scientists that DPM combustion commences at much lower temperatures in the presence of nitrogen dioxide (NO$_2$) than oxygen (O$_2$), some 200°C lower in fact, as illustrated in figure 25 [157, 158].

![Figure 25. Comparison of the combustion onset temperatures of PM in NO$_2$ and O$_2$ [158]](image)

The CRT system consists of a Pt oxidation catalyst coated on a ceramic flow through filter followed by a cordierite or more recently tested SiC wall flow DPF [159]. This configuration allows a portion of the engine out NO to be oxidised to NO$_2$, which in turn is used to combust the DPM. This CRT system however is very sensitive to sulphur in the fuel. This is due to the preferred oxidation of SO$_2$ to SO$_3$ over the Pt catalyst to the required NO to NO$_2$ oxidation [159]. The effect of increased sulphur on NO to NO$_2$ conversion is given in figure 26 [158].
It can be clearly seen that sulphur levels $> 50$ ppm in the fuel greatly affect the NO to NO$_2$ reaction which in turn dramatically reduces the CRT’s performance. The system therefore can only be used with fuels of $< 50$ ppm sulphur. The CRT has undergone extensive engine trials and has proven to be very effective at reducing PM as well as HC and CO emissions [158]. Euro IV PM emission limits are easily reached with this system. However, NOx emissions are not met with the CRT system.

A recent development at Johnson Matthey is in the combination of the CRT system with SCR technology in order to reduce both PM and NOx emissions. This new system is designated SCRT. A schematic of this SCRT technology is given in figure 27 [158]. It consists of a CRT system upstream of a SCR system, which uses urea as a precursor for generating ammonia as a reductant for the NOx. A final oxidation catalyst is used after the SCR system in order to minimise ammonia slip from the system. This configuration of the CRT upstream of the SCR has been found to greatly enhance the low temperature performance of the SCR. This increased performance has been attributed to NO$_2$ generated by the CRT reaching the SCR and having a promoting effect on its activity [160]. Similarly to the CRT, the SCRT system is intolerant of high levels of sulphur in the fuel. Engine tests of SCRT systems have shown it to
successfully reduce PM and NOx emission levels to meet both Euro IV and V regulations, as shown in table 5 [160]. The system has yet to be fully commercialised.

![Catalyst Diagram](image)

**Figure 27. Schematic representation of the SCRT system [158]**

2.3.4.2 PSA Peugeot-Citroen DPF system

In 1999 PSA Peugeot Citroen announced that were introducing a new DPF system to be fitted to their range of light duty HDi (high pressure direct injection) engines fitted to its Peugeot 607 model from the year 2000 onwards [161]. The DPF itself is a SiC WFF that is regenerated by engine throttling that is controlled by the “common rail” injection system to periodically raise the exhaust gas temperature to 450°C. A fuel-borne catalyt (Eolys – which is a ceria containing catalyst) is used to reduce the DPM combustion temperature to 450°C and ensure complete filter regeneration. Regeneration is expected to take place every 400 to 500 km. In addition to the WFF upstream of it there is also a flow through oxidation catalyst that is used to oxidise the excess HC emissions due to the extra fuel injected. This process also helps raise the exhaust gas temperature [161].

2.4 Production of porous ceramics

There are a number of different processing routes for the production of porous ceramics, with both open and closed porosity. A number of the different techniques reported in the literature are discussed below:

**Polymeric foam replication:** By far the most commonly encountered method in the literature, and one that has been adopted by a number of manufacturers, is the polymeric foam
replication method based on work by Schwartzwalder et al [162]. This process essentially entails coating a suitable polymeric sponge with a ceramic slurry to build up a coating of the ceramic onto the polymer network. Once excess slurry has been removed the foam is dried before the polymeric sponge is burnt out at temperatures between 350 – 800°C. The final step is the densification of the resultant ceramic network by sintering [163]. A schematic outlining the process is given in figure 29 [163]. Polyurethane sponges are the most widely used materials in this process. Porous ceramics produced via this route are often referred to as reticulated foams in the literature.

![Figure 29. Step-by-step detail of polymeric sponge method [163]](image)

This method is relatively quick, has good reproducibility and the final foam properties, i.e. pore size, can be controlled by the initial polymeric foam. However, these reticulated foams offer poor mechanical properties due to the large number of flaws and hollow struts in the body as a result of the polymer skeleton being burnt out [164]. Another concern is the quantity and toxicity of the gases released during the burn out stage [165].

**Incorporation of volatile or combustible burn-outs:** A number of materials, including sawdust, wax, rice flour and potato starch can be mixed into a ceramic slurry/paste. These
Chapter 2. Literature Review

Materials are subsequently burnt out during firing with the resultant materials porous nature having been determined by the size, distribution etc of the burnt out phase [165]. Cotton thread has also been used as a fugitive phase in the preparation of porous ceramics with unidirectionally aligned continuous pores as illustrated in the SEM image in figure 30 [166].

Figure 30. SEM image showing the cross sectional microstructure of the unidirectionally aligned continuous pores [166]

Aerogels: Inorganic aerogels, obtained through the supercritical drying of sol derived gels, are highly porous materials that have well-controlled nano-porous structures [167].

Foaming of ceramic suspensions: Another well investigated route for porous ceramic production is through the preparation of a ceramic foam (a foam is defined as group of bubbles separated from one another by thin films, the aggregation having a finite static life [168]). These ceramic foams are prepared by dispersing a gaseous phase into a ceramic suspension that results in the foaming of the ceramic suspension. Generation of these foams can be achieved by a number of means including mechanical foaming, injection of a gas stream or through in-situ gas generation [163, 165]. Since the life of a foam is finite, its lifetime is determined by a number of parameters that will be discussed later, a suitable method to retain the foam structure permanently is needed. This can be achieved either by freezing/drying of the solvent, addition of a gelling agent, e.g. cellulose derivatives, or by the in-situ polymerisation of monomers present in the body before it collapses [165], see section 2.4.1 for further details.

Foaming of pre-ceramic polymer/polyurethane blends: A more recent approach is the foaming of a solution containing a pre-ceramic polymer and polyurethane precursors that can
be subsequently pyrolysed to produce SiC [169], silicon oxycarbide (SiOC) [170, 171] and SiC-Si₃N₄ composite foams [172]. A polyurethane foam is generated that contains the pre-ceramic polymers that on subsequent heating convert to the required ceramic and the polyurethane backbone support is pyrolysed. This polymer-to-ceramic conversion generally occurs with a large amount of shrinkage, weight loss and evolution of gaseous products that result in poor quality bodies [171].

Freeze-drying: A novel process for porous ceramics production is via the freeze drying of aqueous ceramic slurries [173, 174]. The pores are formed in the ceramic from the sublimation of the ice and form a complex dendritic structure as shown in figure 31 below.

![Figure 31. SEM image showing the porous dendritic structure obtained via freeze drying of ceramic slurries [173]](image)

**CVI/CVD of porous vitreous carbon:** A process commercially adapted by Ultramet Corp. USA [175] for the production of porous ceramics is the chemical vapour infiltration/deposition (CVD/CVI) of an extremely porous vitreous carbon body with a refractory material. The process begins with the pyrolysis of a thermoset polymer foam to obtain the carbonaceous skeleton before deposition/infiltration with a wide range of refractory materials including TaC, W, Ta, ZrO₂ and MoSi₂ [176]. The thermomechanical properties of this type of foam are controlled by the properties of the material deposited. These foam structures are typically characterised by hollow triangular struts.
2.4.1 Gel cast foams

The gel casting process has been developed at the Oak Ridge National Laboratory (ORNL) for processing near-net shape, complex, dense bodies from ceramic suspensions [177, 178]. The basis of this technique is the preparation of a ceramic suspension that contains a monomer component that can be triggered to gel in-situ, thus holding the ceramic piece together [179]. The resultant green ceramic body is characterised by very high green strengths. The organic portion is subsequently pyrolysed prior to sintering the ceramic body. This gel casting process was originally developed for the production of complex shaped dense bodies and is presently becoming more widely used as a manufacturing process for such components [180]. It has since been developed as a suitable system to be used with foamed ceramic suspensions, yielding high strength green bodies sufficient to hold structures with porosities >90 vol% [181]. Foam production is usually achieved by mechanical frothing. A flow diagram outlining the gel cast process for porous ceramic production is given in figure 32 [182].

![Flow diagram](Image)

**Figure 32.** Process flow chart for production of gel cast ceramic foams [182]
This process has been successfully applied to a number of ceramic materials, including alumina, zirconia, hydroxyapatite and silicon carbide [165, 182]. Gel casting of porous ceramics has been thoroughly investigated and foams of this type are now commercially available [183].

Some of the advantages offered by gel cast foams are that they have been shown to have much higher mechanical strengths than their reticulated foam counterparts [165]. This is due to gel cast foams having fully dense struts with few defects compared to the hollow struts in reticulated foams with a large number of defects [184]. Also the gel casting route allows great flexibility in the size and complexity of the porous ceramics that can be produced. Due to their different natures of processing, the structures of gel cast and reticulated foams vary quite markedly, as illustrated in figures 33 and 34 [61, 185].

Figure 33. Structure of a reticulated 50 ppi (19.7 ppcm) foam [61]

Figure 34. Structure of a 15 % theoretical density gel cast foam
The gel cast foam is typically characterised by large near spherical pores/cells (that appear as hemispherical like craters due to the way in which the samples have been cut) interconnected to each other by smaller pores/windows within the walls/struts of the foam. Whilst reticulated foams appear to be constructed of an almost web-like network of thin struts with a much smaller surface area that contain a more uniform distribution of pore sizes.

2.4.1.1 Gel cast foam microstructure development

As opposed to reticulated foams whose porous structure is controlled by that of the polymeric sponge used in its production, gel cast foams have many more variables that ultimately determine the final microstructure of the foam. The latter is determined by a number of transformations that occur between foam generation and solidification, since once the monomeric system is polymerised, i.e. foam has become rigid no further alteration to the microstucture is possible.

By definition a foams lifetime is finite. A number of mechanisms exist that result in the destabilising of the bubbles in the foam that act by a process of thinning the liquid film surrounding the bubbles. These include drainage due to gravity, drainage due to capillary pressure, local depression due to hot spots and van der Waals attraction between the surfaces of thin films [185]. During a foams life some bubbles can be seen to grow whilst others shrink and disappear. Bubble growth occurs with time via gas diffusion from smaller bubbles of higher curvature to larger ones, due to differences in their gas pressures [186]. Therefore larger bubbles tend to grow at the expense of smaller ones. Bubble coalescence occurs through film rupture, to produce a bubble with an increased volume that results in a reduction in the free energy of the system [186]. Open-cell foams are produced when the films rupture partially, excessive film rupture can lead to foam collapse.

The most common method employed to inhibit the above thinning mechanisms, thereby increasing the foams lifetime, is through the addition of a surfactant. This acts to reduce the surface tension of the gas-liquid interface that exists between the bubbles of the foam and its surrounding liquid film [187]. By doing so the bubbles become stabilised for a limited period of time. Aside from the use of a surfactant to inhibit the thinning mechanisms, an increase in the viscosity of the liquid in the film also acts to slow down the thinning process [188].
present in large concentrations also stabilise a foam due to the electrostatic repulsion established between the two sides of a very thin film preventing further thinning [186].

A unique ability of the gel-cast process is the level of control over the period between foam generation and its solidification. The time before the onset of polymerisation can be controlled by a number of factors including temperature, concentration of catalyst and initiator added and oxygen concentration [186]. This period after mixing and before the onset of polymerisation, is known as the induction time ($T_i$). By manipulating it, the time afforded to the various mechanisms of foam development mentioned above are changed, this leads to changes in the final microstructure of the foam. In general, a lengthy induction time leads to the development of large pore, more open celled materials. However, due to the stability of the foam being finite there is an upper limit to the induction time period before the foam collapses. Using current manufacturing techniques the maximum pore size consistently achievable is approximately 800 $\mu$m at 15% theoretical density (i.e. 85% porosity) [183].

2.5 Permeability theory of porous media

The back pressure imposed on a system by any filter is a result of the way in which the filters’ microstructure interacts with the air flowing through it. Generally a finer pore size will result in a greater backpressure. In order to understand how a material affects the backpressure an understanding of the theory of fluid flow through a porous media is needed. The following is a discussion of this.

2.5.1 Darcy's law and the Forchheimer equation

Early investigations into the permeability of porous media to fluid flow were initially performed by H.P.G. Darcy in 1856 [188]. Darcy successfully described a relationship between backpressure and fluid velocity through a granular homogeneous and incompressible porous medium given below as equation 1[189]:

$$\Delta P/L = (P_i - P_o)/L = (\mu V_o)/k_1 \quad \text{\textit{Equation 1}}$$

Where $L =$ medium thickness
$\Delta P =$ backpressure
\[ V_s = \text{fluid velocity} \]
\[ \mu = \text{fluid viscosity} \]
\[ k_1 = \text{Darcian permeability constant (m}^2) \]
\[ P_i & P_o = \text{absolute values of pressure at the entrance and exit of the medium.} \]

The parameter \( k_1 \) is a constant for any given porous medium and the above linear relationship between back pressure and fluid velocity is called Darcy's law.

However observations made very early on showed that Darcy's law is valid only for very low fluid velocities, with the relationship between back pressure and fluid velocity becoming non-linear beyond a certain point [188].

Forchheimer, in 1901, gave a modified form of Darcy's law for an incompressible fluid flowing through a homogeneous porous medium that now included a second order term in the velocity, equation 2 [189, 190].

\[
\Delta P/L = \frac{(\mu V_s)k_1}{k_1} + \left(\rho V_s^2\right)/k_2 \quad \text{— Equation 2}
\]

Where \( \rho = \text{fluid mass density} \)
\[ k_2 = \text{non-Darcian permeability or inertial permeability constant} \]

For compressible fluids taken as an ideal gas this relationship is modified to equation 3 below:

\[
\frac{(P_i^2 - P_o^2)}{2PL} = \frac{(\mu V_s)k_1}{k_1} + \left(\rho V_s^2\right)/k_2 \quad \text{— Equation 3}
\]

Equation 3 shows that the backpressure in a porous body is in fact due to the sum of two effects:

- \( (\mu V_s)/k_1 \), describes the energy losses or resistance to flow through viscous attrition between fluid layers and the pore walls.
- \( (\rho V_s^2)/k_2 \), represents the contributions of inertia and turbulence to the resistance of flow.
Both the Darcian and Forchheimer equations show how fluid flow affects the pressure drop and supply permeability constants that allow porous bodies to be compared. They do not describe how the properties of the porous medium affect these permeability constants and ultimately the pressure drop.

2.5.2 Permeability-structure relationships

In a porous body the two primary properties that have an effect on permeability are porosity and pore size. In 1951 Ergun proposed a relationship linking these parameters to the Darcian and non-Darcian permeability constants [191], equations 4.

\[
\frac{(-\Delta P)}{L} = 150 \frac{(1-\varepsilon)^2 \mu V}{\varepsilon^3 d^2} + 1.75 \frac{(1-\varepsilon) \rho V^2}{\varepsilon^3 d} \quad - \text{Equation 4}
\]

Where \( \varepsilon = \) porosity

\( d = \) mean particle diameter of the granular media.

Ergun's work however was done using packed columns of crushed porous solid particles and not cellular solids such as foams. To date there is no equivalent of the above Ergun equation for cellular ceramics. The problem in applying the Ergun equation to cellular ceramics is in defining what parameter to use for the particle size, \( d \), which is clearly defined for granular media. Should for instance it be the cell or window size or some weighted average [192]? Philpse and Schram [193] suggested that a value for \( d \) might be obtained from the ratio \( k_1/k_2 \), which has the dimensions of length [193]. This method in obtaining a value for \( d \) is advantageous as it is easily obtained from pressure drop measurements. Although to date no satisfactory answer has been found for what parameter \( d \) should reflect.

2.5.3 Air-flow through cellular ceramics

There are relatively few works in the literature specifically regarding air flow and air permeability of cellular ceramics. It is the general consensus that for permeability experiments a more realistic approach to curve fitting can be obtained by the use of the Forchheimer or Ergun type equations since these types of equation combine the effects of viscous and inertial
energy losses and can account for fluid compressibility. This is the case especially when using high air velocities. Phlpse and Schram found that above a velocity of approximately 2 ms\(^{-1}\) the air flow became non-Darcian [193]. The use of the Forchheimer equation also gives a greater insight into how the foams' properties i.e. porosity and pore size, influence the pressure drop curves.

A recent report by Innocentini et al [194] examined the general trends shown in previous works dealing with ceramic foam permeability. It illustrates a number of interesting points linking the effect of foam properties to \(k_1\) and \(k_2\). They have shown that \(k_1\) tends to zero as the pore diameter \((d_{pore})\) decreases, i.e. an increase in the nominal pore count (ppi). This is explained through \(k_1\) reflecting the viscous energy losses due to attrition against the walls. Hence a larger surface area is available for attrition as the pore size decreases, resulting in increased viscous energy losses and a subsequent decrease in \(k_1\). They also show \(k_1\) is very sensitive to pore size variation in the region \(1/d_{pore} \sim 0.5\) mm and explain that \(d_{pore}\) has less of an effect on \(k_2\) and that the actual medium curvature can be used to explain the inertial energy losses. In fact there are two factors affecting the pressure drop at increased flow rates. They are a mixing effect (interpassage connections and variations of passage cross sectional area) and the above mentioned curvature effect. However this fluid mixing effect within a porous medium is not yet completely understood and the inertial energy losses have so far been quantified through the medium curvature.

These inertial energy losses during the fluid flow due to the mediums curvature can be explained by looking firstly at the kinetic energy (KE) of the fluid, given by \(PV_i^2\).

Changes in direction of streamline patterns result in a change of the fluids KE. These changes may be reversible when KE transforms into pressure or potential energy or irreversible when KE transforms into heat due to attrition. These changes in direction of the streamlines can be brought about by turbulence (where the streamlines intersect and the motion of the fluid is random, as opposed to laminar or viscous flow where the streamlines are ordered and do not intersect) and by physical barriers to the fluid flow, i.e. struts / pore walls. Medium curvature / tortuosity causes fluid to loose inertial energy through the attrition required for the fluid to alter its direction and the extra pressure required in order for the fluid to regain its initial velocity.
2.5.4 Permeability of Gel cast foams

The vast majority of works in literature have used ceramic foams produced by the replication technique and only one study investigates gel cast foams, making a comparison between the two preparation types [195].

The gel cast work shows similar results to those given in Innocentini [194], with both foam types displaying an increase in both the Darcian and non-Darcian permeability constants with increasing porosity. Ceramic replica permeability was shown to be higher than those of gel cast foams at low velocities with them both being more comparable as the velocity increased.

This work also looks at the relationship between critical velocity $V_*$ (the point at which the contribution of both viscous and inertial energy losses are equal) and the properties of the medium. For both production methods porosity had a similar effect on $V_*$, whilst the $V_*$ was much more dependable on variation in the pore size for gel cast foams.

2.6 Material suitability for application as a DPF

The diesel exhaust environment is a particularly harsh one due to the high temperatures and large number of chemical pollutants it contains. As such, any potential material for use as a DPF must be able to fulfil the following criteria [196]:

- Good thermal shock resistance (i.e. low thermal expansion)
- High temperature stability and oxidation resistance
- High mechanical strength
- Resistance to corrosion at high temperature
- Catalyst compatibility
- Processable into a porous body

These requirements make ceramic materials an obvious choice.

To date the material of choice for ceramic DPFs has been cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$). This material has very good high temperature properties including excellent thermal shock
resistance. Also, the technology exists for it to be processed relatively simply into a suitable porous monolith easily adapted for use as a DPF.

More recently some concerns have been raised over the long term suitability of cordierite due to a number of interactions between itself and some chemical pollutants in the exhaust [197]. The effect of a number of pollutants found in diesel exhaust, viz. Ca, Zn, Fe, S and P emitted from the engine and Cu, V and Fe from catalysts, on the properties of cordierite monoliths' has been evaluated [198]. With the exception of Fe, all the pollutants were found to effect the composition of the support, reacting with the cordierite to form new phases at the monoliths surface. This lead to the formation of microcracks at high temperature due to differences in the thermal expansion coefficient between these new phases and the cordierite [197, 198]. Sodium and lead oxides appear to be the most severe pollutants, since they completely destroyed the cordierite structure at temperatures <900°C [197]. Even so cordierite is still the current main choice material for DPF production.

A number of other materials have also been suggested for use as DPFs including mullite, zirconia (ZrO₂), (α and γ) alumina, zirconia toughened alumina (ZTA), SiC, lithium aluminosilicate, aluminium titanate (Al₂TiO₅) and zirconium phosphate ceramics [41, 43, 199]. As previously mentioned, silicon carbide filters are in fact becoming more commonplace [41, 43], albeit far from as common as cordierite filters, since they have suitable high temperature properties and improved strengths. Although a recent report highlights a concern of their apparent inadequate thermal and chemical resistance at high temperature in the presence of such pollutants as Na₂O, PbO and V₂O₅ [200]. Similar concerns have been raised over the attack of PbO and Na₂CO₃ on mullite [199].
Chapter 3

Objectives

As demonstrated in chapter 2, there is a great need to reduce diesel particulate emissions, for which legislation is now in place enforcing reductions, and at present there is no single perfect solution/product to solve the problem. Therefore the market for diesel particulate reduction technologies is still wide open and looking for innovative and new ideas. Secondly, the process of producing porous ceramic foams via the gel casting route is a novel and relatively new technology that has not yet been applied to this particular application. Although ceramic foam DPFs have been investigated previously, the work has only involved those foams produced by the reticulation process. This combination of factors was therefore the main reasoning why this research on gel cast ceramic foam DPFs was performed.

The overall objective of this study was to determine if gel cast ceramic foam technology could be applied to the production of a passive DPF system. In order to reach this objective the study was broken down in to three work themes:

- Feasibility of using gel cast foam DPFs
- Low operating temperature diesel soot oxidation catalyst development
- Production and testing of a catalysed gel cast foam for soot oxidation

Each of these work themes was again sub divided into individual research topics.
The first work theme involved the investigation of foam permeability and foam filtration efficiency, which are the two most important criteria that a DPF has to meet, to assess whether gel cast foams could be used as DPFs. In order to satisfy these criteria the foams structural properties need to be optimised to give the best combination of both permeability and filtration efficiency. The flexibility of the gel casting process allows the foams’ properties to be altered easily.

The second objective was to develop a suitably active catalyst system that would enable the collected soot particulates to oxidise at temperatures experienced in the exhaust thus continuously regenerating the filter. The final objective of this work was to bring both of the above ideas together to produce a catalytically active gel cast foam that is suitable for use as a DPF and evaluate its regeneration performance.
Chapter 4

Experimental Procedure

The following chapter is split into three main work themes to follow the progressive development of the gel-cast foam diesel particulate filter (DPF), viz. feasibility of using gel cast foam DPFs, low operating temperature diesel soot oxidation catalyst development, production and testing of a catalysed gel cast foam for soot oxidation. The latter, which combines the catalyst and foam filter, is the culmination of the research work and is a combination of the first two work themes.

A list of all the chemical and equipment manufacturers details that were used in this study is given in appendix 1.

4.1 Feasibility of Using Gel Cast Foam DPFs

4.1.1 Ceramic foam production and characterisation

Gel-cast ceramic foam production comprises four primary steps:

1. Preparation of a suitable ceramic slurry
2. Foaming of the slurry
3. In-situ polymerisation of the monomer
4. Drying and sintering of the foam

Each is dealt with in a separate sub-section below.
4.1.1.1 Slurry preparation

Previous work [186] has shown that a combination of the polyacrylic acid based dispersants Versicoll KA11 and Dispex A40 work well together in providing suitably stable and well dispersed alumina slurries for foam preparation. The standard recipe used for alumina foam suspension preparation is given below in Table 5

<table>
<thead>
<tr>
<th>Material</th>
<th>Wt% (±0.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>71</td>
</tr>
<tr>
<td>AA monomer</td>
<td>19</td>
</tr>
<tr>
<td>Water</td>
<td>7.5</td>
</tr>
<tr>
<td>Versicoll KA11</td>
<td>0.5</td>
</tr>
<tr>
<td>Dispex A40</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 5. Composition of standard alumina slurry used in foam production

The aqueous based monomer solution used in the production of foams was used as received from Dytech Corporation and contained approximately 30 wt% ammonium acrylate monomers and approximately 1 wt% methylenebisacylamide monomers. The latter are dienes used to promote cross-linking of the acrylate monomers.

Slurries were prepared by hand mixing the ceramic powder, monomer solution, water and Versicoll KA11 together before allowing this mixture to stand for five minutes prior to the addition of the Dispex A40. After hand mixing with a spatula thorough homogenisation of the slurry was performed using a stirrer with a twin propeller type blade at approximately 1000 rpm.

The rheological properties of slurries were evaluated with a Bohlin V88 viscometer using the C25 and C30 concentric cylinders measuring system. Measurements of shear stress were performed over the range of shear rates 18.9 s⁻¹ to 1122 s⁻¹ in an increasing and then decreasing sweep with an interval of 14.2 s⁻¹ between shear rate increments. The shear stress value was measured and averaged over a 5 s integration time for each shear rate. This data was then analysed using the Bohlin V88 software to calculate the corresponding viscosity values. The latter was an important parameter to monitor since it has a powerful effect on the ability of the slurry to be foamed satisfactorily.
4.1.1.2 Foaming suspensions

The basis for the production of porous ceramics via this technique is the introduction of a gaseous phase into the suspension to create voids/pores. This was achieved by firstly conditioning the prepared slurry by mixing it at high shear using a high shear mixer at approximately 1000 rpm for 5 minutes prior to the addition of a foaming agent and vigorously mechanically foaming the slurry at approximately 2000 rpm.

It has been shown that the presence of oxygen during the foaming process inhibits the polymerisation of the ammonium acrylate monomer used [186]. As such the whole foaming process was performed in a sealed glove box under a nitrogen atmosphere. The purging of the glove box was performed by flowing nitrogen through one of the gas taps on the glove box and using a vacuum pump to draw the air out through another tap, as illustrated in the schematic in figure 35.

![Figure 35. Schematic of system used to purge glove box](image)

Oxygen concentration in the main chamber of the glove box was monitored throughout the foaming procedure using a Servomex 570A Oxygen Analyser calibrated using 21% O₂ in N₂ (air). This oxygen meter was equipped with an internal vacuum pump that allowed purging gas from the glove box atmosphere to be flushed through a paramagnetic cell.

The foaming process was not started until the oxygen level in the glove box had attained a level of approximately < 0.3% (3000 ppm) oxygen. A constant flow of nitrogen was generally required in order to maintain suitably low oxygen levels.
Foaming agent trials

A series of trials were performed on the alumina slurries in which a number of commercially available anionic foaming agents were tested to see what effect they had on cell and widow size. Slurries having a total mass of 100 g were prepared as described in section 4.1.1.1 and foamed by the process described in section 4.1.1.2. Foams were prepared using the formulations shown in table 6.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>B25 (ml g⁻¹)</th>
<th>B29 (ml g⁻¹)</th>
<th>Alpha foamer (ml g⁻¹)</th>
<th>Tergitol (ml g⁻¹)</th>
<th>Tᵢ (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
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<td>0.001</td>
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<td>26</td>
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</table>

Table 6. Commercial foaming agents investigated

4.1.1.3 In-situ polymerisation of foams

The polymerisation of the AA monomer used here has been well studied [177, 178, 179, 185]. From this previous work the chemical initiator and catalyst system chosen for use was
ammonium persulphate (APS) as the initiator and N,N,N',N'-tetramethylethlenediamine (TEMED) as the catalyst. This combination forms a suitable redox system with the catalyst acting as the reductant and the initiator as the oxidiser.

A 25 wt% APS solution was prepared by dissolving the required amount of APS powder in deionised water. Previous work [186] has shown that the initiation performance of APS solution decreases with time so freshly prepared solutions were made daily as and when needed.

Polymerisation of thefoamed slurries was performed by adding the required amount of TEMED to the foamed mix using a micro-pipette and further homogenisation of the slurry using the Kenwood mixer to ensure an even distribution of the catalyst. Finally the APS initiator solution was added and the mixture homogenised in a similar fashion. The amounts of TEMED and APS added were both in the range 33 to 500 μl per 100 g of slurry.

This foamed mixture was then transferred to the required mould during the idle period of the polymerisation reaction. The polypropylene beakers used as moulds did not require the use of any mould release agents as samples were readily ejected. The samples were covered with cling film in order to prevent oxygen leaking into the foam, which would prevent complete polymerisation at the surface of the sample.

The amount of APS and TEMED added to the foamed slurries controlled the length of the idle period, i.e. the time before the foam sets and no more changes in the structure of the foam can take place. Since the onset of polymerisation was accompanied by a rise in the temperature of the foam due to the exothermic nature of the polymerisation reaction, the duration of the idle period was monitored using a digital thermometer.

4.1.1.4 Drying and sintering of foams

As with the majority of ceramic forming processes the final stages of production are drying and densification or sintering of the green body. This is an important stage since a large amount of shrinkage occurs within the sample, which if not properly controlled can lead to warping or cracking of the body.
Chapter 4. Experimental Procedure

Post polymerisation the foams were cooled to room temperature and carefully de-moulded. The elastic nature of the gelled foams and the lack of any reactions between the mould walls and the sample made this an easy process. Samples were placed on metal drying racks and left to dry in air for a minimum period of 24 hours before being dried in an oven at 110°C for a further period of 24 hours.

The dried foams were at this stage suitable for green machining and suitable diameter pieces were core drilled out ready for permeability and filtration testing.

Sintering of the foams was performed in a 1600°C Lenton furnace fitted with a Eurotherm digital controller. The heating cycles used to sinter the alumina foams is given in table 7 below. The term step in the cooling portion of the heating rate meant that the furnace was cooled to room temperature at an unmeasured rate since the cooling was uncontrolled. This step method was the quickest method of cooling the furnace to room temperature.

<table>
<thead>
<tr>
<th>Heating rate / °C min⁻¹</th>
<th>Dwell temperature / °C</th>
<th>Dwell time / min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>250</td>
<td>90</td>
</tr>
<tr>
<td>1</td>
<td>700</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>1550</td>
<td>240</td>
</tr>
<tr>
<td>Step</td>
<td>Room temp.</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 7. Sintering cycle used for alumina foam samples

4.1.1.5 Foam characterisation

Density measurement

Sintered foams were machined into regular shapes and had their % theoretical density calculated using the following relationship:

\[
\% \text{ Theoretical density} = \frac{\text{Bulk density of material}}{\text{Crystallographic density of material}} \times 100
\]
Where \[ \text{Bulk density} = \frac{\text{Mass of sample}}{\text{Volume of sample}} \]

The crystallographic density for alumina was taken as 3.94 g cm\(^3\).

The volume of the samples was calculated from the sample dimensions measured using a micrometer (± 0.01 mm) and the mass of each sample was measured on a four figure Sartorius balance (± 0.0001 g). The values obtained for the % theoretical density of the foams has been related to the total porosity (true porosity), \( \varepsilon_t \), of the sample through the relationship:

\[ \varepsilon_t = 100 - \% \text{theoretical density} \]

The total porosity of the samples is a measure of the volume fraction of both the open and closed pores in the body. However, due to the nature of the materials it can be assumed that this porosity value is a direct measure of the open porosity in the foams [186].

**Cell and window size measurement**

Throughout this work the terms “cell” and “window” size will often be referred to. These parameters are defined as shown in figure 36 below.
Chapter 4. Experimental Procedure

Scanning electron microscopy (SEM) was performed on a Leica Cambridge Stereoscan S360 primarily using a back scattered electron imaging technique to study the topography of the foams surface from which an average for both cell and window size was calculated for each foam sample.

Since the alumina foams were non-conducting a certain amount of sample preparation was required. Foam samples were stuck to aluminium SEM stubs using conductive carbon tabs. Conductive silver paint, silver dag, was also applied down one side of the sample from the surface to the SEM stub. Finally the samples were sputter gold coated for a period of 5 minutes.

4.1.1.6 Permeability testing

One of the main parameters of the foams produced that needed measuring was their permeability to air. This arises from the need for the backpressure generated by the ceramic foam DPF in practice to be minimised and be within certain levels stated by the engine manufacturers. Increased backpressure has a detrimental impact on fuel consumption and in the worst-case scenario can lead to damage to the engine.

To be able to quantify the permeability of a material both the backpressure generated and the air velocity at the face of the material need to be measured simultaneously. A simple permeability test rig was developed for this purpose and a schematic of the system is shown in figure 37. The main piping was manufactured from 2 inch diameter clear PVC and the separable sections were bolted together using PVC flanges and compressed cardboard gaskets.
To be able to fit and remove foam samples easily from the apparatus a split length sample holder was made that could be easily bolted together and made leak free using a gasket.

The test rig was designed to be able to measure backpressures over a range of velocities similar to those experienced by current DPFs, approximately 0 - 7 m s\(^{-1}\). In order to achieve this velocity range two different flow meters of differing flow range measurement were used. Firstly the compressed air was passed through a 50-135 l min\(^{-1}\) flow meter which allowed air velocities up to ~2 m s\(^{-1}\) to be measured before changing to a 1-10 l s\(^{-1}\) flow meter to measure velocities up to ~7 m s\(^{-1}\). The correction factor below was used to calculate the actual flow rate in the pipe:

\[
\text{Actual air flow} = \frac{\text{Indicated air flow}}{(f_1 \times f_2)}
\]

Where \(f_i = \sqrt{8.013 \div (1.013 + \text{operating pressure (bar)})}\)
Chapter 4. Experimental Procedure

\[ f_2 = \sqrt{273 + (\text{operating temperature} (\degree C)) + 293} \]

The air temperature was measured prior to each experiment by blowing the air at a low flow rate on to the bulb of a mercury thermometer for a period of 15-20 minutes. The operating pressure at each required airflow was measured using pressure gauge P1 shown in figure 37.

The air velocity at the face of the foam was calculated using the relationship:

\[ Q = V A \]

Where \( Q \) = flow rate (m\(^3\) s\(^{-1}\))
\( V \) = air velocity (m s\(^{-1}\))
\( A \) = cross sectional area of foam (m\(^2\))

Prior to testing, each foam sample was wrapped in electrical insulating tape in order to prevent radial airflow out of the foam. 48 mm diameter samples were placed in the split length sample holder as illustrated in figure 37 and held in place using two O-rings and blu-tac to ensure a leak free fit was achieved.

Backpressure, measured at point P2, was measured at 10 l min\(^{-1}\) intervals over the range 55 to 135 l min\(^{-1}\) and at 0.25 l s\(^{-1}\) intervals over the range 2.5 to 5 l s\(^{-1}\). A manometer was used to measure backpressure at low flows up to a maximum pressure of approximately 260 mm of water (± 1 mm) whilst for greater back pressures a pressure gauge (0-15 kPa ± 0.1 kPa) was used. The error in measured backpressure results was taken from the standard deviation calculated from three separate measurements on the same foam over the same velocity range.

Effect of varying foam lengths on backpressure

The effect of decreasing foam length on the backpressure generated was determined by measuring the backpressure of a foam sample as a function of velocity at foam lengths of 25, 20, 15 and 10 mm. A belt sander was used to sand down the foams to the required lengths.
4.1.1.7 Filtration experiments

One other very important aspect of a DPF system is the ability to filter out of the exhaust gas as much diesel soot as is possible, i.e. to have a high filtration efficiency. The following sections describe the development of a bench top procedure to test the filtration efficiency of the foams.

Development of filtration test rig

The majority of work in the literature investigating the filtration efficiency of DPFs do so using systems connected to a real diesel engine, i.e. fresh diesel soot is filtered out of the exhaust gas stream. Since we did not have any facilities to allow us to do this until late in the project an alternative system needed to be developed.

Printex U is a commercially produced flame soot and is widely used as a model diesel soot by many in the literature. Transmission electron microscopy (TEM) performed on a Jeol JEM100CX was used to compare Printex U to freshly collected diesel soot (from a 1992 Peugeot 205 XLD). A small amount of each type of soot was dispersed in ethanol using an ultrasonic bath before a single drop was placed onto a thin film of carbon that had been floated onto a TEM grid.

A suitable method of producing an aerosol of Printex U that could then be connected to the permeability test rig, shown in figure 37, was developed and a schematic of this is shown in figure 38 below.
Figure 38. Schematic of system used to develop a Printex U aerosol for filtration experiments

A bed of ballotini (5 mm diameter glass beads) approximately 50 mm in depth was used to aid in breaking up any agglomerates present in the aerosol. The particle size distribution (PSD) of the aerosol generated was measured using a LAS-X laser aerosol spectrometer.

**Effect of foam properties on the filtration efficiency of foams**

A selection of approximately 25 mm long alumina foams with varying density, cell and window size were used to evaluate the effect of foam properties on filtration performance.

Foams were once again sealed with electrical insulating tape and weighed on a four-figure balance prior to being fixed in the split length sample holder using O-rings and Blu-Tac. The exhaust side, post foam filter, of the piping was fed into a gas bubbler containing acetone that acted as a final stage filter to collect any Printex U that passed through the foam filter.

The aerosol generator container was filled with $0.150 \pm 0.0005$ g Printex U before an airflow of $65 \text{ l min}^{-1}$ was passed through the system for a period of 60 seconds. After this loading period was completed the foam was carefully removed from the sample holder and reweighed to calculate the trapped mass of Printex U. The Printex U collected in the acetone and any stuck to the pipe walls post foam filter was collected on Whatman #1 filter paper and allowed
to dry in air for a minimum of 4 hours before being weighed on a four figure balance. The filtration efficiency of the foam filter was then calculated from the relationship:

$$\% E_f = \left[ \frac{(M_d - M_c)}{(M_p + (M_d - M_c))} \right] \times 100$$

Where $\% E_f = \%$ filtration efficiency

- $M_d =$ Mass of dirty foam filter
- $M_c =$ Mass of clean filter
- $M_p =$ Mass of soot passed through filter

The mass of Printex U introduced into the system was not used in the calculation since a large portion did not actually make it to the filter but stuck to the pipe walls instead.

Foam filtration efficiencies were measured at various Printex U loading levels of approximately 1 to 10 g l$^{-1}$ by repeating the above loading procedure. Post testing, the foams were cleaned of Printex U by heating to 800°C at 15°C min$^{-1}$ for a period of 1 hour. The standard error reported was based on the standard deviation for three separate $\% E_f$ measurements on the same foam at a fixed soot loading level.

**Effect of Printex U loading on backpressure**

The effect of Printex U loading on the foams permeability was measured. Foams loaded with a known amount of Printex U were refitted into the sample holder and had their permeability re-measured using the method described previously. Due to some Printex U being blown off the foam during these tests, the foams were reweighed after backpressure readings taken at the following airflow rates, 85 and 125 l min$^{-1}$ and at 3, 4 and 5 l s$^{-1}$.

**Effect of increased foam length on filtration efficiency**

A series of foams were used to measure the effect of increasing the length of foam filter on filtration efficiency. The testing procedure used was exactly the same as that described above except that efficiencies were recorded after only one Printex U loading cycle and not at increased loadings.
4.2 Low Operating Temperature Diesel Soot Oxidation Catalyst Development

4.2.1 Catalyst material production and characterisation

The following section outlines the methods used in the production of a range of potential diesel soot oxidation catalysts and the procedure followed in the selection of a final catalyst material for combination with the foam filter to produce a catalytically coated foam DPF. A range of catalyst materials previously investigated in the literature for use as diesel soot oxidation catalysts as well as a number of previously unreported materials were examined.

4.2.1.1 Preparation of oxidation catalysts

Four main types of catalyst material were produced in the laboratory:

1. Spinel type materials
2. Perovskite type materials
3. Vanadate based materials
4. Alkali metal based materials

Preparation of spinel catalysts

The spinel type catalysts produced and the reagents used in their production are given below in table 8.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reagent 1</th>
<th>Reagent 2</th>
<th>Reagent 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>Copper acetate</td>
<td>Iron nitrate</td>
<td></td>
</tr>
<tr>
<td>CuMn$_2$O$_4$</td>
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<tr>
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<tr>
<td>Cu$<em>{0.5}$Co$</em>{0.5}$Fe$_2$O$_4$</td>
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<tr>
<td>Cu$<em>{0.5}$Co$</em>{0.5}$Mn$_2$O$_4$</td>
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<td>Cobalt acetate</td>
<td>Manganese acetate</td>
</tr>
</tbody>
</table>

Table 8. Spinel catalysts produced and the starting reagents used
Chapter 4. Experimental Procedure

The method used to prepare the spinel catalysts is an adaptation of one used by Shanguan et al [147, 148] and is based on the citric acid-aided process.

Aqueous solutions of the required reagents for each catalyst material were produced and mixed in the correct molar ratios, e.g. for CuFe$_2$O$_4$ Cu-acetate was mixed with Fe-nitrate in a 1:2 molar ratio respectively. Citric acid (C$_6$H$_8$O$_7$. H$_2$O) was then added to the mixture in a 1:1 molar ratio between itself and the total amount of metal cations. This solution was then thoroughly mixed before being evaporated to dryness with vigorous stirring using a combination magnetic stirrer hotplate. The dried powder was then ground in a pestle and mortar. Decomposition of the powder was achieved by heating to 400°C for a period of 1 hour. Post cooling in air the powder was reground in a pestle and mortar. A final calcinations stage was performed in air at 700°C for 4 hours before a final grinding stage.

**Preparation of perovskite catalysts**

Table 9 below shows the perovskite catalyst materials produced and the reagents used in their production.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reagent 1</th>
<th>Reagent 2</th>
<th>Reagent 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.9}$K$</em>{0.1}$FeO$_3$</td>
<td>Lanthanum acetate</td>
<td>Potassium acetate</td>
<td>Iron nitrate</td>
</tr>
<tr>
<td>La$<em>{0.9}$K$</em>{0.1}$MnO$_3$</td>
<td>Lanthanum acetate</td>
<td>Potassium acetate</td>
<td>Manganese acetate</td>
</tr>
<tr>
<td>La$<em>{0.9}$K$</em>{0.1}$CoO$_3$</td>
<td>Lanthanum acetate</td>
<td>Potassium acetate</td>
<td>Cobalt acetate</td>
</tr>
</tbody>
</table>

**Table 9.** Perovskite catalysts produced and the starting reagents used

The method used for perovskite production followed the same process as described for spinel catalysts above until the final calcination stage when the powder was crushed and then decomposed and calcined in one stage by heating the sample in a tube furnace up to 850°C for a period of 10 hours as in the method outlined by Teraoka et al [144].

**Vanadium containing catalysts**

A number of vanadium containing catalyst systems have been investigated by workers in the literature [137, 140]. Two of these systems were included in this catalytic screening programme (a) K$_4$V$_2$O$_7$ and (b) CsVO$_3$-MoO$_3$. 

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**Preparation of K$_4$V$_2$O$_7$**

A similar method to that used by Saracco et al was used [137] in the preparation of potassium pyrovanadate. Vanadium pentoxide (V$_2$O$_5$) and potassium carbonate (K$_2$CO$_3$) were mixed together before being heated in a tube furnace up to 475°C for 2 hours, then cooled and ground before being fused together by melting at 780°C for 4 hours and subsequently ground to a fine powder in a pestle and mortar.

**Preparation of CsVO$_3$-MoO$_3$**

A method similar to that reported by Jelles et al [140] was used in the preparation of CsVO$_3$-MoO$_3$. Firstly, CsVO$_3$ was prepared by calcining stoichiometric quantities of V$_2$O$_5$ and Cs$_2$CO$_3$ at 460°C for 2 hours, followed by melting at 760°C under air for 4 hours, and subsequent crushing in a pestle and mortar. The catalyst was then prepared by mixing CsVO$_3$ and MoO$_3$ together in a 75:25 mol% ratio before heating to 465°C for 1 hour under air, followed by subsequent crushing.

**Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$ (Li/Na/K) catalyst preparation**

A method similar to that described by McKee et al [132] was used to prepare the eutectic mixture 31.5% Li$_2$CO$_3$ / 25% Na$_2$CO$_3$ / 43.5% K$_2$CO$_3$. Referred to here after as Li/Na/K. Finely ground powders of each component were well mixed in the correct molar ratios in a pestle and mortar. Fusion of the mixture was then performed by heating the mixture in an alumina crucible to 520°C, approximately 100°C above the eutectic melting point, for 6 hours at a heating rate of 5°C min$^{-1}$ in air. After cooling in air the fused Li/Na/K mixture was ground up in a pestle and mortar.

**K$_2$CO$_3$-KCl catalyst preparation**

Once again a method similar to that used by McKee et al [132], as described above for Li/Na/K was used to prepare the eutectic mixture 65% K$_2$CO$_3$ – 35% KCl. Fusion of the mixture was performed by heating the mixture to 750°C, approximately 100°C above the eutectic melting point, for 6 hours at a rate of 5°C min$^{-1}$. After cooling in air the fused K$_2$CO$_3$-KCl mixture was ground up in a pestle and mortar.
Other catalyst materials screened

In addition to the catalyst materials produced in the laboratory a selection of other materials obtained direct from a number of chemical suppliers were tested in the screening experiments:

- Alumina (Al₂O₃)
- Zirconia (ZrO₂)
- Iron (II) Oxide (Fe₂O₃)
- Ceria (CeO₂)
- Titania (TiO₂)
- Zinc Oxide (ZnO)
- Lithium aluminosilicate (LAS) (Li₂O·Al₂O₃·8SiO₂)

More information on all the catalyst and catalyst precursor material suppliers used can be found in appendix 1.

4.2.1.2 Catalyst material characterisation

Both laboratory prepared and purchased catalyst powders were passed through a 125 μm sieve and the retained fraction was either discarded or crushed again until it all passed through the sieve. Only the sieved fraction was used for subsequent experiments.

Laboratory prepared catalysts were analysed by X-ray diffraction (XRD) using a Bruker diffractometer with a graphite monochromator and Cu, Kα radiation to check the phases present. Scans of 2θ ranged from 10° to 100° with a step angle of 0.02° and exposure time of 2 s per step.

Catalyst specific surface area measurement was performed on a Quantachrome Monosorb Direct Reading Surface Area Analyser using a modified BET equation for single point surface area determination.
4.2.2 Catalyst screening

The main purpose of a diesel soot oxidation catalyst material is to be able to catalyse the combustion of diesel soot, i.e. reduce the temperature at which combustion occurs. The objective operating temperature range for such a catalyst system was chosen to be 250°C to 450°C therefore ensuring continuous filter regeneration under normal driving conditions.

The aim of the following experiments was to systematically discard potential catalyst materials until one catalyst material could be selected for use in the final stages of the work. This process begun with a thermo gravimetric analysis (TGA) study that was used to rank the materials in terms of their catalytic activity. A number of potentially interesting materials were then selected for further experiments to assess their performance under more specific diesel exhaust type conditions.

4.2.2.1 Preparation of TGA samples

Work reported in the literature by Neeft et al [119] has highlighted the difference that can be obtained in catalytic activity simply through altering the method of TGA sample preparation used. Neeft goes on to define two distinct types of sample preparation method, “tight” and “loose”.

In order to verify Neefts’ work and define standard mixing procedures for this work, samples of Fe₂O₃ and K₂CO₃-KCl were ball milled with Printex U in 125 ml glass sample bottles, using three 8 mm alumina balls at a speed of approximately 60 rpm, for periods of 5, 20, 80, 120 and 160 minutes. Two other sample preparation techniques were also investigated (1) shaking the catalyst and Printex U together in a 100 ml sample bottle and (2) passing the two components through a 125 μm sieve twice. In all cases the total sample mass was maintained at 0.60 g (± 10 mg) and the ratio between catalyst and Printex U was kept constant at 2:1. All of these samples were then analysed by TGA using the method outlined in section 4.2.2.2 below. These mixtures were also characterised by SEM and TEM to try to visually explain the differences in activity.
The resulting preparation methods adopted for use in this study were ball milling the catalyst–Printex U mixtures for 120 minutes to provide “tight” samples and passing the two components through a 125 μm sieve twice for preparation of “loose” samples.

4.2.2.2 TGA of catalyst/soot mixtures

The use of TGA to study potential diesel soot oxidation catalysts is very well documented in the literature [117]. Due to difficulties in obtaining consistent compositions of diesel soot in fairly large quantities most researches use model diesel soot for TGA studies. The most recent studies use Printex U as a model diesel soot as it has been shown to be a good alternative and commercially available, see appendix 2 [201]. The point should be noted that since Printex U contains a lot less adsorbed hydrocarbons on its surface it will appear less reactive in TGA experiments than if real diesel soot were used [201]. Printex U was chosen here as the model diesel soot to be used in the following screening experiments.

TGA was performed on a TA Instruments Hi-Res modulated TGA 2950. Analysis was performed under a steady flow of approximately 100 ml min⁻¹ air using alumina sample pans. Approximately 5-10 mg (± 0.1 mg) of the Printex U–catalyst mixture, prepared as described in section 4.2.2.1, was placed in an alumina sample pan before the balance was zeroed and the mixture heated to temperature. The metal oxide materials were heated at 20°C min⁻¹ up to 300°C then at 10°C min⁻¹ up to 725°C whilst the more active groups of catalyst materials were heated at 20°C min⁻¹ up to 250°C then 5°C min⁻¹ up to 600°C.

Weight loss data from the TGA was collected on a PC connected to the thermo-balance. This data was then analysed using the Universal Thermal Analysis software package. The derivative of the weight loss versus temperature curve, DTGA, was used to compare the catalytic performance of the various materials, using a number of specific points to evaluate and rank catalytic performance as illustrated in figure 39.
Figure 39. Specific points on a typical DTGA curve used to evaluate catalytic performance

Where:

- $T_{ig}$ – ignition temperature
- $T_{max}$ – temperature of the maximum rate of Printex U combustion
- $T_{final}$ – temperature at which the combustion of the Printex U is completed
- $R_{max}$ – maximum rate of Printex U combustion at $T_{max}$

Due to the cost and time required to run each TGA sample it was felt that in order to determine an error in the reported $T_{ig}$, $T_{max}$, $T_{final}$ and $R_{max}$ values the standard deviation in each parameter from 3 separate samples of CuFe$_2$O$_4$-Printex U prepared using both the techniques outlined in section 4.2.2.1 were calculated and would be used throughout.

TGA was performed on all the catalyst materials listed in sections 4.2.1.1. A sample mixed with alumina (Al$_2$O$_3$) powder was used as a control for the non-catalytic combustion of Printex U since alumina has been shown by a number of authors to be inert in the reaction [120,121]. The presence of alumina is also beneficial since it acts as a dilutent in the mixture, this helps to minimise thermal spikes that can occur during the highly exothermic oxidation.
reaction [201]. A number of the most promising active catalysts were selected and used in the next stage of the screening experiments.

4.2.2.3 Sulphur dioxide poisoning

Due to the presence of sulphurous compounds in diesel fuel, sulphur dioxide (SO₂) is present in diesel exhaust gas [5]. A number of diesel soot oxidation catalytic systems have been shown to be sensitive to the presence of SO₂ in the exhaust gas, most notably that of Johnson Matthey’s CRT system [158]. Current EU legislation permits a maximum fuel sulphur content of 350 ppm [202]. This figure is being significantly reduced over the coming years such that zero sulphur (<10 ppm) diesel will be mandatory by 2011 [202]. This reduction is being partly driven by a number of promising diesel exhaust after-treatment devices that are sulphur intolerant.

In order to examine the effect SO₂ had on the selected catalyst materials the following experiment was performed. Approximately 0.8 g of each catalyst was spread in a thin layer over a silica glass slide and placed in a tube furnace. A gaseous mixture of 100 ppm SO₂ at 20 ml min⁻¹ and air at 180 ml min⁻¹ was passed over the catalyst sample in order to provide an SO₂ concentration of approximately 10 ppm in the gas stream. Such a concentration is equivalent to a fuel sulphur content of approximately 250 ppm [5]. Samples were poisoned in this way for periods of 1, 24 and 240 hours at temperatures of 400°C and 600°C. SO₂ delivery did not commence until the required temperature had been reached.

After cooling each sample was prepared for TGA using the method outlined in section 4.2.2.1 and tested using the equipment and procedure described in section 4.2.2.2.

4.2.2.4 Hygroscopicity of alkali metal catalysts

It was noted during the course of the screening experiments that the alkali metal catalysts, in particular K₂CO₃-KCl, appeared to adsorb moisture from the atmosphere, i.e. they exhibited hygroscopic behaviour.

In order to investigate this behaviour a simple experiment was performed. Approximately 0.01 g of both catalysts was weighed onto a glass slide. The slide was then left to stand in the
laboratory for a period of 1 hour during which time its weight was periodically monitored every 5 minutes on a four figure balance. The air temperature was 20°C and 57.5% relative humidity. This experiment was repeated three times to get an average value for the amount of moisture each catalyst adsorbed over 1 hour.

4.2.2.5 Effect of oxygen concentration

Although a diesel engine is a lean burn engine, i.e. it operates with an excess of oxygen, the oxygen concentration present in the exhaust is rarely the same as air (~21% O₂). In general the oxygen concentration in diesel exhaust gas varies between 3 – 17% O₂ [3]. In the previous screening experiments in section 4.2.2.2 all of the TGAs were performed using air.

Selected catalyst materials were once again subjected to TGA but at decreasing oxygen concentrations of 15, 10, 5, 2.5, 0.5 and 0% O₂. The oxygen concentration was set by diluting the air supplied to the furnace of the thermo-balance with pure N₂. The oxygen concentration of the gas exiting the furnace was monitored using a Servomex 570A oxygen analyser. Once the required oxygen level was achieved the TGA experiment was performed as described in section 4.2.2.2.

4.2.2.6 Effect of varying catalyst : model soot ratio

The Printex U – catalyst mixtures prepared as described in section 4.2.2.1 for the TGA screening experiments were all made in a 2:1 (Catalyst : Printex U) by weight ratio. This allowed samples to be compared relative to one another. However, the effect of the ratio of catalyst : Printex U in the mixture on catalytic activity is an important parameter since it is a measure of the catalysts mobility, ω [136].

Selected catalyst materials were used in preparing TGA samples using the method described in section 4.2.2.1 at catalyst : Printex U ratios of 6:1, 4:1, 2:1, 1:1, 1:2, 1:4 and 1:6. In all cases the total sample mass was maintained at 0.6 g. TGA of the samples was performed as described in section 4.2.2.2.
4.2.2.7 Repeated combustion cycling

In practice a diesel soot oxidation catalyst will be used thousands of times during its operational lifetime. The following experiment was performed on the selected catalytic material to get an idea of its stability for repeated use. Although far from conclusive, it was felt such an experiment would give an initial indication of the catalysts expected lifetime.

Approximately 3 g of catalyst was mixed in a 1:1 by weight ratio with Printex U by shaking the two together in a sample jar. This mixture was then placed in an alumina sample boat before being placed in a tube furnace and heated to 500°C at 5°C min⁻¹ and held there for 1 hour before cooling to room temperature. The re-crystallised catalyst was then removed from the boat and reground in a pestle and mortar. The catalyst was then remixed with the correct amount of Printex U to give a 1:1 weight ratio and the above heating procedure repeated. Samples of catalyst were taken after 1, 5, 10 and 50 heating cycles and TGA samples prepared and tested as described in sections 4.2.2.1 and 4.2.2.2 respectively.

4.3 Production and Testing of a Catalysed Gel Cast Foam for Soot Oxidation

At this point in the research work optimisation of foams, both in terms of their permeability and filtration efficiency had been completed and a suitably active catalyst material had also been produced and deemed suitable for use as a potential diesel soot oxidation catalyst. The final stage of the work was therefore the process of combining the above two components; the foam filter and the catalyst, to manufacture and evaluate the performance of a catalysed gel cast ceramic foam filter for the oxidation of a model diesel soot.

4.3.1 Selection of a suitable ceramic support material

An important aspect in producing a DPF is whether the presence of the catalyst material has any effect on the properties of the foam, e.g. mechanical strength, or whether the presence of the ceramic has an adverse effect on the catalytic activity.
Chapter 4. Experimental Procedure

There are a good number of ceramic materials possessing the necessary materials properties required by a DPF, as described in section 2.6. Of these materials the following four were chosen to test their suitability for combination with the chosen catalyst to produce a catalysed DPF: alumina, cordierite, mullite and lithium aluminosilicate.

4.3.1.1 Effect of reacting ceramic and catalyst

Approximately 0.5 g (±0.01 g) of each ceramic material was mixed in a pestle and mortar with a similar amount of catalyst. This mixture was then placed in a 12 mm diameter die and pressed at room temperature to a pressure of 10 MPa. The pellets were then heat treated at temperatures of 500°C and 750°C for periods of 1, 24 and 240 hours. Post cooling in air, visual observations of the pellets were made before the pellets were reground in a pestle and mortar.

A sample of each heat treated mixture was examined by X-ray diffraction (XRD) using a Philips diffractor with a graphite monochromator and Cu,Kα radiation to determine if any phase changes had occurred.

Samples were also examined by TGA to see if catalytic activity had been affected. Sample preparation was the same as that described in section 4.2.2.1 and the TGA procedure used was the same as in section 4.2.2.2.

4.3.2 Production of catalysed DPFs

Two different methods of applying the catalyst to the foam were tested. Since acetone was shown to be a suitable carrier solvent it was used in both preparation techniques. To evaluate the effect of acetone TGA was performed on some Li/Na/K catalyst material that had been left in acetone for 24 hours before being dried and prepared then tested by the methods outlined in sections 4.2.2.1 and 4.2.2.2. The results showed no decrease in catalytic performance compared to fresh catalyst. The catalyst-acetone suspensions were prepared by adding approximately 1 g of catalyst to 150 ml of acetone. An ultrasonic bath was used to aid in the dispersion of the catalyst.
Firstly cylindrical foam pieces approximately 10-12 mm in length were weighed on a four figure balance (± 0.0001 g) and then placed in a flat bottomed funnel attached to a beaker, as shown in figure 40. The acetone-catalyst suspension was repeatedly washed through the foam three times before placing the foam into a drying oven at 45°C for 1 hour to evaporate the acetone. After cooling to room temperature the foam was reweighed. This process was repeated until the required catalyst loading was achieved.

![Diagram](image)

**Figure 40.** Schematic of the apparatus used to prepare catalysed foams via the filtration method

The second method used for catalysed foam production was a simple dipping process. Similar size foam pieces to those used above were weighed dry before being repeatedly dipped into a freshly agitated suspension of acetone-catalyst. Samples were again dried at 45°C for 1 hour prior to cooling and reweighing. This dipping-drying routine was repeated until the required amount of catalyst had been deposited on the foam.

The foams produced via both techniques underwent identical heat treatments prior to characterisation and testing. The foams were heated in a tube furnace to 500°C for 1 hour at
10°C min⁻¹. This heating process was used to melt the catalyst onto the foam with the aim of securing the catalyst to the surface. Prior to and post heating foams were weighed on a four figure balance.

4.3.2.1 SEM and EDX characterisation

SEM examination of the catalysed foams was performed on a Leica Cambridge Stereoscan S360. Samples were examined both pre- and post heat treat at various catalyst loading contents. Sample preparation and SEM operation was the same as that described in section 4.1.1.5.

Energy dispersive X-ray analysis (EDX) was performed in combination with the SEM using a Link AN10000 system. EDX spot analysis was performed on samples using a collection period of 50 seconds. This elemental analysis technique was used to confirm the identity and the location of the catalyst material.

4.3.2.2 Permeability testing of catalysed foams

Permeability measurements were performed on catalysed foam samples prepared using both techniques, in order to determine what effect catalytic coatings had on the foam permeability, following the same procedure outlined in section 4.1.1.6.

4.3.2.3 TGA testing of catalysed foams

A number of catalysed foam pieces were lightly loaded with approximately 1.3 g l⁻¹ Printex U by following the procedure used in the foam filtration experiment work described in section 4.1.1.7. Approximately 10 mm diameter samples were core drilled out of the loaded foams. These pieces were small enough to be able to fit in the alumina sample pans used in the thermo-balance. TGA of catalysed and un-catalysed foams was performed using the procedure described in section 4.2.2.2.
5.1 Feasibility of Using Gel Cast Foam DPFs

This section begins with the characterisation of the alumina aqueous suspensions used in the preparation of foams. Next, the performance of a number of different commercial foaming agents was assessed in terms of their foaming ability and their effect on the foams structural properties. Characterised foams had their permeability and filtration efficiencies measured using dedicated pieces of kit that allowed relationships between the structural properties of the foams and their permeability and filtration efficiencies to be drawn. Finally, the collected data was used to optimise the structural properties of the gel cast foams for suitability to be used as DPFs.

5.1.1 Foam production, characterisation and evaluation

5.1.1.1 Rheological characterisation

Aqueous alumina suspensions, having the composition given in table 5, were produced using the procedure outlined in 4.1.1.1. The rheological behaviour of these suspensions is given by the plots of viscosity and shear stress as a function of shear rate, shown in figure 41. Increasing and decreasing shear rate sweeps were employed for these measurements.

Time dependent effects on slurry rheology were also measured. Figures 42 plots the change in slurry viscosity at shear rates of 80.5 s\(^{-1}\), 205 s\(^{-1}\) and 895 s\(^{-1}\) over a period of 900 s.
Figure 41. Plot illustrating the rheological behaviour of a standard 71 wt% alumina slurry

Figure 42. Standard alumina slurry viscosity plotted as a function of time at shear rates of 80.5 s\(^{-1}\), 205 s\(^{-1}\) and 895 s\(^{-1}\).
5.1.1.2 Foaming slurries

A range of surfactants, given in table 6, were examined to assess their performance in foaming a standard alumina slurry, using the procedure outlined in section 4.1.1.2. The effect of increasing foaming agent concentration on the maximum foam volume generated, after 8 minutes stirring is given in figure 43 below, whilst the plot in figure 44 shows foam volume generation as a function of stirring time at a foaming agent concentration of 0.6 ml per 100 g of standard alumina slurry.

![Figure 43. Effect of increasing foaming agent concentration on the maximum foam volume](image1)

![Figure 44. Foam volume generated as a function of time](image2)
Visual examination of the generated foams in glass measuring cylinders allowed information regarding bubble growth and foam stability to be assessed, the results are summarised below in table 10.

<table>
<thead>
<tr>
<th>Foaming Agent</th>
<th>Foam Collapse Time</th>
<th>Max Bubble Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>B25</td>
<td>Stable after 60 min</td>
<td>&gt; 1000 µm after 30 min</td>
</tr>
<tr>
<td>B29</td>
<td>25 min</td>
<td>~ 500 µm</td>
</tr>
<tr>
<td>Alpha foamer</td>
<td>45 min (visible drainage after 20 min)</td>
<td>&gt; 1000 µm after 30 min</td>
</tr>
<tr>
<td>Tergitol TMN10</td>
<td>Stable after 1 hour</td>
<td>800 µm after 60 min</td>
</tr>
</tbody>
</table>

Table 10. Summary of foam stability and bubble size observations

5.1.1.3 Foam characterisation

All the foams produced were characterised post sintering to determine their % theoretical density, which was then related to foam porosity, as described in section 4.1.1.5. The foams structural parameters, cell and window size were measured using the procedure described in section 4.1.1.5.

The relationship between the cell and window diameters for the produced alumina foams is given in figure 45 and the relationship between % theoretical density and their average cell and window diameters is given in figure 46.

Figure 45. Relationship between the average cell and window diameters for alumina foams
Chapter 5. Results

Figure 46. Relationship between % theoretical density and the average cell and window diameters for alumina foams

Changes in porosity and the cell and window sizes of foams were also accompanied by a resultant change in the structural morphology of the foams. Figure 47 and 48 compare the SEM micrographs of foam #9 with $\varepsilon = 93\%$, $d_{cell} = 0.80$ mm and $d_{win} = 0.24$ mm to that of foam #30 with $\varepsilon = 84.5\%$, $d_{cell} = 0.30$ mm and $d_{win} = 0.10$ mm, respectively. Both foams were prepared using alpha foamer, see table 6 section 4.1.1.2 for details, as a foaming agent but the idle times were different, the first foam, figure 47, had an idle time of approximately 20 minutes and second, figure 48, was approximately 8 minutes.
Figure 47. SEM micrograph of an alumina foam with $\varepsilon = 93\%$, $d_{\text{cell}} = 0.80$ mm
$d_{\text{win}} = 0.24$ mm

Figure 48. SEM micrograph of an alumina foam with $\varepsilon = 84.5\%$, $d_{\text{cell}} = 0.30$ mm and
$d_{\text{win}} = 0.10$ mm
5.1.1.4 Relationship between structural properties and process parameters

The main parameters that influence the cell diameter in foams is (1) the time allowed for bubble growth, i.e. the idle time, and (2) the type of foaming agent used. The effect of changing the type and concentration of foaming agent as a function of idle time used in the manufacture of the foams on cell diameter is plotted in figure 49.

![Diagram showing the effect of varying the type and concentration of foaming agent as a function of idle time on the average cell diameter]

Figure 49. Effect of varying the type and concentration of foaming agent as a function of the idle time on the average cell diameter
5.1.1.5 Foam permeability

The permeability of each of the alumina foams was calculated from the measured values of backpressure and air velocity using the apparatus and procedures outlined in section 4.1.1.5.3. Equation 2 was used to give permeability values not allowing for compressible effects and equation 3 in allowing for compressible effects. Values used for the viscosity, \( \mu \), and density, \( \rho \), of the air and were \( \mu = 1.827 \times 10^{-5} \) Pa s and \( \rho = 1.3 \) kg m\(^{-3} \).

Figure 50 below gives an example of the type of plot and regression analysis curve fitted to the data used to obtain the Darcian and non-Darcian permeability constants, \( k_1 \) and \( k_2 \) respectively.

![Figure 50. Result of curve fitting the Forchheimer equation to data collected for alumina foam sample #18 without allowing for the compressibility of the air](image)

Values for the calculated Darcian, \( k_1 \), and non-Darcian, \( k_2 \), permeability constants are given in Appendix 2.
**Relationship between gel cast foam properties and permeability**

The permeability of any porous media is directly influenced by the macroscopic properties of the body. For gel-cast ceramic foams the primary macroscopic properties influencing permeability are (1) foam porosity, (2) average cell and (3) average window size.

The plots in figures 51, 52 and 53 illustrate the relationship between the Darcian permeability constants, $k_1$, and the average cell and average window diameters and the foams porosity respectively. Figures 54, 55 and 56 illustrate the relationship between the non-Darcian permeability constant, $k_2$, and the average cell and average window diameters and the foams porosity respectively. Permeability constants have all been calculated allowing for the compressibility of air.

![Figure 51. Plot of the relationship between the Darcian permeability constant $k_1$ and foam porosity](image-url)

```plaintext
Figure 51. Plot of the relationship between the Darcian permeability constant $k_1$ and foam porosity
```
Figure 52. Plot of the relationship between the Darcian permeability constant $k_1$ and the average cell diameter

Figure 53. Plot of the relationship between the Darcian permeability constant $k_1$ and the average window diameter
Figure 54. Plot of the relationship between the non-Darcian permeability constant $k_2$ and foam porosity.

Figure 55. Plot of the relationship between the non-Darcian permeability constant $k_2$ and average cell diameter.
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Figure 56. Plot of the relationship between the non-Darcian permeability constant $k_2$ and average window diameter

Predicting gel cast foam permeability

Experimentally determined Darcian permeability constants are compared to those calculated using the relationships proposed by Ergun [191] and Burke [223] in figures 57 and 58 respectively using values for the average cell and window diameters as the particulate diameter, $d$, as a function of foam porosity. Similarly the experimentally determined non-Darcian permeability constants are compared in figures 59 and 60 to values calculated using the Ergun equation, equation 4, and a modified Ergun equation, equation 5, using average cell and window diameters as a value for $d$.

The results of foam backpressure per unit length calculated using a modified Ergun type equation in comparison to experimentally obtained data are given in figure 61 for 94, 89 and 85% porosity foams.
Figure 57. Experimentally determined and calculated Darcian permeability constants using Erguns equation

Figure 58. Experimentally determined and calculated permeability constants using Burkes equation
Figure 59. Experimentally determined and calculated non-Darcian permeability constants using Erguns equation

Figure 60. Experimentally determined and calculated non-Darcian permeability constants using a modified Ergun equation
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Figure 61. Experimental and predicted foam backpressures using the modified Ergun equation for foams of 94%, 89% and 85% porosity

Effect of varying foam length on backpressure

The effect of changing foam length on the backpressure generated in foam sample #26 ($\varepsilon = 92\%$, $d_{\text{cell}} = 670$ $\mu m$ and $d_{\text{window}} = 240$ $\mu m$) is shown below in figure 62.

Figure 62. Effect of changing filter length on backpressure in a single foam sample
5.1.1.6 Filtration performance

The following section begins by presenting results of TEM experiments performed to compare the size and shape of the model diesel soot used to that of freshly collected diesel soot. A filtration rig was developed, see section 4.1.1.7, to simulate as closely as possible on the bench an exhaust similar to that of an actual diesel engine and results of the achieved particle size distribution in the aerosol generated are given. The remainder of this section deals with the effects various foam parameters have on the filtration efficiency and finally the effect the filtered particles have on the backpressure.

TEM examination of Printex U

The micrographs from a TEM study to compare the particle size and shape etc of a model diesel soot, Printex U and freshly collected automotive diesel soot are shown in figures 63 and 64 respectively.

![TEM micrograph of freshly collected diesel soot particulates](image)

**Figure 63.** TEM micrograph (x 160k) of freshly collected diesel soot particulates
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Figure 64. TEM micrograph (x 160k) of Printex U particles

Particle size distribution of generated aerosol

The plot in figure 65 displays the average particle size distribution obtained for the aerosol of Printex U particles generated for use in the filtration experiments.

Figure 65. Particle size distribution of generated Printex U aerosol
Effect of particulate loading on filtration efficiency

The effect of increasing the level of model soot introduced into the filtration system, hence the amount reaching the foam filter, on the filtration efficiency of similar cell and window diameter foams with porosities ranging between 87, 90, 92 and 94 % is shown in figure 66 below.

![Graph showing filtration efficiency as a function of porosity](image)

**Figure 66. Effect of increased soot loading on filtration efficiency as a function of porosity**

Effect of foam properties on filtration efficiency

Since ceramic foam filters are known to act via a deep bed mechanism of filtration, as described in section 2.2.3, in which the whole length of the foam body filters out particles, properties such as porosity and cell and window size are once again expected to be very important determinant factors. A series of filtration experiments were performed on selected foams to enable relationships between the foams’ properties and filtration efficiency to be made.

The plot in figure 67 shows the relationship between foam porosity and the filtration efficiency at increasing levels of soot loading. Relationships between filtration efficiency and foam cell and window diameters are shown in figures 68 and 69 respectively.
Figure 67. Relationship between foam porosity and filtration efficiency at soot loading levels of 1.5, 5.3 and 6.6 g/l (d_{cell} \sim 0.6 - 0.8 \text{ mm}, d_{win} \sim 0.2 - 0.4 \text{ mm})

Figure 68. Relationship between the average cell diameter and filtration efficiency at soot loading levels of 1.5, 5.3 and 6.6 g/l (\varepsilon \sim 88-90\%)
Figure 69. Relationship between the average cell diameter and filtration efficiency at soot loading levels of 1.5, 5.3 and 6.6 g/l (ε ~ 88-90%)

Effect of increasing foam length on filtration efficiency

As previously mentioned in section 2.2.3, foam filters act by a deep bed filtration mechanism, i.e. the whole body acts as a filter, as such, an important parameter affecting filtration efficiency is the filter length. Figure 70 below shows the relationship between filter length and filtration efficiency. Since individual foam samples were prepared at lengths of approximately 25 mm a series of four foams, samples #10, 12, 15 and 16, were combined in order to obtain filtration efficiency results at approximately 25, 50, 75 and 100 mm lengths.
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Figure 70. Effect of increased filter length on filtration efficiency

Effect of filtered soot on backpressure

Particles of Printex U that were filtered out of the gas stream by the foam filter were trapped within the tortuous bubble like structure of the gel-cast foam as illustrated by the SEM image in figure 71.

Figure 71. SEM micrograph of trapped Printex U particles within a gel cast foam
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The effect the presence trapped Printex U particles had on the back pressure is graphically quantified in figure 72, using a foam with 89% porosity and 0.7 mm average cell and 0.2 mm average window diameter as an example.

![Graph](image)

Figure 72. Effect filtered Printex U particles have on the backpressure

5.1.1.7 Selection of gel-cast foams for use as DPFs

Previous experiments have shown that the structural parameters of the foam; porosity, cell and window size, play a major role in defining both the permeability and filtration properties of the foam. The following section runs through an example selection procedure that might be used to select foams applicable for use as DPFs.

If the assumption is made that a foam DPF system were to be enclosed using the current diameters of WFFs, given in table 11, then the backpressure can be calculated using the permeability constant data calculated in section 5.1.1.5, for typical gas flow rates (Q) experienced in practice by DPFs, as shown in table 12. These gas flow rates have been calculated using the method outlined in appendix 4.
Chapter 5. Results

<table>
<thead>
<tr>
<th>WFF diameter / mm (in)</th>
<th>WFF length / mm (in)</th>
<th>WFF volume / l</th>
</tr>
</thead>
<tbody>
<tr>
<td>143.8 (5.66)</td>
<td>152.4 (6)</td>
<td>2.5</td>
</tr>
<tr>
<td>190.5 (7.5)</td>
<td>203.8 (8)</td>
<td>5.8</td>
</tr>
<tr>
<td>228.6 (9.0)</td>
<td>304.8 (12)</td>
<td>12.5</td>
</tr>
<tr>
<td>266.7 (10.5)</td>
<td>304.8 (12)</td>
<td>17.0</td>
</tr>
<tr>
<td>285.8 (11.25)</td>
<td>304.8 (12)</td>
<td>19.6</td>
</tr>
</tbody>
</table>

Table 11. Standard WFF dimensions as produced by Corning [41]

<table>
<thead>
<tr>
<th>Engine size / litres</th>
<th>Gas flow rate @ 2000 rpm / m³ h⁻¹</th>
<th>Gas flow rate @ 4000 rpm / m³ h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>102</td>
<td>204</td>
</tr>
<tr>
<td>4</td>
<td>204</td>
<td>408</td>
</tr>
<tr>
<td>6</td>
<td>306</td>
<td>612</td>
</tr>
<tr>
<td>10</td>
<td>510</td>
<td>1020</td>
</tr>
<tr>
<td>14</td>
<td>714</td>
<td>1428</td>
</tr>
</tbody>
</table>

Table 12. Gas flow rates (Q) calculated for typical diesel engine sizes

The resultant backpressure calculated for foam #26 ($\varepsilon = 92\%$, $d_{cell} = 0.7$ mm and $d_{window} = 0.2$ mm) over the range of gas flow rates experienced in practice by heavy duty DPFs for a variety of filter diameters is given in figure 73 below.

Figure 73. Backpressure generated by a 50 mm long gel-cast foam with $\varepsilon = 92\%$, $d_{cell} = 0.7$ mm and $d_{window} = 0.2$ mm
5.2 Low Operating Temperature Diesel Soot Oxidation Development

This section begins with the characterisation of the catalyst materials included in the screening study. A number of potential diesel soot oxidation catalyst materials were studied next, initially by TGA, and the most active selected for further trials that included investigating poisoning effects by SO₂, their performance under a low oxygen atmosphere and the effect the amount of soot present had on their activity. Potential catalyst materials have been classified into five groups for discussion purposes; metal oxides, spinels, perovskites, alkali metal and vanadium based materials.

5.2.1 Catalyst characterisation

5.2.1.1 XRD

XRD was performed on all catalyst materials produced in the laboratory, as outlined in section 4.2.1.2. The resultant traces are given in figures 74 to 86. Where possible the phases present have been identified and labelled, the corresponding JCPDS file numbers are given in brackets.

![XRD trace for CuFe₂O₄]

Figure 74. XRD trace for CuFe₂O₄
Figure 75. XRD trace for CuMn$_2$O$_4$

Figure 76. XRD trace for CoFe$_2$O$_4$

C = Cubic
(22-1086)
Chapter 5. Results

Figure 77. XRD trace for CoMn$_2$O$_4$

Figure 78. XRD trace for Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$
Chapter 5. Results

Figure 79. XRD trace for Cu$_{0.5}$Co$_{0.5}$Mn$_2$O$_4$

$C = $ Cubic
(47-0324)

Figure 80. XRD trace for La$_{0.9}$K$_{0.1}$FeO$_3$

$O = $ Orthorhombic
(88-0641)
Chapter 5. Results

Figure 81. XRD trace for La$_{0.9}$K$_{0.1}$CoO$_3$

R = Rhombohedral
(84-0848)

Figure 82. XRD trace for La$_{0.9}$K$_{0.1}$MnO$_3$

O = Orthorhombic
(50-0591)
Chapter 5. Results

C = Cubic KCl
(41-1476)

M = Monoclinic K$_2$CO$_3$
(16-0820)

Figure 83. XRD trace for K$_2$CO$_3$ - KCl

M* = Monoclinic LiKCO$_3$
(34-1148)
M = Monoclinic LiNaCO$_3$
(34-1193)

Figure 84. XRD trace for Li/Na/K
**Figure 85.** XRD trace for CsVO$_3$-MoO$_3$

**Figure 86.** XRD trace for K$_4$V$_2$O$_7$
5.2.1.2 Specific surface area (BET method)

The specific surface areas of each catalyst material, both those metal oxides purchased and the other four groups of catalyst produced in the laboratory, are given for each of the five groups of materials in table 13.

<table>
<thead>
<tr>
<th>Catalyst Material</th>
<th>Specific Surface Area (BET) / m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metal Oxide Catalyst Materials</strong></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.3</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>2.8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.3</td>
</tr>
<tr>
<td>CeO₂</td>
<td>7.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>9.5</td>
</tr>
<tr>
<td>ZnO</td>
<td>5.0</td>
</tr>
<tr>
<td>LAS</td>
<td>3.3</td>
</tr>
<tr>
<td><strong>Spinel Catalyst Materials</strong></td>
<td></td>
</tr>
<tr>
<td>CuFe₂O₄</td>
<td>1.1</td>
</tr>
<tr>
<td>CuMn₂O₄</td>
<td>7.0</td>
</tr>
<tr>
<td>CoFe₂O₄</td>
<td>7.4</td>
</tr>
<tr>
<td>CoMn₂O₄</td>
<td>3.9</td>
</tr>
<tr>
<td>Cu₀.₅Co₀.₅Fe₂O₄</td>
<td>2.0</td>
</tr>
<tr>
<td>Cu₀.₅Co₀.₅Mn₂O₄</td>
<td>2.7</td>
</tr>
<tr>
<td><strong>Perovskite Catalyst Materials</strong></td>
<td></td>
</tr>
<tr>
<td>La₀.₉K₀.₁FeO₃</td>
<td>12.8</td>
</tr>
<tr>
<td>La₀.₉K₀.₁MnO₃</td>
<td>3.0</td>
</tr>
<tr>
<td>La₀.₉K₀.₁CoO₃</td>
<td>1.6</td>
</tr>
<tr>
<td><strong>Alkali Metal Based Catalyst Materials</strong></td>
<td></td>
</tr>
<tr>
<td>K₂CO₃ – KCl</td>
<td>0.4</td>
</tr>
<tr>
<td>Li/Na/K</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>Vanadium Based Catalyst Materials</strong></td>
<td></td>
</tr>
<tr>
<td>K₂V₂O₇</td>
<td>0.5</td>
</tr>
<tr>
<td>CsVO₃-MoO₃</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Table 13. Specific surface areas of the five groups of catalyst materials
5.2.2 Study on how variations in mixing affect catalytic activity

The effect on $T_{\text{max}}$ values by altering the catalyst – Printex U TGA sample preparatory methods is illustrated below in figure 87 using Fe$_2$O$_3$ and K$_2$CO$_3$ – KCl as examples.

![Graph showing effect of sample preparation method on $T_{\text{max}}$ values](image)

**Figure 87.** Effect of sample preparation method on $T_{\text{max}}$ values (zero milling time represents the shaken samples)

A visual examination of both Fe$_2$O$_3$ and K$_2$CO$_3$-KCl samples ball milled for 5 minutes and 120 minutes was performed using SEM and TEM, micrographs of which are shown in figures 88 to 96 below.
Figure 88. SEM of Fe$_2$O$_3$ particles

Figure 89. SEM of Fe$_2$O$_3$ particles ball milled with Printex U for 5 minutes
Figure 90. SEM of Fe$_2$O$_3$ particles ball milled with Printex U for 120 minutes

Figure 91. High magnification SEM of Fe$_2$O$_3$ particles ball milled with Printex U for 120 minutes
Figure 92. TEM of Fe$_2$O$_3$ & Printex U mixture after 5 minutes ball milling

Figure 93. TEM of Fe$_2$O$_3$ & Printex U mixture after 120 minutes ball milling
Figure 94. SEM of the surface of an $\text{K}_2\text{CO}_3$-$\text{KCl}$ agglomerate

Figure 95. SEM of the surface of an $\text{K}_2\text{CO}_3$-$\text{KCl}$ agglomerate after 5 minutes ball milling with Printex U
5.2.3 Catalyst screening

Samples of Printex U and the potential catalyst materials were prepared using the two different techniques as described in section 4.2.2.1. As previously described in section 4.2.2.2, plots showing the rate of change in the weight loss curve as a function of temperature allowed information regarding the rate of the combustion reaction to be obtained, i.e. $R_{\text{max}}$, along with values of $T_{\text{max}}, T_{\text{lg}}, T_{\text{final}}$, which are stated in the accompanying tables for each material group.

5.2.3.1 TGA errors

In order to report a realistic error in the parameters $T_{\text{max}}, T_{\text{lg}}, T_{\text{final}}$ and $R_{\text{max}}$ obtained in the TGA experiments three different batches of 0.6g CuFe$_2$O$_4$-Printex U were prepared using both the techniques outlined in section 4.2.2.1 and run according to the protocol in section 4.2.2.2. The standard deviation obtained for each mixing technique, as reported in tables 14 and 15 below, were used throughout as the error in each of these parameters.

Figure 96. High magnification SEM of the surface of an K$_2$CO$_3$-KCl agglomerate after 5 minutes ball milling with Printex U
Table 14. Standard deviation in the parameters $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ for CuFe$_2$O$_4$ samples ball milled with Printex U for 120 minutes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>St Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{max}}$</td>
<td>489</td>
<td>494</td>
<td>488</td>
<td>2.0</td>
</tr>
<tr>
<td>$T_{\text{ig}}$</td>
<td>406</td>
<td>412</td>
<td>407</td>
<td>3.2</td>
</tr>
<tr>
<td>$T_{\text{final}}$</td>
<td>519</td>
<td>521</td>
<td>517</td>
<td>2.0</td>
</tr>
<tr>
<td>$R_{\text{max}}$</td>
<td>0.62</td>
<td>0.57</td>
<td>0.60</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 15. Standard deviation in the parameters $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ for CuFe$_2$O$_4$ sieved with Printex U

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>St Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{max}}$</td>
<td>542</td>
<td>548</td>
<td>550</td>
<td>4.2</td>
</tr>
<tr>
<td>$T_{\text{ig}}$</td>
<td>442</td>
<td>444</td>
<td>452</td>
<td>5.3</td>
</tr>
<tr>
<td>$T_{\text{final}}$</td>
<td>561</td>
<td>580</td>
<td>568</td>
<td>9.6</td>
</tr>
<tr>
<td>$R_{\text{max}}$</td>
<td>0.29</td>
<td>0.35</td>
<td>0.28</td>
<td>0.04</td>
</tr>
</tbody>
</table>

5.2.3.2 Metal oxide materials

Figure 97 illustrates the rate of change in the weight loss curves as a function of temperature for all the metal oxide materials screened when well mixed with Printex U and the values obtained for $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ are given in table 16. Since all these materials had very little or no catalytic effect on the combustion of Printex U only the three most active along with the alumina sample, which was used as a reference, were tested under poorly mixed conditions, figure 98 and table 17.
Chapter 5. Results

**Figure 97.** Plot of the rate of change in weight loss as a function of temperature for various metal oxide materials well mixed with Printex U

<table>
<thead>
<tr>
<th>Catalyst material</th>
<th>$T_{\text{max}}$ / °C</th>
<th>$T_{\text{ig}}$ / °C</th>
<th>$T_{\text{final}}$ / °C</th>
<th>$R_{\text{max}}$ / mg min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>622</td>
<td>500</td>
<td>650</td>
<td>0.57</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>620</td>
<td>500</td>
<td>670</td>
<td>0.42</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>597</td>
<td>470</td>
<td>630</td>
<td>0.42</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>570</td>
<td>440</td>
<td>590</td>
<td>0.85</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>600</td>
<td>485</td>
<td>635</td>
<td>0.48</td>
</tr>
<tr>
<td>ZnO</td>
<td>596</td>
<td>480</td>
<td>630</td>
<td>0.90</td>
</tr>
<tr>
<td>LAS</td>
<td>622</td>
<td>485</td>
<td>635</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Table 16.** Values of $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ for metal oxide materials well mixed with Printex U
Figure 98. Plot of the rate of change in weight loss as a function of temperature for four of the most active metal oxide materials poorly mixed with Printex U.

Table 17. Values of $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ for metal oxide materials poorly mixed with Printex U.

<table>
<thead>
<tr>
<th>Catalyst material</th>
<th>$T_{\text{max}}$ / °C</th>
<th>$T_{\text{ig}}$ / °C</th>
<th>$T_{\text{final}}$ / °C</th>
<th>$R_{\text{max}}$ / mg min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>623</td>
<td>500</td>
<td>668</td>
<td>0.34</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>624</td>
<td>500</td>
<td>680</td>
<td>0.25</td>
</tr>
<tr>
<td>$\text{CeO}_2$</td>
<td>621</td>
<td>500</td>
<td>682</td>
<td>0.30</td>
</tr>
<tr>
<td>$\text{ZnO}$</td>
<td>620</td>
<td>500</td>
<td>685</td>
<td>0.20</td>
</tr>
</tbody>
</table>

5.2.3.2 Spinel materials

Figures 99 and 100 illustrate the rate of change in the weight loss curves as a function of temperature for the spinel materials screened when well mixed and poorly mixed with Printex.
Tables 18 and 19 provide values for $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ obtained from these plots.

![Graph showing weight loss as a function of temperature for various spinel materials](image)

**Figure 99.** Plot of the rate of change in weight loss as a function of temperature for various spinel materials well mixed with Printex U

<table>
<thead>
<tr>
<th>Catalyst material</th>
<th>$T_{\text{max}}$ / °C</th>
<th>$T_{\text{ig}}$ / °C</th>
<th>$T_{\text{final}}$ / °C</th>
<th>$R_{\text{max}}$ / mg min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>489</td>
<td>406</td>
<td>519</td>
<td>0.62</td>
</tr>
<tr>
<td>CuMn$_2$O$_4$</td>
<td>520</td>
<td>385</td>
<td>552</td>
<td>0.31</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>584</td>
<td>407</td>
<td>615</td>
<td>0.11</td>
</tr>
<tr>
<td>CoMn$_2$O$_4$</td>
<td>571</td>
<td>393</td>
<td>619</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Co$</em>{0.5}$Fe$_2$O$_4$</td>
<td>506</td>
<td>414</td>
<td>540</td>
<td>0.34</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Co$</em>{0.5}$Mn$_2$O$_4$</td>
<td>565</td>
<td>405</td>
<td>584</td>
<td>0.30</td>
</tr>
</tbody>
</table>

**Table 18.** Values of $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ for spinel materials well mixed with Printex U
Figure 100. Plot of the rate of change in weight loss as a function of temperature for various spinel materials poorly mixed with Printex U

<table>
<thead>
<tr>
<th>Catalyst material</th>
<th>$T_{\text{max}} / ^\circ\text{C}$</th>
<th>$T_{\text{ig}} / ^\circ\text{C}$</th>
<th>$T_{\text{final}} / ^\circ\text{C}$</th>
<th>$R_{\text{max}} / \text{mg min}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>543</td>
<td>443</td>
<td>568</td>
<td>0.29</td>
</tr>
<tr>
<td>CuMn$_2$O$_4$</td>
<td>574</td>
<td>452</td>
<td>607</td>
<td>0.22</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>589</td>
<td>402</td>
<td>646</td>
<td>0.10</td>
</tr>
<tr>
<td>CoMn$_2$O$_4$</td>
<td>603</td>
<td>452</td>
<td>647</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Co$</em>{0.5}$Fe$_2$O$_4$</td>
<td>565</td>
<td>447</td>
<td>600</td>
<td>0.25</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Co$</em>{0.5}$Mn$_2$O$_4$</td>
<td>593</td>
<td>462</td>
<td>628</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Table 19. Values of $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ for spinel materials poorly mixed with Printex U

5.2.3.3 Perovskite materials

Figures 101 and 102 illustrate the rate of change in the weight loss curves as a function of temperature for the perovskite materials screened when well mixed and poorly mixed with Printex U respectively. Tables 20 and 21 provide values for $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ obtained from these plots.
Figure 101. Plot of the rate of change in weight loss as a function of temperature for various perovskite materials well mixed with Printex U

<table>
<thead>
<tr>
<th>Catalyst material</th>
<th>$T_{\text{max}}$ / °C</th>
<th>$T_{\text{ig}}$ / °C</th>
<th>$T_{\text{final}}$ / °C</th>
<th>$R_{\text{max}}$ / mg min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}_0.9\text{K}_0.1\text{CoO}_3$</td>
<td>464</td>
<td>321</td>
<td>485</td>
<td>0.19</td>
</tr>
<tr>
<td>$\text{La}_0.9\text{K}_0.1\text{FeO}_3$</td>
<td>564</td>
<td>388</td>
<td>591</td>
<td>0.14</td>
</tr>
<tr>
<td>$\text{La}_0.9\text{K}_0.1\text{MnO}_3$</td>
<td>479</td>
<td>337</td>
<td>521</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 20. Values of $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ for perovskite materials well mixed with Printex U
Figure 102. Plot of the rate of change in weight loss as a function of temperature for various perovskite materials poorly mixed with Printex U

<table>
<thead>
<tr>
<th>Catalyst material</th>
<th>$T_{\text{max}}$ / °C</th>
<th>$T_{\text{ig}}$ / °C</th>
<th>$T_{\text{final}}$ / °C</th>
<th>$R_{\text{max}}$ / mg min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$La_{0.9}K_{0.1}MnO_3$</td>
<td>517</td>
<td>376</td>
<td>572</td>
<td>0.13</td>
</tr>
<tr>
<td>$La_{0.9}K_{0.1}FeO_3$</td>
<td>538</td>
<td>426</td>
<td>627</td>
<td>0.10</td>
</tr>
<tr>
<td>$La_{0.9}K_{0.1}CoO_3$</td>
<td>522</td>
<td>390</td>
<td>555</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Table 21. Values of $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ for perovskite materials poorly mixed with Printex U

5.2.3.4 Alkali metal and vanadium containing materials

Figures 103 and 104 illustrate the rate of change in the weight loss curves as a function of temperature for both the alkali metal and vanadium containing materials screened when well mixed and poorly mixed with Printex U respectively. Tables 22 and 23 provide values for $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ obtained from these plots.
Figure 103. Plot of the rate of change in weight loss as a function of temperature for alkali metal and vanadium containing materials well mixed with Printex U

<table>
<thead>
<tr>
<th>Catalyst material</th>
<th>$T_{\text{max}}$ / °C</th>
<th>$T_{\text{ig}}$ / °C</th>
<th>$T_{\text{final}}$ / °C</th>
<th>$R_{\text{max}}$ / mg min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_4\text{V}_2\text{O}_7$</td>
<td>388</td>
<td>300</td>
<td>436</td>
<td>0.17</td>
</tr>
<tr>
<td>$\text{CsVO}_3$-$\text{MoO}_3$</td>
<td>428</td>
<td>338</td>
<td>470</td>
<td>0.16</td>
</tr>
<tr>
<td>$\text{K}_2\text{CO}_3$-$\text{KCl}$</td>
<td>394</td>
<td>336</td>
<td>441</td>
<td>0.32</td>
</tr>
<tr>
<td>Li/Na/K</td>
<td>376</td>
<td>326</td>
<td>437</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Table 22. Values of $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ for alkali metal and vanadium containing materials well mixed with Printex U
Figure 104. Plot of the rate of change in weight loss as a function of temperature for alkali metal and vanadium containing materials poorly mixed with Printex U.

![Plot of the rate of change in weight loss as a function of temperature for alkali metal and vanadium containing materials poorly mixed with Printex U.](image)

<table>
<thead>
<tr>
<th>Catalyst material</th>
<th>$T_{\text{max}}$ / °C</th>
<th>$T_{\text{ig}}$ / °C</th>
<th>$T_{\text{final}}$ / °C</th>
<th>$R_{\text{max}}$ / mg min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_4V_2O_7$</td>
<td>503</td>
<td>325</td>
<td>542</td>
<td>0.15</td>
</tr>
<tr>
<td>$CsVO_3-MoO_3$</td>
<td>480</td>
<td>341</td>
<td>527</td>
<td>0.14</td>
</tr>
<tr>
<td>$K_2CO_3$-KCl</td>
<td>426</td>
<td>336</td>
<td>481</td>
<td>0.11</td>
</tr>
<tr>
<td>Li/Na/K</td>
<td>431</td>
<td>323</td>
<td>481</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 23. Values of $T_{\text{max}}$, $T_{\text{ig}}$, $T_{\text{final}}$ and $R_{\text{max}}$ for alkali metal and vanadium containing materials poorly mixed with Printex U.

5.2.3.5 Catalyst materials selected for further evaluation

Based on the TGA results, the following materials were selected for use in the latter stages of the screening process. The $T_{\text{max}}$ values when well mixed are also given.

- CuFe$_2$O$_4$ ($T_{\text{max}} = 489^\circ$C)
- La$_{0.9}$K$_{0.1}$CoO$_3$ ($T_{\text{max}} = 479^\circ$C)
- $K_2CO_3$-KCl ($T_{\text{max}} = 394^\circ$C)
- Li/Na/K ($T_{\text{max}} = 376^\circ$C)
5.2.4 Sulphur dioxide poisoning of selected catalysts

The effects on the catalytic activity of the four selected catalyst materials after exposing them to sulphur dioxide, by the method described in section 4.2.2.3, is illustrated by the plot given in figure 105.

![Figure 105. The effect of sulphur dioxide poisoning on T_max values](image)

Based on the above SO_2 poisoning results, the two alkali metal based catalyst materials, Li/Na/K and K_2CO_3-KCl were selected for further investigation.

5.2.5 Hygroscopicity of selected catalysts

Figure 106 illustrates the measured weight gain in the chosen catalysts when left to stand in air over a period of 60 minutes. The weight gain seen in Li/Na/K was only 1% after 60 minutes whilst that of the K_2CO_3-KCl material was greater than 50 wt%. On this basis Li/Na/K was selected as being the most suitable material on which to perform the final series of experiments.
5.2.6 Effect of reduced oxygen atmosphere on catalytic activity

The concentration of the oxygen being fed into the furnace chamber of the TGA was gradually reduced in stages from that of air i.e. 21% O₂, to 15%, 10%, 5%, 2.5%, 0.5% and 0% O₂ (pure N₂). The plot in figure 107 below shows what effect this had on the values of $T_{\text{max}}$ for Li/Na/K ball milled for 120 minutes with Printex U.
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Figure 107. The effect of reducing the concentration of oxygen present in the TGA on Li/Na/K’s $T_{\text{max}}$ values

The results of differential scanning calorimetry (DSC) measured for the catalytic oxidation of Printex U with Li/Na/K in the presence of 21% and 0% oxygen are given in figures 108 and 109 respectively.

Figure 108. DSC trace for the catalytic oxidation of Printex U in air (≈21% $O_2$)
Figure 109. DSC trace for the catalytic oxidation of Printex U in nitrogen (0% O₂)

5.2.7 Effect of altering catalyst: model soot ratio

Figure 110 shows the effect on the $T_{\text{max}}$ value of well mixed Printex U and Li/Na/K samples in which the weight ratio of the Li/Na/K catalyst to that of Printex U was varied in the following manner: 1:1, 1:2, 1:4, 1:6 and 1:1, 4:1, 6:1.

5.2.8 Useful catalyst lifetime experiments

Figure 111 shows the change in Li/Na/K $T_{\text{max}}$ values for samples that were repeatedly mixed and heated to 500°C with Printex U 1, 5, 10 and 50 times.
Figure 110. Plot of the rate of change in weight loss as a function of temperature for Li/Na/K when well mixed with Printex U at decreasing levels of catalyst content.

Figure 111. Plot illustrating the effect on the $T_{\text{max}}$ value through the repeated use of the Li/Na/K catalyst over a number of combustion cycles.
5.3 Catalysed Gel Cast Foams

This section begins by firstly identifying a material with which to make the combined foam filter and catalyst support that is not detrimentally affected by the presence of the Li/Na/K catalyst and vice versa causes no detrimental effect on catalytic performance. Importantly any material also has to be compatible with the gel casting process. Different techniques employed in applying a catalytic coating to the foam were next assessed before a TGA study of the performance of catalysed foams for Printex U combustion were performed. Finally the performance of Li/Na/K catalysed foam filters was examined in a real diesel exhaust system.

5.3.1 Selection of a suitable support / filter ceramic material

5.3.1.1 TGA of Li/Na/K – ceramic support materials

Plots of rate change in weight loss as a function of temperature for Li/Na/K – ceramic support materials mixtures heated at 500°C and 750°C for periods of 1, 24 and 240 hours are given in figures 112 to 119 for alumina, cordierite, LAS and mullite respectively.

Figure 112. Plot of the rate of change of weight loss as a function of temperature for an alumina – Li/Na/K mix heated to 500°C for periods of 1, 24 and 240 hours
Figure 113. Plot of the rate of change of weight loss as a function of temperature for an alumina – Li/Na/K mix heated to 750°C for periods of 1, 24 and 240 hours.

Figure 114. Plot of the rate of change of weight loss as a function of temperature for an cordierite – Li/Na/K mix heated to 500°C for periods of 1, 24 and 240 hours.
Figure 115. Plot of the rate of change of weight loss as a function of temperature for a cordierite – Li/Na/K mix heated to 750°C for periods of 1, 24 and 240 hours

Figure 116. Plot of the rate of change of weight loss as a function of temperature for a lithium aluminosilicate – Li/Na/K mix heated to 500°C for periods of 1, 24 and 240 hours
Figure 117. Plot of the rate of change of weight loss as a function of temperature for a lithium aluminosilicate – Li/Na/K mix heated to 750°C for periods of 1, 24 and 240 hours

Figure 118. Plot of the rate of change of weight loss as a function of temperature for a mullite – Li/Na/K mix heated to 500°C for periods of 1, 24 and 240 hours
Figure 119. Plot of the rate of change of weight loss as a function of temperature for a mullite–Li/Na/K mix heated to 750°C for periods of 1, 24 and 240 hours

5.3.1.2 XRD of Li/Na/K–ceramic support materials

XRD traces of the as received raw ceramic powders are given in figures 120 to 123. Phases present have been identified and the corresponding JCPDS file number is given in brackets.

Figure 120. XRD trace for alumina
Figure 121. XRD trace for cordierite

Figure 122. XRD trace for LAS

$O = \text{Orthorhombic (13-0294)}$

$SP = \text{Spodumene (76-0921)}$

$P = \text{Petalite (75-1716)}$
Comparison of the XRD traces obtained when the Li/Na/K catalyst was heated with alumina, cordierite, LAS and mullite for periods of 1, 24 and 240 hours at temperatures of 500°C and 750°C are given in figures 124 to 127 and 128 to 131 respectively. Phases un- attributable to either the Li/Na/K catalyst or base ceramic are identified and the corresponding JCPDS file number is given in brackets.

**Figure 123.** XRD trace for mullite

**Figure 124.** XRD traces for Li/Na/K-alumina heated and held at 500°C for set time periods

(* 44-0224 – LiAlO₂*)
Figure 125. XRD traces for Li/Na/K-cordierite heated and held at 500°C for set time periods (* 47-0027 – γ LiAlSiO₄)

Figure 126. XRD traces for Li/Na/K-LAS heated and held at 500°C for set time period (* 30-0766 – Li₂SiO₃/Li₂O·SiO₂) (Φ 14-0667 – LiAlSiO₄)
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Figure 127. XRD traces for Li/Na/K-mullite heated and held at 500°C for set time periods
(* 47-0027 – γ LiAlSiO₄)

Figure 128. XRD traces for Li/Na/K-alumina heated and held at 750°C for set time periods
(* 44-0224 – LiAlO₂) (Φ 38-1464 – LiAlO₂)
Figure 129. XRD traces for Li/Na/K-cordierite heated and held at 750°C for set time periods
(*43-0230 Li$_2$AlSiO$_4$) (Φ 47-0027 – γ LiAlSiO$_4$)

Figure 130. XRD traces for Li/Na/K-LAS heated and held at 750°C for set time periods
(* 30-0766 Li$_2$SiO$_3$) (Φ 11-0579 KAISiO$_4$) (δ 02-0897 KAIO$_2$)
Figure 131. XRD traces for Li/Na/K-mullite heated and held at 750°C for set time periods

(* 11-0579 KAlSiO₄) (Φ 50-1675) (δ 14-0667 LiAlSiO₄) (π 32-0731)

5.3.2 Preparation and characterisation of catalysed foams

5.3.2.1 Selection of a suitable solvent carrier liquid

Both the methods used to prepare catalysed foams employed the use of a solvent carrier liquid that needed to be quick drying, easily available, low cost and most importantly had no effect on the performance of the catalyst. Acetone was chosen as it fulfilled all these criteria and had no effect on catalyst activity as shown in figure 132.
5.3.2.2 Preparation of catalysed foams

Two methods of applying the Li/Na/K catalyst powder onto the alumina foam were tested both began with the preparation of a suspension of the catalyst in acetone. Suspensions were prepared with a concentration of 15 g dm\(^{-3}\). This suspension was then either washed through the foam, method 1, or the foam was dipped into the suspension, method 2. A typical plot of the catalyst concentration on an 8 % theoretical density foam as a function of the number of dips or washes received is shown in figure 133.
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Figure 133. Catalyst concentration on foams as a function of the loading method employed

5.3.2.3 Evaluation of loading methods

Typical catalyst depositions seen on the front and back faces of foam #28 ($\varepsilon = 90\%$, $d_{\text{cell}} = 800 \ \mu m$ and $d_{\text{win}} = 250 \ \mu m$) prior to heat treatment, for both loading methods, described in section 4.3.2, are shown in the SEM micrographs in figures 134 to 139 respectively. Where the front face refers to that facing skywards during both dipping and filtering.

Post heat treatment, performed as outlined in section 4.3.2, the front and back surfaces of the foams was again characterised by SEM and the resulting micrographs are given in figures 140 to 145 respectively.

5.3.2.4 Characterisation of catalyst coating

High magnification SEM combined with EDX analysis was used to examine more closely the morphology and chemistry of the applied catalytic coating, the results of which are presented in figures 146 to 155.
Figure 134. 55 g l⁻¹ of Li/Na/K catalyst powder loading on the front face using method 1

Figure 135. 55 g l⁻¹ of Li/Na/K catalyst powder loading on the front face using method 2
Figure 136. Higher magnification micrograph showing the rod like fibres found in amongst the Li/Na/K catalyst

Figure 137. EDX analysis result on the rod like fibres found in amongst the Li/Na/K catalyst
Figure 138. 55 g l\(^{-1}\) of Li/Na/K catalyst powder loading on the rear face using method 1

Figure 139. 55 g l\(^{-1}\) of Li/Na/K catalyst powder loading on the rear face using method 2
Figure 140. Post heat treatment upper side loaded with 55 gl⁻¹ Li/Na/K using method 1 (■ and △ represent the EDX analysis areas in figures 142 and 143)

Figure 141. Post heat treatment upper side loaded with 55 gl⁻¹ Li/Na/K using method 2
Figure 142. EDX analysis result for the area marked □ in figure 140

Figure 143. EDX analysis result for the area marked ▲ in figure 140
Figure 144. Post heat treatment underside loaded with 55 g/l\textsuperscript{1} Li/Na/K using method 1.

Figure 145. Post heat treatment underside loaded with 55 g/l\textsuperscript{1} Li/Na/K using method 2.
Figure 146. Large Li/Na/K crystal and much smaller crystallites on the surface of the underside of an alumina foam post heat treatment (▲ represents the area of EDX analysis shown in figure 148)

Figure 147. Higher magnification image of the Li/Na/K crystallites shown in figure 148 on the alumina surface (■ represents the area of EDX analysis shown in figure 149)
Figure 148. EDX analysis result for the area marked ▲ in figure 148

Figure 149. EDX analysis result for the area marked ■ in figure 149
Figure 150. SEM image showing the Li/Na/K catalyst morphology formed on the strut on the underside of an alumina foam

Figure 151. High magnification image showing Li/Na/K plate-like crystals formed on the surface of the upper side an alumina foam
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Figure 152. SEM image showing the interface seen on the upper surface between areas of catalyst coating and the base alumina ceramic.

Figure 153. High magnification SEM showing in greater detail how the Li/Na/K catalyst crystals formed during heat treatment interact with the alumina support (△ and ■ represent the areas examined by EDX as shown in figures 154 and 155).
Figure 154. EDX analysis result for the area marked ■ in figure 153

Figure 155. EDX analysis result for the area marked ▲ in figure 153
5.3.2.5 Effect of coating on permeability

The effect of applying the catalytic coating to the permeability of the ceramic foam compared to the un-catalysed state was measured for both methods at loading levels of 35 g/l and 55 g/l, the results of which are shown below in figure 156.

![Figure 156. Effect of increased catalyst loading on foam permeability](image)

5.3.2.6 TGA evaluation of catalysed foams

Catalysed foams were loaded with Printex U and their performance for Printex U oxidation was evaluated by TGA in accordance with the procedure described in section 4.3.2.3.

Figure 157 below shows the difference seen in the combustion profiles when Printex U was oxidised on two 8% theoretical density foams with Li/Na/K coatings loaded on using methods 1 and 2.
Figure 157. The effect of loading method on the Printex U combustion profile for 55 g l\textsuperscript{-1} Li/Na/K coated alumina foams

Figure 158 below shows the rate of change in weight loss as a function of temperature for samples #9 (ε = 93\%, d_{cell} = 792 \, \mu m and d_{win} = 236 \, \mu m) and #24 (ε = 92.6 \%, d_{cell} = 786 \, \mu m and d_{win} = 292 \, \mu m) loaded with 35 g l\textsuperscript{-1} and 55 g l\textsuperscript{-1} of the Li/Na/K catalyst prepared using method 1 in comparison to the combustion profile seen on an un-catalysed alumina foam.

Figure 158. Combustion profile for catalysed and un-catalysed foams
5.3.2.7 Comparison of TGA sample preparation technique

The effect of the mixing technique employed in preparing catalyst-Printex U mixtures is an important parameter that needs to be clearly defined as quite marked differences in results can be achieved, as shown in section 5.2.2.

The plot in figure 159 shows the comparison between the combustion profiles seen for Li/Na/K -Printex U mixtures prepared using the two different mixing techniques of ball milling and sieving employed within this study to that of Printex U combusted on a 55 g l\(^{-1}\) Li/Na/K catalysed alumina foam. The Printex U on the catalysed foam was applied via a realistic filtration method as described in section 4.1.1.7. The data for the rate of change of weight loss for the alumina foam has been magnified by a factor of 100 to allow for an easier visual comparison to be made. The lower values seen in the rate of change of weight loss for the catalysed foam are a result of the lower mass of Printex U present on the foam filter.

![Combustion profile for Li/Na/K - Printex U mixtures in tight and loose contact compared to Printex U combustion on a 55 g l\(^{-1}\) Li/Na/K catalysed 8% theoretical density alumina foam](image)

**Figure 159.** Combustion profile for Li/Na/K - Printex U mixtures in tight and loose contact compared to Printex U combustion on a 55 g l\(^{-1}\) Li/Na/K catalysed 8% theoretical density alumina foam
5.3.2.8 Effect of foam structure on combustion

The TGA analysed combustion of Printex U on a un-catalysed alumina foam in comparison to combustion of the Printex U - alumina powder mixtures, as prepared by the two different techniques used for the catalyst screening experiments as described in more detail in section 4.2.2.1 is given in figure 160 below.

Similarly to the previous data presented the values for the rate of change of weight loss for the alumina foam has been magnified by a factor of 50 in order to allow an easier visual comparison to be made. Again the lower values seen in the rate of change of weigh loss for the catalysed foam are a result of the lower mass of Printex U present on the foam filter.

![Graph showing combustion profile](image)

**Figure 160.** Combustion profile for alumina - Printex U mixtures prepared to give tight and loose contact in comparison to Printex U combustion on a un-catalysed 8% theoretical density alumina foam.
Chapter 6

Discussion

In line with the experimental procedure and results, chapters 4 and 5 respectively, this chapter has been divided up into three parts. The first section, 6.1, is a discussion of the results obtained for production of the foams, their structural characterisation and subsequent evaluation of their permeability and filtration efficiency for suitability for use as DPFs. The second section, 6.2, begins with a brief discussion of the characterisation of the catalytic compounds produced before going through each stage of the selection procedure used to identify a suitable catalyst material for the catalytic oxidation of the diesel soot. Finally the production and characterisation of foam filters catalysed with the chosen catalyst material and the evaluation of these catalysed gel cast foams for diesel soot oxidation using TGA and a model diesel soot is discussed in section 6.3.

6.1 Feasibility of using gel cast foam DPFs

6.1.1 Rheology of suspensions

Sepulveda [186] and work at Hi-Por Ceramics Ltd [183] have thoroughly investigated the preparation of suitable suspensions, as a result only a brief discussion is presented here.

A prerequisite of the gelcasting process is the production of a ceramic suspension, usually aqueous. For porous foam manufacture, a suitably low viscosity suspension is required in order for mechanically foamed suspension to be produced, typically viscosities $<200 \text{ mPa s}$ are required as these have been shown to be suitable for foaming using the technique
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employed within this study [186]. Figure 41 shows that the suspensions prepared here are well below this value.

A plot illustrating the relationship between the viscosity and shear stress to shear rate of alumina suspensions was also given in figures 41. The alumina suspensions produced showed decreasing viscosities and increasing shear stresses with increasing shear rate, this behaviour is typical for pseudoplastic/shear thinning fluids. These viscosity values and the shear thinning behaviour of these suspensions is in agreement with Sepulveda [186].

Time dependent effects on the alumina suspensions were shown in figure 42, this allows information regarding the thixotropy of the suspensions to be derived. When a thixotropic suspension is sheared at a constant rate the apparent viscosity decreases with time as structures within the suspension are broken apart until eventually a balance between structural breakdown and reformation is achieved. Upon removal of the shearing force the suspensions viscosity returns to its original value prior to the application of shearing [217]. The alumina suspensions produced display such thixotropic behaviour, which is again in agreement with Sepulveda [186]. This thixotropic behaviour was the reason for the adoption of a five minute pre-shear conditioning operation, prior to foaming agent addition.

6.1.2 Foaming of alumina slurries

The performance of a range of commercially available anionic foaming agents for foaming the standard 71 wt% alumina suspension was assessed in terms of foam generating ability, foam stability and achievable bubble size. The majority of studies, Sepulveda [186] and at Hi-Por Ceramics Limited [183], have focussed on the use of Tergitol TMN10, it was therefore included as a baseline for comparative purposes.

Previous studies by Sepulveda [186] and Ortega [218] have shown that the type of foaming agent used in the preparation of porous gel cast ceramic foams play a significant role whilst parameters such as stirring speed and time and the concentration of foaming agent used also have an effect. Stirring speed was not investigated here since Sepulveda [186] noted that the speed used to generate the foams, ~900 rpm, is below the critical value beyond which rupture of the foam films occurs, resulting in lower foam volumes.
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The effect of increasing the concentration of foaming agent in the alumina suspension was illustrated in figure 43. The results clearly show that the surfactant molecules in alpha foamer are far more effective at reducing the surface tension in this system than the other three foaming agents. The powerful foaming ability of alpha foamer has also been noted in its use for the production of foamed calcium sulphate suspensions, for gypsum board manufacture [219]. In all cases maximum foam volume generation increases with increasing concentration of foaming agent due to the increased reduction in surface tension facilitating the formation of stable gas-liquid interfaces thereby allowing a greater volume of gaseous phase to be incorporated into the suspension.

Except in the case of alpha foamer, the rate of foam volume increase gradually decreases with increasing foaming agent addition, and beyond a certain point the addition of extra foaming agent has very little effect on the foam volume generated. It can be assumed that at this point the solubility limit of each surfactant has been reached, i.e. the critical micelle concentration (CMC) is achieved. This suggests that even at a concentration of $1 \text{ ml} / 100 \text{ g}$ of suspension alpha foamer has yet to reach its CMC.

Beyond the CMC the foaming agent molecules no longer orientate themselves with the hydrophobic portion of their structure towards the gaseous surface, therefore no longer lower the surface tension of the liquid gas-interface. Instead the foaming agent molecules now collect into groups, called micelles, with the hydrophobic portion of their structure facing inwards.

The effect of stirring time on the volume of foam generated for the six foaming agents examined was given in figure 44 for a foaming agent addition level of $0.6 \text{ ml}$ per $100 \text{ g}$ of suspension. Both B29 and Tergitol TMN10 required approximately 4 minutes to reach maximum foam volume whilst B25 and alpha foamer required approximately twice this. These findings are in agreement with Sepulveda [186] who achieved a maximum foam volume after approximately 4 minutes using Tergitol TMN10.

It is believed that the reason for finding a maximum foam volume as a function of stirring time may be explained as follows. During the initial stirring period gas is dissolved into the suspensions and liquid is drawn around each bubble until a thin film is formed. Upon shearing, the surfactant molecules of the foaming agent move from the interior of the
suspensions toward the newly created surfaces, establishing forces that prevent further film thinning. When most surfactant molecules have attached themselves to the gas-liquid interfaces, the stabilisation of newly created films is no longer possible and foam volume no longer increases. Therefore at maximum foam volume the thickness of the liquid film surrounding each bubble is at its minimum. The longer times required by B25 and alpha foamer to reach maximum foam volume are probably due to them both containing similarly bulky, longer chain length surfactant molecules that would necessitate more mixing time for transport to the required interfaces. In reality, bubbles may still be continuously generated, but they dissipate almost instantly after agitation has ceased. In addition to the lack of stabilisation due to surfactant molecules being used up, the effect of continuous shearing also requires consideration. Although the amount of agitation increases the amount of gas brought into the suspension, it also has a destabilising effect on the foam already formed. Therefore, the ultimate foam volume produced depends on the steady state balance between the rates of foam production and that of foam breakdown [220].

Foam stability and bubble size observations have been summarised in table 10. In terms of their stability both B25 and Tergitol TMN10 performed excellently well with no signs of drainage or collapse even after one hours standing. Alpha foamer was also shown to be suitably stable with visible signs of drainage after 20 minutes and foam collapse after 45 minutes. As expected comparison of B25 and B29 showed B29 to be the most unstable foaming agent. The instability of foaming agents with a molecular composition like B29s compared to those with a composition like B25s has previously been noted [221].

Approximate measurements of the maximum bubble size observed was studied with the aim of establishing if any foaming agent could generate bubbles >1000 μm before collapse, since bubble growth rate using Tergitol TMN10 was found to be very slow. Both B25 and alpha foamer demonstrated similar abilities to grow bubbles >1000 μm in less than 30 minutes.

Bubble growth rate is governed by bubble coalescence and coarsening. The coalescence of neighbouring bubbles is a consequence of the displacement of liquid around neighbouring bubbles up to the point that the films separating them are so fine that rupture occurs. Coarsening of bubbles occurs via gas diffusion from smaller bubbles of higher curvature to larger ones due to differences in gas pressure. Therefore larger bubbles grow at the expense of smaller ones [222].
Accelerated bubble growth was most probably seen for both alpha foamer and B25 due to their surfactant molecules being more effective at reducing the surface tension of the alumina suspension thereby allowing more highly foamed suspensions with reduced liquid film thickness to be formed.

6.1.3 Foam characterisation

All the foams produced were characterised using the techniques outlined in the experimental procedure chapter, section 4.1.1.5. These techniques allowed information regarding the foams' sintered structural parameters, i.e. cell and window diameter and the porosity of the foam, to be calculated. The following is a discussion of the relationships between the structural parameters of the foams and effects various foaming agents and foaming parameters had on the foams sintered microstructure.

6.1.3.1 Structural parameter relationships for alumina foams

The relationship between the average cell and window diameters for the foams was given in figure 45. This shows that a linear relationship existed between these two structural parameters over the range of densities examined. The relationship between the % theoretical density, which can be used as a measure of foam porosity, and both the average cell and window diameters of the foams was illustrated in figure 46. Again an apparently linear relationship existed with both diameters increasing as the % theoretical density decreases. This behaviour is a result of the more porous samples, i.e. those that have been foamed to a greater volume, having less ceramic material to construct the cell walls giving rise to larger open windows. The larger cell size associated with increased porosity is due to the longer idle periods used in their manufacture, which allows more time for bubble growth in the foamed suspension. This behaviour was also noted by Sepulveda [186] for gelcast alumina foams over a similar range of densities, as illustrated in figure 161 below. However, it may be observed that a non-linear relationship becomes evident over the broader range of densities examined by Sepulveda.
Figure 161. Mean cell size of alumina foams of increasing solids loading [186]

Figure 46 shows a high degree of scatter about the line of the linear relationship for both the average cell and window diameters that becomes more pronounced as the density decreases, i.e. porosity increases. This may be explained as a result of gelcast foams having a wider distribution of cell and window diameters at lower density values, as reported by Sepulveda [186]. Also the variety of foaming agents and idle times used to produce the foams examined here would have had an affect on the relationship, this is discussed in section 6.1.3.2.

Changes in the structural parameters of the foam were also accompanied by visible changes in their surface morphology. Evidence of this was given in figures 47 and 48 that showed SEM micrographs of two foams produced using similar concentrations of alpha foamer but different idle times. Figure 48 shows the type of microstructure and morphology seen for a foam produced with a theoretical density of 15.5 %. The structure looks fairly uniform with the circular contours of both the cells and windows clearly visible, whilst the surface of the solid portion of the cell walls and strut areas is quite smooth. In comparison figure 47 is of a foam with a theoretical density of 7%. Aside from differences in cell and window size, the morphology of the foam is much less uniform, with the contours of each cell in particular appearing less circular and more fragmented and angular. Also the surface of the solid area in
the cells and the struts appears to be more uneven and granular. Such changes cannot be attributed to differences in starting suspension or the foaming agent used, as all were identical. A possible explanation for this is that the structure seen in figure 48 is of a foam that was polymerised whilst the structure was becoming unstable and the process of foam collapse i.e. liquid drainage, was in progress. The more uneven/angular surfaces of such a foam can be explained by particles in the foamed suspension agglomerating together as fluid in the suspension is draining away due to gravitational forces. This theory is backed up by the observations presented in table 10, of drained liquid being clearly visible after 20 minutes when alpha foamer was used. The idle time for this particular foam was approximately 20 minutes.

6.1.3.2 Relationship between foam structure and process parameters

The unique ability of the gel casting process to control the time period up to permanent foam stabilisation, i.e. the idle time, allows foams with controlled properties to be produced. The effect of various types of foaming agents used on the achieved average cell diameter of the sintered alumina gelcast foams as a function of the idle time was presented in figure 49. Two distinct groupings can be made; foams produced using Tergitol TMN10 and secondly those produced using alpha foamer and B25, for both groupings a near linear relationship between idle time and the cell diameter is seen.

Figure 49 shows that the idle time required to achieve similar average cell diameters is much shorter for foams produced using alpha foamer and B25 than Tergitol TMN10, for the reasons discussed in section 6.1.2. For example to achieve a foam with an average cell diameter of approximately 0.6 mm took approximately 30 minutes using Tergitol TMN10 whilst a foam of similar cell diameter was produced using alpha foamer or B25 in less than half that time.

6.1.4 Foam permeability

Foam permeability is of paramount importance when developing a foam filter for use as a DPF since exhaust gases need to flow through the filter with as little resistance as is possible to minimise the backpressure. Since increased backpressures have the undesirable effects of increasing fuel consumption and can lead to engine damage. Therefore it is vital to study the
effect various foam parameters have on the foam permeability in order to successfully tailor a foam for use as a DPF.

Air flowing through the prepared gel cast ceramic foams has been shown to be non-Darcian over the range of velocities studied here, figure 50, i.e. the relationship between the air velocity and backpressure is non-linear and is best described using the Forchheimer equation that takes into account inertial effects of the air flow. In all cases the correlation coefficient \( r^2 \) was greater than 0.99. This is in agreement with the work of Philippse et al [193] who found that non-Darcian air flow occurred at velocities >0.2 ms\(^{-1}\) in work performed using reticulated alumina foams.

6.1.4.1 Relationships between the structural parameters of foams and their permeability

The effect of foam porosity, the average cell and window diameters on the Darcian permeability constant, \( k_I \), were shown in figures 51-53 respectively.

Figure 51 shows that the relationship between foam porosity and Darcian permeability constant is non-linear, with increasing porosity resulting in increased \( k_I \) values. This result is in agreement with a review of reticulated foam permeability results presented by Innocentini et al [194] and a comparative study between the permeability of gel cast versus reticulated foams as illustrated in figure 162, again by Innocentini et al [195]. Beyond a porosity of approximately 88% the degree of variability seen in the \( k_I \) values increases substantially.
Figures 52 and 53 show that values for the Darcian permeability constant, $k_1$, increases as both the average cell and window diameter increase in a non-linear fashion, again a sharp increase in the degree of variability amongst $k_1$ values was seen beyond a cell diameter of approximately 0.8 mm and an average window diameter of approximately 0.3 mm. This non-linear trend is again in agreement with the results for average pore diameter presented by Innocentini et al [194].

These three relationships might well be explained by the following. The Darcian permeability constant represents the viscous energy losses of the air that arise due to attrition between the air and the solid surfaces of the foam. Therefore a decrease in any of the three variables
effectively increases the amount of solid surface area in the foam. This increased solid surface area will result in higher viscous energy losses that are reflected in lower $k_1$ values.

The relationship between the non-Darcian permeability constant, $k_2$, and foam porosity is given in figure 54. Similarly to $k_1$, a non-linear relationship between the two exists, with both $k_2$ and porosity increasing together. Similarities between the relationships shown previously for $k_1$ continue for $k_2$ with both the average cell and window diameter showing non-linear dependencies on $k_2$, as shown in figures 55 and 56. These trends are again in agreement with those of Innocentini et al [194] and [195], shown in figure 162.

The variability shown in $k_2$ for all three foam parameters is once again shown to increase quite dramatically beyond a porosity of approximately 88%, an average cell diameter of 0.8 mm and window diameter of 0.3 mm, as was the case for $k_1$.

The relationships shown for the non-Darcian permeability constant can be explained as follows. Non-Darcian permeability represents the inertial energy losses during air flow within the foam. It is generally accepted that these energy losses arise from the medium's curvature or tortuosity, with a more tortuous path leading to increased inertial energy losses that are reflected by a lower $k_2$ value. Increasing the porosity, average cell or window size in the foams decreases the tortuosity of the air flows path through the foam resulting in higher $k_2$ values.

The increased variability in both the Darcian and non-Darcian permeability constants above certain porosity, average cell and window diameters is probably a result of the increased variability seen in these parameters due to their method of manufacture. Results in figure 46 showed that the variability in both cell and window diameter increases as the porosity increased. This increase in variability was also noted by Sepulveda, [186], and possible reasons for this were discussed in section 6.1.3.1.

The reason why the values for both $k_1$ and $k_2$ should increase so markedly beyond a porosity of 88%, a cell diameter of 0.8mm and a window diameter of 0.3 mm is as yet unclear.

The most commonly encountered relationship between the permeability of a porous medium and its' structural properties is that proposed by Ergun [191], see equation 4 section 2.5.2. To
date however, the problem in applying this equation has been what parameter should be used for the particulate diameter, \( d \), and a number of variables have been proposed as discussed in section 2.5.2.

Figure 57 compares values for the Darcian permeability constants obtained using the Forchheimer equation, equation 3, applied to experimental data against Darcian permeability constants calculated using Ergun's equation for \( k_f \) determination, using values of the average cell and window diameters for the characteristic length \( d \). The result clearly shows that using either the average cell or window diameter as the characteristic length \( d \) in the Ergun equation, does not allow a close prediction of the Darcian permeability constant to be made, especially at porosity levels <88%. This result is not surprising if one considers that the Ergun equation was experimentally determined at very low gas flow rates through packed beds of granular solids and not cellular materials [191].

A much better correlation exists between the experimentally determined Darcian permeability constant and those calculated using the relationship proposed by Burke et al [223], in which the viscous energy losses are proportional to \( (1-\varepsilon) / \varepsilon^2 \), using the average window diameter as the critical length \( d \), as shown in figure 58. Similarly to the result in figure 57 the use of the average cell diameter as a value for \( d \) does not result in a satisfactory relationship in predicting a value for \( k_f \). However Burke et al [223] did not recognise that the total pressure drop is additive of both the viscous and inertial energy losses, which was subsequently demonstrated by Ergun [191].

Comparison of experimentally obtained values for the non-Darcian permeability constant to those predicted using the Ergun relationship were given in figure 59. In both scenarios where the average cell and window diameters were used as the critical length \( d \) neither were shown to result in a good correlation between the experimentally obtained results. However, if the empirical coefficient of 1.75, experimentally determined by Ergun at low gas flow rates using columns packed with uniform granular media, is increased to 6.0 then a much closer correlation between the measured and calculated non-Darcian permeability constants is achieved, as shown in figure 60, again using the average window diameter as the critical value for length. This increase in the inertial coefficient of the Ergun equation is most likely related to the increased surface roughness of the gel cast foams used here in comparison to the media used by Ergun, as discussed by Macdonald et al [224].
It is therefore suggested that the pressure drop across gel cast ceramic foams is best described using a modified version of the Ergun equation, equation 5 below, in which the additive nature of the viscous and inertial energy losses are still recognised and his proposed relationship for \( k_2 \) still stands but the relationship of Burke et al [223] is used to describe the viscous energy losses.

\[
\frac{(-\Delta P)}{L} = \frac{150(1-\varepsilon)}{\varepsilon^2 d^2} \frac{\mu V}{\varepsilon^2 d^2} + 6\frac{(1-\varepsilon)\rho V^2}{\varepsilon^3 d} \quad \text{— Equation 5}
\]

A comparison between experimentally obtained backpressure and calculated backpressures using equation 5, for foams of 85, 90 and 94% porosity, were given in figure 61.

The result clearly shows a good correlation between the experimentally measured and calculated results at high porosities. However, below approximately \( \varepsilon = 90\% \) the above relationship becomes less adequate. This is due to an increase in variation between the measured and calculated \( k_2 \) values at lower porosity, as shown in figure 60, combined with the fact that at the high velocities studied here inertial energy losses are dominant, by factors of \( 10^2 \) to \( 10^3 \) difference.

Although not conclusive, as a much larger study involving more samples over a broader range of porosities and window diameters would be required, equation 5 does appear to be a very useful method for approximating the backpressure in highly porous gelcast foams using easily obtainable data.

6.1.4.2 Effect of altering the foam length

Altering the length of the foam filter through which the air must pass will have no effect on the permeability of the foam, i.e. \( k_1 \) and \( k_2 \) would remain constant. However there is a subsequent effect on the resultant backpressure in the system. The effect of increasing foam length on backpressure at increasing air velocities was shown in figure 62. As would be expected the backpressure increases linearly as the foam length and air velocity are increased. This increase in backpressure is simply due to the air having to travel a greater distance through the foam resulting in greater viscous and inertial energy losses. This linear relationship is in agreement with the work of both Watabe et al [53] and Mizrah et al [54].
6.1.5 Filtration performance

When developing a DPF system a filter medium is needed that is permeable enough in order to give a suitably low backpressure, whilst having a filtration efficiency suitably high enough to justify its use. The following section begins by discussing the type of model soot that was used in comparison to diesel soot before the variables that affected filtration efficiency; soot loading, structural parameters and filter length, are discussed. Finally the effect the trapped soot had on backpressure is discussed.

6.1.5.1 Comparison of model soot to actual diesel soot

Micrographs of the TEM characterisation of both the model diesel soot, Printex-U, and actual diesel soot collected from a 1.8 litre Peugeot diesel car were given in figures 63 and 64 respectively. Both samples appear very similar in consisting of agglomerates of individual carbon particles, with the real diesel soot having a slightly smaller average particle diameter of approximately 20 nm than that of Printex-U at approximately 25-30 nm. A previous study by Neeft [201] on the characterisation of diesel particulates and Printex-U provided a similar result to this, and concluded that aside from differences in the amount of adsorbed hydrocarbons and metal impurities present in diesel soot, Printex-U was well suited for use as a model diesel soot.

6.1.5.2 Development of a filtration system

As discussed above in section 6.1.5.1, Printex-U is similar enough to diesel soot in respect to its particle size and morphology to be used as a substitute. However, in order to be used successfully for filtration studies the particles of Printex-U needed to be fluidised in a manner that replicated the kind of aerosol particle size distribution seen in actual diesel exhaust gas streams. This proved a very difficult task to achieve in a “bench top” type rig. However a system was finally developed. The result of the particle size distribution generated in this aerosol was given in figure 65. In comparison to a typical particle size distribution of diesel exhaust (total solids, soluble organic fraction and sulphate portions), shown below in figure 163, the generated aerosol appears to have a broader distribution with a higher proportion of larger agglomerates of Printex-U particles. The aerosol generated does however also contain a significant range of the smaller particles encountered in diesel exhausts.
6.1.5.3 Soot loading effects

Since foam filters operate via a deep bed filtration mechanism the effect of increased soot loading on filtration efficiency was studied on four different foams and the results were presented in figure 66. In all the tests, filtration efficiencies can be seen to decrease as the soot loading on the foams increases. This observed behaviour is the opposite of what is to be expected from deep bed filters, filtration efficiency would be expected to increase as the trapped particulate content increases as a result of pores in the bed blocking up. It is believed that this observed phenomena is due to soot “blow off”, where by the high velocity gases passing through the foam erode away built up layers of soot previously collected in the foams structure. This result is not unusual for foam DPFs as the phenomena of soot blow off has previously been noted by Arai et al [226] and Helfriech et al [57]. The results in figure 66 also show that filtration efficiencies >80% could be achieved at low soot loading levels using foams with ε<90%, however this efficiency tails off due to the above “blow off” effect. These results are in agreement with recent results for low level loading of reticulated foams reported by Ambrogio et al [227], who used a similar bench top rig to that described here in section 4.1.1.7.
6.1.5.4 Effect of foam properties on filtration efficiency

The relationship between foam porosity and filtration efficiency was presented in figure 67. The plot shows that as the porosity increases the filtration efficiency decreases quite markedly, with a porosity change of some 6% resulting in a filtration efficiency decrease of approximately 30%. The reason for such behaviour is probably best explained by increased foam porosity resulting in a reduction in available solid surfaces on which to trap the soot. Figures 68 and 69 presented the relationship between the average cell and window diameter of the foam to filtration efficiency. In both cases the effect of increasing the average cell or window diameter results in a decrease in filtration efficiency that again is probably best explained through a decrease in solid surfaces being available for soot filtration.

6.1.5.5 Effect of foam length on filtration efficiency

The effect of increasing foam filter length on the resultant filtration efficiency was shown in figure 70. The result clearly shows that increasing the length of the foam through which the soot laden air stream is forced to pass greatly improves filtration efficiency, with efficiencies >90% achievable for a 89% porosity foam. Intuitively such a result can be explained as a result of the dirty air stream having to pass through a greater volume of foam thereby presenting much more solid surfaces on which to trap the soot particles. Figure 70 also shows that beyond a certain length no great increase in filtration efficiency is seen, this is probably a result of the filtration profile gradient seen in foam filters, as previously shown in figure 11. The above is in agreement with the results reported by Tutko et al [51], as shown in figure 10, section 2.2.5.

6.1.5.6 Effect of filtered soot on backpressure

The location of filtered Printex U particles in gel cast alumina foam was visualised in the SEM image shown in figure 71. Agglomerates of Printex U particles can clearly be seen on the solid surfaces of the cell walls in the foam. What is also evident in this image is the Printex U blocking up some windows in the foam, exemplified by the circled window in figure 71. Such behaviour would be expected to have a negative impact on the backpressure in the system.
The results of experiments monitoring backpressure as a function of Printex U loading and air velocity were given in figure 72. This plot shows that trapped soot does indeed have a negative impact on the backpressure as would be expected, with the backpressure increasing linearly as a function of increased soot loading. However, the negative effect on backpressure as a result of these trapped particulates is small, approximately 0.1 kPa at a loading of 3 g l⁻¹ Printex U at 3 ms⁻¹.

6.1.6 Sizing and selecting a foam filter suitable for use as a DPF

An optimised foam filter system requires a low back pressure combined with a high filtration efficiency. In the previous section on foam permeability, section 6.1.4, it was demonstrated that in order to increase the permeability of gel cast foams, hence lower the backpressure, short length high porosity foams with large average cell and window diameters were required. In the previous section, section 6.1.5, it was shown that in order to achieve high filtration efficiency the complete opposite was required. As such when designing a foam filter for use as a DPF, or indeed any filtration application, a trade off exists between backpressure and filtration efficiency.

However, one variable in a DPF system that serves to increase filtration efficiency and decrease backpressure is the foam filter diameter. Altering the diameter (Φ) of the foam filter in the exhaust has the effect of changing the gas velocity (v) at the filter face through their relationship with the gas flow rate (Q) given below:

\[ Q = v \times \pi \left( \frac{\Phi}{2} \right)^2 \]

The resultant backpressure generated by the foam filter varies accordingly in line with the Forchheimer equation, equation 3.

Examples of calculated gas flow rates experienced for a variety of engine displacements at varying engine speeds was given in table 11. The table shows that gas flow rates can vary between approximately 100 to 1000 m³h⁻¹ depending on engine size and speed. The expected air velocity range, for a particular sized engine, can now be calculated from these flow rate
figures for foams of varying diameters using the dimensions of currently used WFF as a guide shown in figure 12, using equation 6.

6.1.6.1 Example of sizing a gel cast foam for use as a DPF

Typically the maximum allowable backpressure for a clean DPF system at full power is approximately 10 kPa increasing to 20 kPa loaded, although these values vary depending on engine size and manufacturer.

Previous data for a foam with $e = 89\%$, $d_{\text{cell}} = 0.7$ mm and $d_{\text{win}} = 0.21$ mm, given in figure 70, showed that in order to achieve a filtration efficiency $>90\%$ a filter bed length of 50 mm is required. Increasing the filter length beyond this was shown to have no significant improvement on filtration efficiency.

The plot in figure 73 illustrates the backpressure as a function of varying foam diameter for the same foam at a length of 50 mm, calculated using experimentally obtained values for $k_1$ and $k_2$, over a typical gas flow rate range experienced in practice by foam DPFs on heavy duty vehicles. The plot illustrates that such a foam would generate an acceptably low backpressure in its clean state throughout the complete gas flow rate range shown, at a diameter of 266.7 mm or greater. The effect of particulate loading on this foam was previously given in figure 72 and shown to raise the backpressure by approximately 0.2 kPa on a 25 mm length of foam at a particulate loading of 3 g l$^{-1}$, at these levels it is believed that the backpressure would not be raised sufficiently in the loaded state to cause a problem.
6.2 Potential catalyst material screening

6.2.1 Catalyst characterisation

X-ray diffraction patterns for all laboratory produced catalyst compounds were given in figures 74 to 86. For both the spinel and perovskite compounds, all the major peaks were identifiable except in the case of CuMn$_2$O$_4$ for which no reference data from the JCPDS database was available. The diffraction pattern for Cu$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$, figure 78, was notable in that the compound was isomorphous to both CuFe$_2$O$_4$ and CoFe$_2$O$_4$, both of which are face centred cubic structures with very similar lattice parameters.

No reference diffraction data was available for either of the alkali metal compounds produced. However, for K$_2$CO$_3$-KCl the strongest lines in the diffraction pattern could be attributed to its constituent compounds, cubic KCl and monoclinic K$_2$CO$_3$ whilst the closest matches for the strongest lines in the Li/Na/K pattern was for data from LiKCO$_3$ and LiNaCO$_3$.

In the case of the CsVO$_3$-MoO$_3$ catalyst no suitable reference data was able to be fitted to the pattern, undoubtedly this is due to the wide range of possible stoichiometries with both vanadium and molybdenum compounds, as previously noted by van Setten [228]. The XRD pattern for K$_4$V$_2$O$_7$ shows it to be primarily composed of a mixture of both the mono- and di-hydrate forms of K$_4$V$_2$O$_7$, which is in agreement with the results of Badini et al [209], and can be explained by the compounds sensitivity to moisture and hygroscopic nature.

The specific surface areas (SSA) of all the catalysts were given in table 12. Interestingly the spinel and perovskite catalysts that were all produced using the same citric acid aided process and calcined in a similar fashion had a broad range of surface areas from 1.1 to 12.8 m$^2$g$^{-1}$. This might have arisen due to differences in the concentrations of the individual salt solutions prepared, the temperature and times used for evaporation and speed of mixing, all factors which have been shown to affect particle size [203, 204] and were not kept constant in this study.
6.2.2 Development of TGA sample preparation method

As previously mentioned in section 2.3.2.2, Neeft et al [117, 119] have studied the “influence of contact between soot and catalyst” on catalytic activity through altering the method of sample preparation. Mechanically milling the mixtures was used to provide “tight” contact and physically shaking the two components together was used for “loose” contact with the former method resulting in higher catalytic activities.

In order to verify these effects reported by Neeft, the effect of mixing technique on T$_{\text{max}}$ values was studied using the procedures outlined in section 4.2.2.1, using Fe$_2$O$_3$ and K$_2$CO$_3$-KCl as examples, the results of which were given in figure 87.

The figure shows that both compounds initially behave similarly, with a steep decrease in T$_{\text{max}}$ from the initial shaken samples (zero minutes ball milling time). As the ball milling time increases the T$_{\text{max}}$ value for Fe$_2$O$_3$ begins to plateau out at a constant value of approximately 585°C, whilst T$_{\text{max}}$ continues to decrease in the K$_2$CO$_3$-KCl sample although the rate of change gradually lessens with time. These results are in good agreement with Neefts’ work [201] as shown in figure 164 below.

![Figure 164. Effect of milling time on T$_{\text{comb}}$ for an Fe$_2$O$_3$ catalyst [201]](image)

Neeft suggests that the differences seen in ball milling behaviour might be a result of the materials properties such as hardness, elasticity and compressibility and also the presence of
crystal defects that lead to catalyst "break up". In order to clarify what exactly NeefMean terms "tight" and "loose" meant and explain the differences seen in ball milling, SEM and TEM of the samples was performed.

Comparison of figures 88 and 89 show that after 5 minutes ball milling clusters of Printex U particles are clearly evident on the agglomerates of Fe₂O₃ whilst figure 90 shows that after 120 minutes ball milling the Fe₂O₃ particles are much more difficult to distinguish. High magnification SEM, figure 91, reveals that the particles of Fe₂O₃ are indeed present but the increased milling time has lead to a more even dispersion of Printex U over the Fe₂O₃ surface. The TEM images in figures 92 and 93 show that the increasing ball milling time has had no visible effect on the average Fe₂O₃ particle size.

SEM of K₂CO₃-KCl, figure 94, showed it to be composed of large agglomerates of fine particles. Comparison of figures 95 and 96 for K₂CO₃-KCl show distinct differences to those seen in Fe₂O₃. After only 5 minutes ball milling the agglomerate samples were covered in Printex U particles and no distinction between 5 and 120 minute samples could be made. This is possibly a result of the hygroscopicity of these particles aiding the adherence of a layer of Printex U. High magnification SEM, figure 96, showed the agglomerate structures to be intact and porosity visible between the particles. Unfortunately TEM on K₂CO₃-KCl was not done, as it was soluble in the ethanol used to mount samples on to a TEM grid.

This visual study suggests that the differences seen in catalytic activity through the different preparation techniques can be attributed to the degree of homogenisation achieved between the two components leading to differences in the number of soot – catalyst surface contact points, with a greater number of catalyst – soot contact points giving increased activity.

Neeft demonstrated that “tight” sample preparation techniques evaluated in the laboratory can grossly exaggerate the performance of a catalyst when in use on a DPF, and demonstrated that “loose” contact provides a more realistic outcome [119]. A series of experiments were performed in the final stages of this work to compare laboratory TGA sample preparation techniques to actual catalysed foam combustion. Therefore at this stage in the work it was felt that Printex U-catalyst samples should be prepared using both a sieving method and 120 minute ball milling technique in order to compare catalytic activity.
6.2.3 Catalyst screening

6.2.3.1 Metal oxides

Of the seven metal oxides examined only CeO₂ showed any reasonable activity for the catalytic combustion of the Printex U when well mixed together, lowering the $T_{\text{max}}$ by approximately 40°C, see figure 97 and table 16. ZnO and Fe₂O₃ also had some activity in comparison to the others and as such these three materials were the only ones used in producing poorly mixed samples, the results of which are given in figure 98 and table 17. The catalytic activity of CeO₂ previously seen was no longer evident, in fact none of the materials displayed any catalytic activity towards Printex U combustion when mixed in this fashion.

A number of researchers have investigated the use of similar metal oxides to those looked at here for the catalytic combustion of various carbonaceous materials, an overview of which was given in section 2.3.2. The poor activity of ZnO seen here is in agreement with results given by Neeft et al [117, 119], whilst the similarly poor activity found for Fe₂O₃ more closely matches that of Neri et al [121] than Neeft et al [117]. The latter found a $T_{\text{max}}$ value of approximately 480°C some 100°C lower than that found here [117]. Neeft's study [117, 119] also found CeO₂ to have a $T_{\text{max}}$ value of approximately 567°C, which is in good agreement with the value of 570°C found here. Ceria has been shown to be more successful when applied to the catalytic oxidation of the liquid portion of DPM [205]. The relatively poor activity displayed by these materials is surprising since both cerium and iron based catalysts have been successfully commercialised as fuel borne catalysts. This is probably due to the latter allowing the active species much more intimate contact with individual soot particles, as opposed to the contact achieved here.

6.2.3.2 Spinel materials

When well mixed with Printex U, the spinel materials examined were considerably more active for its catalytic combustion than the simple metal oxides discussed in the previous section, see figure 99 and table 18. All the spinel materials examined had similar $T_{\text{ig}}$ temperatures of approximately 400°C. However, changing the metal at both the A and B sites in the AB₂O₄ spinel structure had pronounced effects on the $T_{\text{max}}$ and $T_{\text{final}}$ values seen and hence the overall shape of the curves.
Comparison of well mixed materials that contain only Cu ions and 50% Cu ions at the A site in the spinel structure to those with only Co ions show that the Cu containing species have much lower $T_{\text{max}}$ and $T_{\text{final}}$ values, resulting in them having narrow and sharp shaped curves in comparison to the much broader and flatter curves in Co containing materials, see figure 99 and table 18. In addition the Cu-less species all have $T_{\text{final}}$ temperatures in excess of 600°C.

The effect of altering the B site ion in the spinel structure from Fe to Mn is also displayed in figure 99 and table 18. The structures that had Fe ions at B sites within the spinel structure all had lower values of $T_{\text{max}}$ in comparison to similar materials with Mn ions at the B site. This was also found when the catalyst and Printex U were poorly mixed, figure 100 and table 19.

The use of spinel type materials for the catalytic oxidation of diesel soot has only been studied in detail by Shangguan et al, [147, 148], who focused primarily on their ability to simultaneously remove soot and NOx emissions. Their findings suggest that CoFe$_2$O$_4$ and CoMn$_2$O$_4$ are more active in terms of soot oxidation with respect to their $T_{\text{ig}}$ values than CuFe$_2$O$_4$. The values of $T_{\text{ig}}$ found here also suggest this, but the opposite is true when their $T_{\text{max}}$ values are considered, which has been used here as the main selection parameter. However the values of $T_{\text{ig}}$ reported by Shangguan et al [148] are over 120°C lower. This difference is probably due to a combination of them having used soot collected from the incomplete combustion of diesel fuel and employing a different mixing method to the one used here. The ratio of catalyst to soot is not mentioned and if different would also have an effect on the results. Unfortunately Shangguan does not report $T_{\text{max}}$ values for these materials, preventing a direct comparison.

CuFe$_2$O$_4$ was chosen from this group of materials as being the most active in terms of its $T_{\text{max}}$ and $R_{\text{max}}$ values and hence was considered worthy of inclusion in further experiments.

### 6.2.3.3 Perovskite materials

All the perovskite materials studied had the same constituent A site elements in the ABO$_3$ structure; lanthanum and potassium. Partial substitution of potassium at the A sites was used as this had been shown to improve catalytic activity of perovskites for soot oxidation [143, 144]. The effect of altering the B site ion on catalytic activity when the catalyst and Printex U
were well mixed is shown in figure 101 and table 20. The results show that catalytic activity increases following the trend Co>Mn>Fe. The shapes of all three curves are very similar.

Altering the mixing method had no change on the catalytic activity rankings, see figure 102 and table 21, with Fe still performing the worst, though there was very little difference in the $T_{\text{max}}$ values for Co and Mn. The Co catalyst appears to be better as its $R_{\text{max}}$ value was twice that of the Mn catalyst. As previously seen for all the catalytic materials, the curves for poorly mixed materials were much broader than those of the well mixed materials.

The effect of altering the type of element at the B site in rare earth perovskite structures e.g. La, has been shown in a number of studies to influence the catalytic properties [206]. Co, Fe and Mn for instance, have all been reported as very beneficial in increasing the catalytic activity of perovskites for methane oxidation [207]. The catalytic ranking Co>Mn>Fe found here for the catalytic oxidation of Printex U is in agreement with volcano-type activity pattern theory for the oxides of the first row metals that states "the catalytic activity of base metals increases as its reducibility increases (e.g. Co, Mn > Fe, Ni> Al)" [206].

Only Teraoka et al [144] had previously investigated these three catalysts for the oxidation of diesel soot. Their findings, based on $T_{\text{ig}}$ values, suggested that catalyst activity increased with Co>Mn>Fe in agreement with current work. Hong et al [208] reported a similar such ranking for Cs substituted lanthanoid perovskite catalysts. These results all suggest Co is the most active element to have at the B site in the perovskite structure for soot oxidation. Differences in the $T_{\text{ig}}$ values reported here and in Teraokas' study most likely arise from the latter's work using soot derived from the incomplete combustion of diesel fuel which would tend to be more reactive than the Printex U used here due to the presence of hydrocarbon species. As with Shagguans' [147, 148] work on spinels, the ratio of catalyst : soot is not given but would have an effect on the results obtained.

$\text{La}_{0.9}\text{K}_{0.1}\text{CoO}_3$ was chosen from this group of materials for further study as it had a suitably low $T_{\text{max}}$ value and offered higher $R_{\text{max}}$ values under both mixing conditions.
6.2.3.4 Alkali metal and vanadium containing materials

In comparison to the previously tested metal oxide, spinel and perovskite type materials, this group of catalysts were by far the most active; with the exception of CsVO$_3$-MoO$_3$ all had $T_{\text{max}}$ values < 400°C when well mixed with Printex U, as shown in figure 103 and table 22. The results for the catalyst materials poorly mixed with Printex U, figure 104 and table 23, show that the potassium pyrovanadate was the most poorly performing material, with $T_{\text{max}}$ increasing over 100°C to 503°C. Whilst the two alkali metal-containing catalysts had $T_{\text{max}}$ values < 450°C. It should be noted that this value is still lower than the $T_{\text{max}}$ value for the best spinel and perovskite materials when well mixed with Printex U.

For discussion purposes the two groups of materials, vanadium and alkali metal containing catalysts will be discussed separately.

6.2.3.5 Vanadium containing catalysts

Both the CsVO$_3$-MoO$_3$ and K$_4$V$_2$O$_7$ materials have been thoroughly investigated by workers at Delft and Torino Universities respectively for use as diesel soot oxidation catalysts, specifically with the idea of applying them as catalytic coatings on ceramic foams, as reviewed in section 2.3.2.2. The catalyst systems both groups have developed and studied are the most active non-precious metal based systems reported for diesel soot oxidation in the open literature.

Jelles et al [140] reported a $T_{\text{max}}$ of 382°C for CsVO$_3$-MoO$_3$ in their TPO (temperature programmed oxidation) experiments approximately 40°C lower than the value of 428°C obtained here for the well mixed samples. This result is surprising as the only apparent difference is in the method of mixing the catalyst and Printex U, with Jelles [140] using a spatula to mix, i.e. he produced poorly mixed samples, which would be expected to provide a higher $T_{\text{max}}$ value.

Saracco et al [137] reported a $T_{\text{max}}$ value for K$_4$V$_2$O$_7$ of 437°C, which is some 50°C higher than the result of 388°C obtained in the current work. This difference in $T_{\text{max}}$ values might have arisen due to differences in the soot used, they used an amorphous carbon powder and also the different preparation technique employed; Saracco et al mixed and crushed the
constituents together in a pestle and mortar. A value of 360°C was reported by Badini et al [209] for the peak temperature seen in the carbon combustion curve catalysed by K₄V₂O₇ as determined by TPO. No results in the literature are given on the catalytic activity of K₄V₂O₇ when poorly mixed with soot, so comparisons cannot be made.

The large difference seen in K₄V₂O₇ T max values for well and poorly mixed samples, in comparison to those for CsVO₃-MoO₃, can be explained by considering the catalytic mechanism for the oxidation of the soot and most importantly the physical state of the catalyst at these temperatures. Saracco et al [137] proposed a mechanism based around a combination of the V-O bonds in the catalyst acting as “oxygen pumps” through repeated reduction-oxidation cycles and the C-C bond weakening and C-O bond promotion forming effects associated with the presence of an alkali metal for K₄V₂O₇. This mechanism proceeds whilst both catalyst and the soot are in the solid state and in order for it to proceed, catalyst soot contact is required and it is therefore highly sensitive to any effects that might alter this contact, i.e. the method of mixing. This is supported by the present observations for K₄V₂O₇, a shift in T max of approximately 120°C occurring by altering the mixing conditions.

In comparison the catalytic oxidation of soot by CsVO₃-MoO₃ occurs at temperatures greater than its’ melting point, i.e. in the liquid phase. Jelles et al [140] has proposed a Mars and van Krevelen type catalytic mechanism, i.e. rapid transport of electrons and ions through the ionic liquid. In comparison to the K₄V₂O₇ catalyst any advantage of such a catalytic mechanism is unapparent when the two components are well mixed. However once the method of mixing is altered and a more realistic poorly mixed system is achieved the CsVO₃-MoO₃ performs better. The improved catalytic activity under more realistic conditions is most probably attributed to the fact that a liquid phase forming catalyst will have a greater mobility, due to its liquid state thereby allowing the active species present to get in contact with the soot and catalyse the oxidation reaction. The development of increased mobility catalysts for diesel soot oxidation have in recent years been led by the groups at Delft and Torino Universities and a number of their systems were reviewed in section 2.3.2.2.

6.2.3.6 Alkali metal containing catalysts

The idea of improving catalyst – reactant contact through the formation of a liquid phase that contains active species for carbonaceous material oxidation is not entirely new, for instance it
has previously been investigated by McKee et al [210]. The majority of work in the literature on this subject is based on the oxidation of graphite and coal chars [211, 212] and none of the materials investigated had specifically been applied to diesel soot oxidation, probably as a result of the environmental concerns and legislation associated with diesel emissions not being around at this time. Therefore it was decided to include two alkali metal species into the screening programme; one liquid phase forming and one solid state, to see how they performed against the vanadium containing species that had been specifically developed for the purpose of diesel soot oxidation.

The results for the catalysts well mixed with the Printex U, figure 103 and table 22, showed that Li/Na/K is the most active of the two alkali metal-containing materials with a $T_{\text{max}}$ of 376°C approximately 20°C lower than the 394°C seen for the solid state $K_2CO_3$-$KCl$. In comparison to the vanadium species it is again the most active material investigated, approximately 10°C lower than the value found for $K_4V_2O_7$ (388°C) and approximately 50°C lower than that of the liquid phase forming $CsVO_3$-$MoO_3$ (428°C).

Interestingly the Li/Na/K material has a $T_{\text{max}}$ value lower than its melting point of 400°C, therefore catalytic oxidation is occurring in the solid state as is seen with the $K_2CO_3$-$KCl$ material. This suggests that the catalytic mechanism is unlikely to be a Mars and van Krevelen type mechanism as has been suggested for the liquid phase oxidation of soot by $CsVO_3$-$MoO_3$.

The superiority of the alkali metal containing catalysts is maintained when the materials are poorly mixed with Printex U, with both having $T_{\text{max}}$ values lower than the vanadium containing materials. However, the benefit of having a liquid phase forming catalyst to facilitate better contact with the soot when poorly mixed, as was shown with the vanadium containing materials, is not displayed here, in fact the difference between $T_{\text{max}}$ values is greater for the Li/Na/K catalyst. The shapes of the curves shown in figure 105 for both alkali metal catalysts are almost identical, with both displaying considerably more activity at temperatures $< 450°C$ than either of the vanadium materials. The identical shape of the curves suggests that even when Li/Na/K does become molten this has no great beneficial effect on the rate of soot oxidation, further proof that the mechanism is unlikely to be that of a Mars and van Krevelen mechanism and that both alkali metals have similar catalytic mechanisms.
These results suggest that these alkali metal catalysts facilitate the oxidation of the soot through a mechanism that isn't totally dependent on having good catalyst soot contact as observed for K₄V₂O₇, suggesting that an active mobile species is formed that is independent of the physical state of the catalyst.

A number of mechanisms have been suggested in the literature that are in possible agreement with the proposed mechanism ideas. McKee et al [213] elucidated a mechanism involving a redox cycle with the intermediate formation of the associated alkali metal peroxide or higher oxide that was the active species as is shown below:

\[
\begin{align*}
M_2CO_3 + C + O_2 & = M_2O + 2CO_2 \\
M_2O + \frac{n}{2}O_2 & = M_2O_{1+n} \quad \text{Where } n = 1, 2 \text{ or } 3 \\
M_2O_{1+n} + nC & = M_2O + nCO
\end{align*}
\]

Haga et al [214] suggest that K₂CO₃ catalyses carbon combustion by reduction into potassium metal, whilst Mims et al [212] showed that the potassium in K₂CO₃ interacted with the carbon surface to form surface salt complexes at temperatures well below that of the bulk melting point. This is analogous to potassium phenolate structures and it was suggested that these complexes were the active species, although the exact mechanism by which these surface complexes facilitated the oxidation of carbon was not given.

Without further extensive investigation that is beyond the scope of this work it is unclear which, if any, of the suggested mechanisms is occurring. However the mechanism proposed by Mims et al [212] would appear the most likely route as the T_{max} temperatures found are markedly lower than those at which McKee [213] proposes the formation of peroxide and higher oxide species and more similar to the temperatures proposed by Mims et al [212] for the formation of the surface salt complexes.

The results found here suggest that alkali metal species are very reactive towards soot oxidation and, more importantly, the mobility of these active species and the mechanism, whichever it is, by which they oxidise the soot is far more effective than that seen in both solid state and liquid phase forming vanadium containing materials.
Aside from the increased activity displayed by the alkali metal containing catalysts another factor that was considered was toxicity and the health and safety issues associated with the use of systems. From this perspective the vanadium containing species were thought unsuitable for this purpose, as the alkali metal catalysts were in comparison much friendlier. The alkali metal catalysts are also more attractive as they are much cheaper than the vanadium materials.

The result of this was that both of the alkali metal containing materials, Li/Na/K and K₂CO₃-KCl, were chosen for inclusion in further selection experiments.

6.2.4 Sulphur dioxide poisoning of catalysts

The effect of the presence of sulphur dioxide on catalytic activity was monitored using the methodology outlined previously in section 4.2.2.3 and the results of the experiments on the four selected catalysts were given in figure 105.

The detrimental effect of SO₂ on the performance of both the spinel and perovskite catalysts is clearly apparent, with both their Tₚₑₚ values increasing by over 60°C after 240 hours in the presence of approximately 100 ppm SO₂. This result is in agreement with Li et al [229], who noted that LaCoO₃ oxidation catalysts were sensitive to the presence of sulphur dioxide whilst studying its use for CO oxidation. For this reason both the spinel and perovskite compounds were discontinued from further investigations, although legislation is moving towards the introduction of sulphur less diesel fuels, which might permit the use of spinel and perovskite compounds in the future. Fortunately both the alkali metal compounds were shown to be resistant to SO₂ poisoning, with negligible increases in their Tₚₑₚ.

6.2.5 Hygroscopicity of alkali metal based catalysts

During the course of the TGA screening programme it was noticed that the K₂CO₃-KCl material was very hygroscopic. For instance a sample of the finely ground powder left open to the atmosphere would transform to a fluid like suspension in less than 24 hours. An experiment to quantify this behaviour was performed on both of the selected materials and the result was shown in figure 106.
The take up of moisture from the atmosphere onto the K$_2$CO$_3$-KCl catalyst is clearly visible with a weight gain of greater than 50% seen after less than one hour’s exposure to the atmosphere. Interestingly the Li/Na/K catalyst saw a negligible increase in weight over the same time period.

The hygroscopic nature of the K$_2$CO$_3$-KCl mixture means that the use of this material is impractical due to the catalyst becoming very fluid, allowing the material to readily flow to the lowest point of the support filter due to gravity. Therefore it would be practically impossible to maintain an even distribution of this catalyst on a foam. For these reasons Li/Na/K was chosen as the catalyst material for further study.

### 6.2.6 Oxygen concentration effects

In the first stage of the catalytic screening process TGA was performed on all the catalyst Printex U mixtures in air, having an oxygen concentration of approximately 21%, to rank catalytic activity. However the oxygen concentration in an actual diesel exhaust is very rarely this high and is more likely to be in the range 3-17% [3]. The effect of lowering the oxygen concentration of the feed gas entering the TGA on the catalytic activity of Li/Na/K is shown in figure 107.

The curve shows that lowering the oxygen concentration down to 2.5% had very little effect on the $T_{\text{max}}$ values. However once the oxygen concentration decreased below 2.5% O$_2$ the $T_{\text{max}}$ values increased sharply, reaching temperatures $>800^\circ\text{C}$ for the combustion of Printex U without any oxygen present. It appears that at these low oxygen concentrations Li/Na/K looses its catalytic activity towards Printex U combustion. This result supports theories like that proposed by McKee [213] and many others, [215], that alkali metals extract oxygen from the reactant gas that is then supplied in an active form to the carbon surface.

It is interesting to note in figures 108 and 109, which are DSC plots for the combustion of Printex U in air and in nitrogen respectively, the change in the thermodynamics of the reaction. Figure 108, for the reaction in air, clearly shows a sharp exothermic peak, with a maximum value corresponding very closely to that of the $T_{\text{max}}$ value. In comparison the same reaction performed in the absence of any oxygen, figure 109, shows a much broader endothermic reaction is occurring. The heat flow change seen at 500$^\circ\text{C}$ corresponds to a
decrease in the heating rate used. This endothermic reaction emphasises the loss in catalytic activity seen and that the Printex U is now being destroyed in a thermodynamically unfavourable manner.

Overall the result shows that a Li/Na/K catalyst would maintain its high catalytic activity towards diesel soot combustion throughout the range of oxygen concentrations seen in an exhaust, making it well suited for application in DPFs.

6.2.7 Ratio of catalyst to Printex U

The effect of altering the ratio of Li/Na/K to Printex U in the oxidation mixture on catalytic activity was determined by TGA in the usual manner and the result is shown in figure 110.

The results clearly show that having excess catalyst present in the reaction greatly reduces the $T_{\text{max}}$ value whilst the opposite is true if there is an excess of Printex U, with $T_{\text{max}}$ values shifted to higher temperatures. This trend is seen for all the measured parameters, $T_{\text{lg}}$, $T_{\text{final}}$ and $R_{\text{max}}$. The increasing trend seen in the $R_{\text{max}}$ values as the mass of catalyst is decreased is a direct result of there being a greater mass of soot available for combustion.

These trends are in agreement with those published by both Badini et al [209] and Saracco et al [136] for KVO$_3$ + KI and CsVO$_3$ + KCl respectively. In the latter case, Saracco et al [136] found that increasing the amount of catalyst beyond the ratio 2:1 had very little effect on $T_{\text{max}}$ whilst a ratio of 1:1 was determined optimum by Badini et al [209], the difference was only 8°C between the ratios 8:1 and 1:1. In the case of KVO$_3$ + KI this ratio of 1:1 was deemed insufficient to allow complete solid-solid contact between the components suggesting some degree of catalyst mobility during the reaction. Saracco et al [136] suggests that for the CsVO$_3$ + KCl catalyst at ratios greater than the optimum 2:1 sufficient liquid is formed to rapidly wet and promote combustion of the carbon particulates. Saracco [136] terms this ratio a mobility index, $\omega$, with the optimum ratio denoted $\omega^*$ and states the higher the $\omega^*$ ratio the higher the catalyst mobility.

However a similar optimum ratio between Li/Na/K and Printex U is not as clearly definable since the decrease in the $T_{\text{max}}$ seen is still approximately 10°C between the ratios of 6:1 and 4:1. This suggests that the mechanism involved is rather more dependent on solid-solid
contact, i.e. surface area and the active species in Li/Na/K are less mobile than those present in the vanadate based catalysts.

6.2.8 Catalyst lifetime

In order to get an idea of the useful lifetime of the Li/Na/K catalyst when in operation, repeated combustions were performed as outlined in 4.2.2.7 and the results given in figure 111.

The plot shows that even after the catalyst had been used in 50 oxidation reactions there was no apparent loss in activity, i.e. no significant increase in the $T_{\text{max}}$ value. This result was encouraging but far from conclusive as much lengthier trials, in the order of tens of thousands cycles, would need to be performed to obtain conclusive proof that Li/Na/K would have a lifetime suitable for commercial DPF use.
6.3 Catalysed Gel Cast Foams

6.3.1 Selection of a suitable support material

The four materials that were selected for evaluation at this stage of the work were alumina, cordierite, mullite and lithium aluminosilicate (LAS). These four materials were selected for a number of reasons, as discussed in section 2.5; that included their cost, suitability for use with gel casting and having appropriate mechanical and thermal properties.

The chosen material would not only have to be engineered to provide suitable permeability and filtration, but would also be required to act as an inert or perhaps performance enhancing catalyst support surface. Work in the previous section identified Li/Na/K as being the most promising catalyst material studied and this section now discusses the work performed in establishing a suitable material to support it.

In order to assess the chemical compatibility between various ceramic support materials and the Li/Na/K catalyst, mixtures of the ceramic and catalyst were prepared, as described in section 4.3.1.1, and heated to 500°C and 750°C for increasing lengths of time. At 500°C, which is experienced in the exhaust gases of heavy-duty vehicles during some driving conditions, the Li/Na/K catalyst is just above its melting point. Whilst the effect of heating to 750°C can be considered a little extreme for diesel exhaust gases, although not unseen.

These samples were then characterised by XRD analysis, as described in section 4.3.1.1, in order to determine if any new phases were formed through reaction of the support ceramic and Li/Na/K. Samples were also analysed by TGA, as described in sections 4.2.2.1 and 4.2.2.2 to determine if any change in catalytic activity had occurred.

The results for alumina heated to 500°C, figure 112, show that there is very little change in $T_{\text{max}}$ values observed from that of the pure Li/Na/K catalyst, $T_{\text{max}} = 376°C$, with a maximum increase of just 9°C seen after 240 hours. This suggests that there is minimal interaction between the catalyst and alumina at this temperature over these time periods. This is supported by the XRD results, figure 124, that showed no discernible change in the materials...
up to 240 hours, at which point the presence of a LiAlO$_2$ was detected indicating that the base ceramic and catalyst are reacting.

However, a more noticeable shift in $T_{\text{max}}$ values was observed when the alumina-Li/Na/K mixture was heated to 750°C, figure 113. All the $T_{\text{max}}$ values were increased in excess of 30°C, with the 240 hour sample having a $T_{\text{max}}$ of 413°C as opposed to 376°C for the unsupported catalyst. These results suggest that a reaction between the alumina and Li/Na/K has occurred that has a detrimental effect on catalytic performance. XRD in figure 128, clearly shows that at this higher temperature even after 1 hour of heating the alumina and catalyst reacted to form lithium aluminate phases that become more prominent as time increased. The trend of decreasing catalytic activity with increasing time at temperature is probably due to the increasing loss of catalyst species available for soot oxidation due to the formation of lithium aluminate rather than an increase in the eutectic temperature of the catalyst, for reasons discussed in section 6.2.3.6.

Both the 500°C and 750°C results for cordierite, figures 114 and 115, show that there is a moderate increase in $T_{\text{max}}$ values from 376°C to approximately 390-400°C suggesting that some catalyst deactivation has occurred through the presence of the cordierite support. Similarly to alumina at 500°C, only after 240 hours is the presence of a small amount of newly formed $\gamma$-eucryptite phase detectable whilst at 750°C the formation of this phase and another lithium aluminosilicate phase is discernible after 1 hour. The formation of $\gamma$-eucryptite appears to have a negative effect on catalytic performance, once again believed to be as a result of loss of catalyst species for the intended reaction.

An odd result is seen for the cordierite mixture heated to 500°C for 24 hours as the plot in figure 114 shows it having two peaks at 366°C and 404°C respectively, this result might be due to inadequate mixing of the sample with Printex U prior to analysis. This was possibly a result of moisture on the mixing balls post washing allowing a layer of Printex U to stick to the balls surface and prevent proper mixing with the catalyst.

The effect of reacting LAS with the catalyst at 500°C was given in figure 116 shows quite a pronounced difference to all the other plots. Instead of having well rounded broad peaks the LAS mixtures all show very sharp intense peaks, as a result of the rapid oxidation of the Printex U, as part of the overall curves at temperatures of approximately 380-400°C. Similar
results to this were noted by Neeft [201] for the oxidation of Printex U on various metal oxides and were described as "thermal runaways". This phenomenon was attributed to limited heat transportation in combination with large heat production during soot oxidation. Neeft [201] minimised this effect by diluting the mixtures with SiC and employing smaller sample sizes, 2 mg soot, 4 mg catalyst and 54 mg SiC.

Thus far these thermal runaways have been avoided by using very small masses of undiluted samples in the TGA, typically 5-10 mg in weight as described in section 4.2.2.2. This suggests that for all three samples to display such behaviour it is highly likely that some reaction has occurred between the LAS and the Li/Na/K when heated to 500°C that promotes an increased rate of oxidation of the Printex U. This promoting effect does not unfortunately reduce the $T_{\text{max}}$ values which are all similar to that of the unsupported Li/Na/K.

However the results of the LAS mixtures heated to 750°C for increasing periods of time given in figure 117 does not show such behaviour, suggesting that the previous oxidation enhancing effect is no longer evident. In fact the peaks are now much broader with $T_{\text{final}}$ values $> 480°C$, which is the worst of all the mixtures tested.

Comparison of XRD results for LAS-Li/Na/K mixtures heated to 500°C and 750°C were given in figures 126 and 130 respectively. The results at 500°C clearly show that even after 1 hour two new lithium rich phases, Li$_2$SiO$_3$ and LiAISiO$_4$, are formed with increasing intensity as the reaction time increases, whilst at 750°C the LiAISiO$_4$ phase is not formed, instead the Li$_2$SiO$_3$ phase is accompanied by the formation of a number of intense potassium rich phases. This suggests that the LiAISiO$_4$ phase formed might be responsible for increasing the rapid oxidation of the model soot.

The mullite supported samples heated to 500°C, figure 118, show an increasing trend in $T_{\text{max}}$ values from 376°C after 1 hour of heating, exactly the same as the unsupported catalyst, to 394°C as the time at temperature is increased to 240 hours. This suggests that the catalyst is deactivated with time at this temperature. XRD results in figure 127 show no change after 1 hour and the increased formation of a γ-eucryptite phase after 24 and 240 hours heating, in agreement with the TGA observations. This result is in agreement with the previous results on cordierite that the formation of γ-eucryptite has a detrimental effect on catalytic activity.
Whilst the opposite effect is seen for the samples heated to 750°C, figure 119, with the 1 hour sample having a $T_{\text{max}}$ of 410°C and the 240 hour sample having a $T_{\text{max}}$ of 390°C. XRD results, figure 131, showed the increasing formation of LiAlSiO$_4$ not previously formed with time at temperature alongside various potassium rich phases. The beneficial effect on catalytic activity through the formation of LiAlSiO$_4$ is in agreement with results previously noted for LAS-Li/Na/K.

The above study has shown that no material is totally inert to the Li/Na/K material over the complete range of temperatures studied, although by no means did any of the materials have any major detrimental deactivation effects on the activity of Li/Na/K. The LAS material was shown to promote the rapid oxidation of the Printex U when heated to 500°C with the catalyst through the formation of LiAlSiO$_4$. However, alumina was chosen as the support material of choice for two reasons. Firstly, it was shown to be one of the most inert supports when studied at 500°C, which is a more frequently experienced temperature in a diesel exhaust as opposed to the more extreme 750°C. Secondly, most work on optimising foam properties for use as DPFs has been done on alumina and at the time LAS foams with suitable density and cell/window sizes could not be manufactured.

### 6.3.2 Preparation and characterisation of catalysed foams

A wide variety of methods for applying catalyst coatings to various support substrates have been proposed in the literature. Historically, one of the most commonly encountered approaches applied to ceramic foams is via the aqueous impregnation of the foam support with solutions of the salts used to prepare the catalyst followed by a drying and calcination step to form the catalyst in-situ. van Setten et al [60] suggest that this classical impregnation method might not be best suited in preparing catalytic foams for use as DPFs for two reasons. Firstly the distribution of filtered soot in the foam is far from homogeneous. Impregnation leads to a very homogeneous distribution of catalyst in the foam structure, which is disadvantageous for this purpose, as the catalyst needs to be located where the filtered soot is most likely to be trapped in order to promote combustion. Secondly, with the classical impregnation method it can be difficult to ensure the correct amounts of precursor material have been applied to the support to produce the correct composition catalyst.
An alternative approach is the direct deposition of the prepared catalyst. This technique allows the correct composition catalyst to be prepared prior to application, therefore minimising any potential chemical composition errors and allows an uneven distribution of the catalyst on the foam similar to that of the filtered soot particulates to be produced.

Recent direct deposition techniques for the application of liquid phase forming diesel soot oxidation catalysts to ceramic foams have been explored by van Setten et al [228]. Catalysed foams were prepared by dipping the foam into a bath of the molten catalyst, however this technique proved unsatisfactory as the foams became completely saturated with catalyst. Some excess was removed by blowing air at temperature through the foam. Another method employed by van Setten [60] involved mixing the catalyst powder with oxalic acid powder and mechanically and/or ultrasonically forcing this mixture into the porous structure. This method proved successful for small $<10$ mm diameter foams but the penetration depth was poor on larger samples.

van Setten et al [60] demonstrated a more successful technique involving the direct filtration of catalyst particles out of a solvent liquid being pumped through the foam. This technique formed the basis of the methods employed here.

For both the direct deposition methods studied here, described in more detail in section 4.3.2, acetone was employed as the carrier solvent due to its ease of availability, high evaporation rate at low temperature and its inertness to the catalyst as shown in figure 132. van Setten et al [60, 228] used heptane as their carrier solvent.

Both direct deposition methods involved numerous loading and drying stages to achieve the desired catalyst loading concentrations. Figure 133 shows that by simply dipping the alumina foam, method 2, into a well dispersed suspension of catalyst the required loading level was reached must faster than by filtering the catalyst out of the acetone, method 1. A possible reason for this was the slight difference in drying method employed between the two. In method 1 the alumina foam was kept in place in the filter funnel whilst drying while in method 2 the alumina foam was placed on a glass petri dish. This latter method led to excessive catalyst loading on the back face of the foams in comparison to those loaded by method 1, as illustrated by the SEM images in figures 138 and 139. This was probably a result of the excess catalyst and acetone being unable to drain away as easily as it was able to do so.
in method 1. SEM analysis of the front face of the filters, figures 134 and 135 show little
difference between the two techniques with catalyst particles being collected on the solid cell
wall areas. These results suggest that loading via method 1 would supply the best distribution
of catalyst material in order to provide the necessary catalyst-soot contact required for
oxidation of the trapped soot particles.

Interestingly fibrous particles were observed on some samples, as shown in more detail in
figure 136, subsequent EDX analysis, figure 137, showed these fibres to be alumina based.
This contamination of the samples is believed to be from SAFFIL alumina fibres that were
being used in the laboratory at the time the samples were being prepared for SEM analysis.
Their presence should not have any detrimental effect on subsequent experiments.

The loaded alumina foams were heat treated at 500°C for 1 hour in order to melt the catalyst
to allow it to redistribute and secure itself over the alumina foam. Post heat treatment the
foams were reweighed and none showed any appreciable loss that suggested a loss of catalyst
through evaporation or flow out of the foam structure.

SEM analysis of the front faces of the catalysed alumina foams post heat treatment, figures
140 and 141 show a significant change in the distribution and appearance of the Li/Na/K
catalyst. In both figures acicular crystallites can be seen on the surface of the alumina that are
a result of melting and re-crystallisation of the catalyst on the cell walls of the foams in a
similar fashion irrespective of the loading method. EDX analysis, figures 142 and 143, on the
base alumina and crystallites in figure 140, confirmed that the crystallites seen on the surface
were in fact potassium rich and could therefore be attributed to the Li/Na/K catalyst.
Unfortunately, the newly formed catalyst coating was found to be patchy and did not
uniformly cover the surface of the cells. Judging by the amount of filtered catalyst, figures
134 and 135, to the amount visibly present on the surface walls of the cells post heat
treatment, figures 140 to 141, it seems likely that either some catalyst is adsorbed into micropores
in the foam or due to its liquid nature it redistributes itself through the foam due to
gravitational forces. The latter would be preferred for encouraging good catalyst – soot
contact. This behaviour would also explain the fact that very little difference in catalyst
coverage was seen as the loading level was increased from 35 g l\(^{-1}\) to 55 g l\(^{-1}\), since any
redistribution of the catalyst inside the foam would not be visible by microscopy.
SEM examination of the rear faces of the catalysed alumina foams showed similar patchy areas of catalyst crystallites of a similar size to those seen on the upper face along with much finer areas of catalyst, figures 144 to 145. The amount of catalyst crystallites was visually more predominant on the rear faces of the foams. This suggests that the applied material becomes mobile and migration to the rear face as a result of gravity occurs and the Li/Na/K is not anchored in its place of deposition.

It was noted however in a number of samples prepared by method 2, figure 145, that some of the windows appeared to be filled up with the re-crystallised catalyst material. This is possibly a result of the excessive amount of catalyst entrapped by the structure due to poor drainage during drying as previously discussed in combination with any re-distribution of the liquid phase by gravity to this face.

The result of an excess of catalyst material blocking the connecting windows is shown in figure 156. As expected the application of increasing amounts of catalyst material to the foams causes an increase in backpressure, resulting from the extra resistance to the air flow through the foam windows that have become partially or fully blocked with catalyst material. Figure 156 also shows the difference seen between loading methods. Method 2 clearly shows much higher foam permeability in comparison to method 1 for similar loading levels, which is a direct reflection of what was observed by SEM, figure 145.

The results of these experiments suggest that both the methods employed were suitable for the direct deposition of Li/Na/K onto ceramic foam filters. However, method 1 was the more attractive route due to its filters having improved permeability due to it maintaining open windows for air flow and having a more favourable distribution of catalyst. Unfortunately neither method gave an even coating of the cell walls at the loading levels studied. It was felt that improvements in the drying procedure used for method 2 could be made that would alleviate the clogging of the windows whilst surface roughening of the cell walls might aid in anchoring the catalyst in position and preventing excessive build up on the underside.
6.3.3 Characterisation of catalyst coatings

SEM combined with EDX analysis was used to examine the topography and chemical composition respectively of the post heat-treated catalysed foams. A wide variety of interesting catalyst crystal morphologies were seen as illustrated in figures 146 and 150.

Figure 146 shows a large crystal, >20 µm, of Li/Na/K on the surface of the rear face of an alumina foam loaded via method 1, out which there appears to have grown much finer, < 1 µm in width, blade like crystals giving the crystal an almost sea urchin type appearance. Interestingly, these very fine crystals also appear to be growing out of the surface of the alumina ceramic as better illustrated in the higher magnification image in figure 147. EDX analysis in figures 148 and 149 shows a high potassium concentration present in these crystals in comparison to the base alumina suggesting that they are composed of pure Li/Na/K catalyst. This type of crystal morphology is suggestive of a vapour phase deposition mechanism. In terms of the intended application this kind of catalyst formation would be advantageous due to the increase in surface contact area available to the diesel soot whilst it might also serve to increase filtration efficiency, especially of very fine particulates, by acting like a mini fibrous filter. This type of behaviour was also seen in certain areas of foams loaded via method 2, also on the rear face, as shown in figure 150. In general these areas of fine blade like crystals were formed independent of the type of loading method used and were always found close to areas of the foam that had much larger crystals, typically in excess of 20 µm in size and always on the rear face. These fine crystals were never seen on the front face.

This above phenomena might have arisen from the fact that the top face of the filter would be at a slightly higher temperature than the bottom face facilitating the formation of a catalyst liquid and associated vapour phase that due to gravity and increased vapour density would subsequently migrate to the rear face and condense to give the fine blade like crystals and solidify to give the much larger crystallites on to the ceramic due to the cooler surface temperature on the bottom face.

The catalyst coatings found on the upper face of the foams were always in the form of flat narrow elongated crystals growing in the same plane as the ceramic grains, as shown in the SEM micrograph in figure 151, as opposed to the blade like crystals found on the rear face that appeared to grow out of the ceramic almost at right angles. However, it was noticed that
in some areas the interface between the catalyst crystal and the base alumina contained porosity as illustrated in figure 152. Closer inspection of these areas, figure 153, does reveal the presence of porosity and also the apparent presence of a third phase bridging between the alumina and the large catalyst crystal that appears to be more elongated than the alumina grains and rougher round its periphery. Subsequent EDX analysis, figures 154 and 155, show that this third phase present is predominantly alumina but also has an appreciable amount of potassium present. The XRD results for alumina heated to 500°C for 1 hour, figure 124, do not reveal the presence of this new phase probably due to the amounts formed being below the limits discernible by XRD.

This porosity and the presence of a third phase was not noticed on the rear faces of the foams. This might again be explained by the previous theory that the upper surface of the foam is hotter than the bottom and at a high enough temperature so as to allow a reaction between the catalyst and alumina to occur that results in the formation of a third phase that leads to the formation of porosity.

6.3.4 TGA Evaluation of catalysed foams

Unfortunately very little evidence has been found in the literature reporting on TGA studies of ceramic foam supported catalytic combustion of carbonaceous materials. A number of studies have been made on the use of catalysed foams for soot combustion but all were studied in pilot plant / engine test rigs and don’t allow comparisons between results to be made [136].

In order to evaluate the performance of the catalyst whilst supported on the alumina foam support catalysed foam samples were loaded with Printex U, as described in section 4.3.2.3. Out of these loaded discs small cylindrical samples, small enough to be able to fit inside the alumina sample pan of the TGA, were core drilled out and TGA was performed as described in section 4.2.2.2.

The rate of change in weight loss as a function of temperature seen for foams loaded via methods 1 and 2 were given in figure 157. A clear difference is seen between the two loading methods. Both have similar T_{ig} points, < 350°C, but method 2 shows a much more gradual increase in its rate of change of weight loss up to approximately 470°C before a sharp rise in the rate is seen with a T_{max} at approximately 520°C. However, the curve for method 1 is much
more trapezoid in shape with two maximums, the first at approximately 400°C and the second at approximately 495°C.

Similarly shaped curves to these have been reported by Saracco et al [137], which he explains as being a result of a two step combustion process. The initial combustion arises from carbon particles in direct contact with the catalyst whilst the second stage is the combustion of carbon articles that due to imperfect mixing are not in direct contact.

A similar explanation can be postulated here. Since in method 2 it was shown that the majority of the catalyst was present at the rear face, the opposite face to where the greater proportion of the Printex U was collected, the initial combustion rate would be expected to be low due to the low concentration of soot in intimate contact with catalyst. However as the temperature increases the catalysts mobility increases therefore allowing it to come into contact with more and more soot resulting in an increase in the rate of combustion. In use the foam would simply be rotated to present the most catalysed surface to the oncoming soot particulates.

Whereas loading method 1 is more favourable as it allows a greater proportion of the trapped Printex U to have an initial intimate contact with the catalyst, due to both catalyst and soot loading methods employing the same deep bed filtration mechanism. This is reflected in the higher initial combustion rate seen. The rate slightly decreases as the number of intimate catalyst-carbon contacts decreases. However, due to the catalyst being located in close proximity to the soot particles, combined with increasing catalyst mobility as a result of increasing temperature, ensures that this rate stays constant as the catalyst comes into contact with surrounding carbon particles before a slight increase in rate is seen at the end as the ratio of catalyst to soot changes to an excess of catalyst before decreasing as all the soot feeding the reaction is used up.

The effect of increasing the catalyst loading on the rate of change in weight loss for foams loaded using method 1 is shown in figure 158. The 55 gl⁻¹ curve clearly shows in the initial stage of the combustion process, at temperatures < 450°C, an increased rate compared to the 30 gl⁻¹ foam, whereas the effects later on at higher temperatures are relatively minimal. This increase in the rate at lower temperatures can be explained by there being more catalyst available at higher loading levels in positions easily accessible to the filtered out Printex U
particles therefore allowing a greater number of initial intimate contact points between catalyst and carbon particles. As the temperature increases above 450°C and catalyst mobility increases then the increased loading effects and associated initial catalyst-soot contact points become more irrelevant. Also shown in figure 158 for comparative purposes is the combustion profile seen for Printex U on an un-catalysed foam. This result clearly demonstrates the effectiveness of the Li/Na/K catalysed foams for Printex U oxidation with both the $T_{ig}$ and $T_{fmal}$ values approximately 100°C lower using catalysed foams. The ideal situation would be to have the same shape combustion curve displayed by the un-catalysed foam but shifted to the lower temperatures associated with Li/Na/K catalytic combustion. This could only be achieved through the preparation of a catalyst coating that had good initial intimate contact with the filtered soot at approximately 380°C, when the Li/Na/K displays a high activity and prior to it become molten and possibly flowing out of the reaction area.

6.3.5 Comparison of TGA sample preparation technique to catalysed foam combustion

As previously discussed in section 6.3.4, the methods used to prepare the TGA samples were shown to result in rather marked differences in the combustion curve profiles seen. In summary it has been demonstrated that in-homogeneous mixing of both the components generally results in the catalyst displaying a higher $T_{max}$ value and lower $R_{max}$ value, $T_{ig}$ values are less susceptible to change, whilst much more favourable results for exactly the same catalyst material can be obtained by thorough mixing to produce a more homogeneous sample. These differences have been attributed to the number or amount of catalyst-soot contact points that are achieved via the different mixing regimes employed. With the more homogeneous mixtures a greater proportion of carbon particles are in direct contact with the catalyst surface thereby facilitating their combustion through the proposed redox type mechanism. The less homogeneous mixtures display a lower catalytic activity due to fewer catalyst-soot contacts.

Work in the literature by Neeft [201] demonstrated that under practical loading conditions, using an actual diesel exhaust to load a filter, TGA analysed catalytic combustion on a section of cordierite wall flow filter monolith had a much closer resemblance to “loose” contact type conditions i.e. in-homogeneous mixing than “tight” contact conditions. In order to asses how the laboratory mixing conditions used within this study compared to catalysed combustion on a ceramic foam the TGA results from all three experiments have been plotted, as shown in
figure 159. What is clearly obvious is that neither the well or poorly mixed TGA samples is a suitable method for accurately modelling the actual result seen for combustion of Printex U loaded, using realistic aerosol filtering conditions, onto a catalysed foam.

The $T_{max}$ value for the first peak of the catalysed foam combustion profile lies approximately midway between those of the well and poorly mixed samples. This suggests that during this early stage of combustion the number of intimate catalyst – Printex U contact points must lie somewhere in between that achieved during both mixing regimes. Neither of the preparation methods reflects the plateau section or second peak seen in the catalysed foam combustion, which has been attributed to the combustion of Printex U particles not in direct contact with the catalyst and only reached through the catalysts increasing mobility at increasing temperature.

6.3.6 Effect of support structure on combustion

Mizrah et al [54] noted that one of the benefits of using reticulated foam DPFs in comparison to wall flow filters was that both the catalysed and un-catalysed combustion of diesel soot occurred at lower temperatures. This phenomena was explained by the foam having a more open porosity and isotropic structure thereby allowing easier flame front propagation through the structure.

A similar finding can be seen in the plot in figure 160, in which combustion profiles for well and poorly homogenised alumina – Printex U mixtures are compared to that for combustion of Printex U on an uncatalysed alumina foam. The alumina foam has a $T_{max}$ approximately 20°C lower than that seen in both the other samples. Alumina has been shown to be inert towards Printex U combustion in this study, section 6.2.3.1, and for soot combustion by many in the literature [230] and due to this lack of catalytic activity appears insensitive to the mixing technique employed, as shown by the results in tables 16 and 17. This decrease in $T_{max}$ can therefore be attributed to the open porous structure facilitating oxidation of the Printex U as it allows a good transport of oxygen to the Printex U reaction front that is needed to maintain the un-catalysed reaction. Whilst in both the other examined cases oxygen transport to Printex U particles at the centre of the sample mass becomes limited.
Chapter 7

Conclusions

The aim of this chapter is to draw conclusions from the three main work themes; (1) Feasibility of using gel cast foam DPFs, (2) Low operating temperature diesel soot oxidation catalyst development, (3) Production and testing of a catalysed gel cast foam for soot oxidation, from the results and discussion sections.

7.1 Feasibility of gel cast foam DPFs

A series of foaming experiments on alumina suspensions, with a suitable rheology for foaming, was undertaken to evaluate the performance of a number of commercial foaming agents. Two foaming agents, alpha foamer and B25, were shown to be far superior for foaming the suspension and achieving large bubble sizes in a short period of time.

Characterisation of the foams revealed linear relationships between the porosity of the foam and both the average cell and window diameter. Visual changes in the structure of the foam were seen as the porosity increased, with foams becoming less cellular in appearance; that was attributed to a decrease in foam stability at increased idle times. It was also shown that the idle time to achieve larger celled foams could be halved by using B25 or alpha foamer instead of Tergitol TMN10.

Airflow through the foams produced was shown to be non-Darcian and obeyed the Forchheimer equation over the range of velocities studied. The relationship between calculated Darcian and non-Darcian permeability constants and the structural parameters of the foam was found to be in agreement with work in the literature.
The Ergun equation was used to predict the permeability constants using the measured foam porosity values and either the average cell or window diameter as the characteristic length, $d$, neither of which proved satisfactory. However, for Darcian permeability constant determination it was shown that a close correlation existed between measured $k_1$ values and those predicted using Burkes equation and the average window diameter as a value for $d$. It was also found that increasing the empirically determined coefficient value of 1.75, used by Ergun to predict $k_2$ values, to 6 and again using the average window diameter as the critical length, $d$, yielded a close correlation between the measured constants. This increase in the inertial coefficient of the Ergun equation was explained by a difference in the surface roughness of the media.

A new equation combining Burkes relationship and a modified Ergun equation was proposed and shown to be accurate in determining backpressure across gelcast foams at porosity values $>90\%$.

Equipment suitable for fluidising Printex U and providing an aerosol of Printex U particles was developed and used in a series of filtration experiments. It was shown that the filtration efficiency of the foams appeared to decrease as the amount of soot loaded on them increased which is the opposite to normal deep bed filter behaviour and was attributed to soot “blow off”, a process by which loosely bound clusters of soot particulates are eroded away from the bulk of the trapped material by air flowing through.

Filtration efficiency was found to increase as porosity and the average cell and window sizes decreased, this was due to the result of increasing solid surface area on which to trap soot particles. This is in direct contradiction to the foam properties required for increasing foam permeability, hence a trade off between the two was shown to exist.

Increasing filtration efficiency could also be achieved by increasing the length of the foam filter, however this had its limitations and beyond a certain length no appreciable increase in filtration efficiency was noticed and served only to detrimentally increase back pressure.

Filtered particles of model diesel soot were visually shown to block up the windows of the foams resulting in a decrease in foam permeability. This negative effect was shown to be pretty inconsequential on the overall backpressure generated.
7.2 Low operating temperature diesel soot oxidation catalyst development

The catalyst screening program began with the TGA ranking of a number of potential catalyst materials, including various metal oxide, perovskite, spinel, vanadium and alkali metal based compounds, and resulted in the following materials being selected for further study (listed in order of activity when well mixed):

Li/Na/K, K₂CO₃/KCl, La₀.₉K₀.₁CoO₃ and CuFe₂O₄

These four selected materials were next tested for their tolerance to sulphur poisoning. Both the spinel and perovskite compounds were shown to be in-tolerant to sulphur dioxide, at a concentration level currently experienced in diesel exhaust, with a significant increase in their $T_{\text{max}}$ values. However, both the alkali metal based catalysts were unaffected by the presence of sulphur dioxide. On this basis both CuFe₂O₄ and La₀.₉K₀.₁CoO₃ were discarded from further trials.

During the course of the work it was noticed that the two selected alkali metal based materials displayed some hygroscopic behaviour. Experiments were performed to quantify the extent of this behaviour. The results of this work showed that the K₂CO₃/KCl material was extremely hygroscopic in nature, a weight gain of >50% in less than one hour was observed, that resulted in the material become visibly quite fluid. It was felt that such behaviour in a catalyst material would be unsuitable for use as a coating on foam DPF due to relocation of the material through moisture absorption from the ambient air whilst the engine was not in operation. Therefore Li/Na/K was selected as the material of choice.

Since all previous TGA experiments were performed in air, at an oxygen concentration of approximately 21%, and under realistic operating conditions the oxygen concentration in a diesel exhaust is rarely at this level and more realistically varies from 3-17%, a series of TGA runs were performed at decreasing oxygen concentration levels. It was shown that the performance of the Li/Na/K catalyst material was unaffected within this lower range of oxygen concentration and $T_{\text{max}}$ values were maintained at $\leq 400^\circ\text{C}$ down to an oxygen concentration of 2.5%. However, once the oxygen content did fall below 2.5% catalytic performance was greatly inhibited.
The effect of repeated oxidation cycling on Li/Na/K catalytic performance was measured and it was shown that its catalytic activity was unaffected up to 50 cycles.

No previous studies have been performed on Li/Na/K looking specifically at its use as a diesel soot oxidation catalyst. Only its use as a catalyst for coal and coal char gasification has been investigated. The results given here suggest that Li/Na/K offers an alternative material to the diesel soot oxidation catalysts studied in the literature with a number of additional beneficial properties such as low cost and low toxicity in comparison to other potential systems investigated, making it a worthy candidate for future study.

### 7.3 Production and testing of a catalysed gel cast foam for soot oxidation

The first stage of this section of the work program began by investigating the compatibility between the chosen Li/Na/K catalyst material and a number of potential ceramic materials, alumina, cordierite, mullite and lithium aluminosilicate, that could be used for the production of a gel cast foam DPF. This was done via combined TGA and XRD studies to determine what effect combining Li/Na/K with the four support materials chosen for inclusion in this study had on the chemistry and catalytic performance of the material.

Unfortunately none of the four support materials were shown to be totally inert to the Li/Na/K catalyst material over the time periods and exposure temperatures employed and the majority of the reactions that occurred had detrimental effects on catalytic performance. Only lithium aluminosilicate was shown to have an interesting promotion effect on the rate of Printex U oxidation when mixtures had been pre-heated to 500°C prior to testing, this was lost when the pre-heating temperature was raised to 750°C. XRD studies showed that this might have been due to the formation of a LiAlSiO₄ phase.

Alumina was finally decided upon as the material of choice for the progression of this study since it was the most inert substrate out of the four when tested at 500°C, a more commonly encountered exhaust gas temperature than the extreme of 750°C, and also the majority of the previous work on foam optimisation for use as a DPF had been done using alumina.

The second stage in this section of the work was the development of a suitable method for applying the Li/Na/K catalyst to the foam and the characterisation of the obtained catalytic
coatings. A direct deposition route was chosen as opposed to aqueous impregnation as it was felt such a route would result in a catalyst distribution similar to that obtained for the filtered soot therefore aiding catalyst soot contact.

Two techniques were evaluated here; dipping the foam into a catalyst/acetone suspension and filtering catalyst particles out of such a suspension. The former method was shown to be prone to excessive loading on one side of the filter that resulted in clogging up of the windows that had a net effect of leading to an unwanted decrease in foam permeability. This was believed to be due to an inappropriate drying technique, whilst the latter method was chosen for future experiments since it provided foams with a more even graded concentration distribution of Li/Na/K that did not have such a detrimental effect on foam permeability. Unfortunately SEM examination of the catalysed surfaces revealed that neither method resulted in an even catalytic coating on the foam.

SEM and EDX analysis revealed differences in the applied Li/Na/K coatings topography and chemistry that was believed to have arisen due to temperature differences across the foam during heat treatment. The result was the formation on the cooler side of the foams of areas containing very fine, <1 μm, blade like crystals that appeared to be growing out at 90 degrees to the alumina surface, suggestive of vapour phase deposition/growth. Examination of the hotter side of the foams revealed the presence of larger Li/Na/K crystals, grown in the same plane as the alumina grains. The hotter side of the foams also displayed areas of porosity, discovered using high magnification SEM, and EDX analysis showed these areas of porosity to be associated with the formation of a new potassium aluminate phase.

The formation of this almost “grass” like catalyst coating would be most advantageous for application in DPFs, since it should aid filtration of the finer soot particles, in a method similar to that of fibrous based filters, about which there is currently considerably great concern and no proven answer, whilst also providing a greater catalytic surface area on which to promote the oxidation of the trapped particles.

The final stage of this work program was the performance evaluation of the prepared Li/Na/K catalysed alumina foams for Printex U oxidation. This evaluation was performed by a series of TGA experiments on small sections of catalysed foams loaded with Printex U filtered from an aerosol stream.
The combustion profile seen for catalysed foam combustion was completely different to those previously seen for un-supported catalytic oxidation of Printex U, with the foams having two peaks. This two-stage combustion process was postulated as being a result of the high degree of in-homogeneity between the Printex U and catalytic coating on the foams. With the first peak corresponding to particles in close contact and the second peak a result of mobile species in the catalyst reaching particles of soot that had no initial contact with the coating.

TGA work revealed that the two different loading methods employed, dipping and filtering, resulted in subtle but distinct differences in their combustion profiles. These differences were attributed to the differences in catalyst distribution profiles previously mentioned with the filtering method yielding a more preferable combustion profile as a result of it having a catalyst distribution similar to that of the filtered soot thereby increasing catalyst – Printex U contact and activity.

The effect of increasing catalyst loading was shown to be of importance during the early stages of oxidation of the Printex U due to the increased number of catalyst soot contact points whereas it became less significant at higher temperatures due to increased catalyst mobility.

Previous work in the literature, and work in this study, has shown that differing laboratory catalyst-soot TGA sample preparatory methods can greatly influence catalytic performance as a result of differences in homogeneity of the mixtures. This work has shown that neither of the techniques employed within this study can be used to reliably prepare laboratory TGA samples that allow direct comparison to catalytic combustion on foams. The first peak of the combustion profile has been shown to lie somewhere in-between that of poorly and well mixed Li/Na/K-Printex U mixtures, whilst the rest of the catalysed foam combustion profile is not reflected in either laboratory preparation technique.

Combustion of Printex U supported on un-catalysed alumina foams was shown to be advantageous over Printex U combustion supported on alumina powder, as it produced $T_{\text{max}}$ values approximately 20°C lower. This enhanced combustion is believed to be a direct result of the foams open porous structure facilitating oxygen transport to the reaction zone.
Overall this work has demonstrated that the flexibility of gel cast foaming technology allows foams with tailored permeability and filtration efficiencies to be produced that are suitable for use as DPFs. These foams can achieve suitably high filtration efficiencies and low back pressures over much shorter lengths than current wall flow filter technology, making them ideally suited for applications where space is at a premium.

Such foams can be successfully coated with a diesel soot oxidation catalyst which in conjunction with their open structure facilitate the oxidation of trapped diesel soot particulates at lower temperatures. Using an alkali metal based catalyst system previously unreported for use as a diesel soot oxidation model diesel soot laden catalysed foams have been demonstrated capable of initiating filter regeneration at temperatures less than 400°C, under laboratory type conditions, that present the potential for their use in current passenger and heavy truck diesel engine vehicles.
Chapter 8

Further Work

The following is a brief description of possible areas where future work might be performed within each of the work themes.

8.1 Feasibility of using gel cast foams DPFs

- Further develop and prove the equation proposed for gel cast foam backpressure determination by including a larger number of samples encompassing a much broader range of porosity and window diameters.

- Investigate the surface roughness effect on the inertial coefficient as a function of foam material and foaming agent used.

- Compare the filtration efficiency of foams when used under more realistic conditions to determine if the phenomena of soot “blow off” still occurs with wetter soot particulates.

8.2 Low operating temperature diesel soot oxidation catalyst development

- Develop more sulphur dioxide tolerant spinel and perovskite catalysts.

- Determine the difference in catalytic performance when fresh diesel soot is used in comparison to the model diesel soot used.
• For the chosen Li/Na/K catalyst develop a better understanding of the mechanism by which it catalyses the combustion of the model diesel soot.

• Perform accelerated ageing trials on Li/Na/K to establish its long term stability under more realistic conditions for use as a diesel soot oxidation catalyst.

8.3 Production and testing of catalysed gel cast foams for use as DPFs

• Establish what the long term effects of supporting Li/Na/K on alumina are on catalytic performance and the mechanical and thermal properties of the support material.

• Perform TGA on LiAlSiO$_4$-Printex U mixtures to establish if the rapid oxidation seen on LAS-Printex U was due to its formation.

• Develop a laboratory TGA sample preparation method that more closely resembles the combustion profile displayed by catalysed foam combustion.

• Determine the optimum catalyst loading level for successful “trapless trap” operation.

• Perform trials under more realistic diesel exhaust conditions and temperatures.

This final area of future work is the natural progression from the laboratory work performed here and has been initiated at Hi-Por Ceramics Ltd.


exhaust in rats. Toxic and carcinogenic effects of solid particles in the respiratory tract”, 4th International Inhalation Symposium, Hannover, Germany, 1993

28. ECE Regulation No.49 (UNECE, 1982)

29. EC Directive 91/542/EEC

30. EC Directive 1999/96/EC


37. Conversation with Fiat, Torino, Italy


45. S Miwa, F Abe, T Hamanaka, T Yamada & Y Miyairi, “Diesel particulate filters made of newly developed SiC”, SAE 2001-01-0192


47. R Bloom, “The development of fibre wound diesel particulate filter cartridges”, SAE 950152


49. A Mayer, A Buck & H Bressler, “The knitted particulate trap: field experience and development progress”, SAE 930362


52. K Yoro, S Itsuaki, H Saito, S Nakajima & S Okamoto, “Diesel particulate filter made of porous metal”, SAE 980187

53. Y Watabe, K Irako, T Miyajima, T Yoshimoto & Y Murakami, “Trapless trap” – a catalytic combustion system of diesel particulates using ceramic foam, SAE 830082


56. Y Niura, K Ihkubo & K Yagi, “Study on catalytic regeneration of ceramic diesel particulate filter”, SAE 860290

57. R L Helferich & R C Schenck, “Evaluation of a stacked element diesel particulate trap using newly developed membrane covered ceramic foam filtering media”, SAE 890787


64. D P Thimsen, K J Baumgard, T J Kotz & D B Kittelson, "The performance of an electrostatic agglomerator as a diesel soot emission control device", SAE 900330
65. D B Kittelson, J Reinertsen & J Michalski, "Further studies of electrostatic collection and agglomeration of diesel particles", SAE 910320
68. R M Heck & R J Farrauto, "Catalytic air pollution control commercial technology", van Nostrand & Rheinhold, Amsterdam, 1995
69. P Zelenka, W Kriegler, P L Herzog & W P Cartellieri, "Ways toward the clean heavy-duty diesel", SAE 900602
70. M Wyatt, W A Manning, S A Roth, M J D'Aniello, E S Andersson & S C G Fredholm, "The design of flow through diesel oxidation catalysts", SAE 930130
74. W R Wade, J E White & J J Florek, "Diesel particulate trap regeneration techniques", SAE 810118
75. N Higuchi, S Mochida & M kojima, "Optimised regeneration conditions of ceramic honeycomb diesel particulate filters", SAE 830078
76. W R Wade, J E White H A Cikanek & J J Florek, “Thermal and catalytic regeneration of diesel particulate traps”, SAE 830083
80. O A Ludecke & D L Dimick, “Diesel exhaust particulate control system development”, SAE 830085
82. V D Rao, J E white, W R Wade, M G Alimone & H G Cikanek, “Advanced techniques for thermal and catalytic diesel particulate trap regeneration”, SAE 850014
83. K Ohno, N Taoka, T Ninomiya, H Sungtae, M Kojima & T Komori, “SiC diesel particulate filter application to electric heater system”, SAE 1999-01-0464
84. P Kojetin, F Janezich, L Sura & D Tuma, “Production experience of a ceramic wall flow electric regeneration diesel particulate trap”, SAE 930129
85. T Yamada, M machida & Y Ichikawa, “Development of wall flow type diesel particulate filter system with reverse pulse air regeneration”, SAE 940237
86. A Matsunama, T Takizawa, K takeuchi & K Yokota, “Status of particulate trap system for a heavy duty diesel truck”, SAE 910132
88. Y Goto, T Abe, T sato & M Hayashida, “Study on regeneration of diesel particulate trapper by electrical self-heating type filter”, SAE 920140
89. Z Ning & Y He, “Experimental study on microwave regeneration characteristics of diesel particulate after-treatment system”, SAE 1999-01-1470
91. F B Walton, P J Hayward & D J Wren, “Controlled energy deposition in diesel particulate filters during regeneration by means of microwave irradiation”, SAE 900327


94. J B Dementhon, B Martin, P Richards, M Rush, D Williams, L Bergonzini & P Morelli, “Novel additive for particulate trap regeneration”, SAE 952355


100. D T Dally, D L McKinnon, J R Martin & D A Pavlich, “A diesel particulate regeneration system using copper fuel additive”, SAE 930131

101. Eolys, Rhodia


110. D W McKee and D Chatterji, Carbon, 1975, 13, 381-390

111. T Miyazaki, N Tokubuchi, M Inoue, M Arita & I Mochida, “Catalytic activities of \( K_2CO_3 \) supported on several oxides for carbon combustion”, Energy and fuels, 1998, 12, 870-874


114. D W McKee, “Chemistry and Physics of carbon”, vol. 16


149. G Sarraco, V serra, M Vallino, A Delmastro & V Specchia, “Catalytic materials for high temperature processes”, Ceramic transactions 73

150. B J Cooper & J E Thoss, “Role of NO in diesel particulate emission control”, SAE 890404

151. P Ciambelli, V Palma, P Russo & S Vaccaro, “The role of NO in the regeneration of catalytic ceramic filters for soot removal from exhaust gases”, Cat. Today, 2000, 60, 43-49


156. California air resources board, Summary of products reported to reduce particulates from diesel engines,
http://arbis.arb.ca.gov/toxics/diesel/ss/summary_2.htm, January 2002


168. “Gas-in-liquid dispersions”, In: Perry’s chemical engineers handbook, Ch.18, p.68


175. www.ultramet.com, March 2001
180. L M Sheppard, “Gelcasting enters the fast lane”, Ceramic Industry, April 2000, 26-34
183. Hi-Por Ceramics, Stubley Lane, Dronfield, Sheffield, UK
188. A E Scheidegger, “The physics of flow through porous media”, Ch. 4, 3rd Edn., University of Toronto Press, Canada, 1974
206. M Misono & N Mizuno, "Design of catalysts based on perovskite type mixed oxides", Catalyst materials for high temperature processes, 67-83
207. P Ciambelli, S Cimino, S De Rossi, L Lisi, G Minelli, P Porta & G Russo, "AFeO₃ (A= La, Nd, Sm) and LaFe₃₋ₓMgₓO₃ perovskites as methane combustion and CO oxidation catalysts: structural, redox and catalytic properties", App. Cat. B: Env., 29, 239-250, 2001
208. S Hong & G Lee, "Simultaneous removal of NO and carbon particulates over lanthanoid perovskite-type catalysts", Cat. Today, 63, 397-404, 2000
219. US Patent US5240639
221. US patent US5643510
Appendix 1

Manufacturer details for all the chemicals and items of equipment used in the experimental sections are given below.

**Foam preparation and characterisation**

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**Equipment**

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**Catalyst preparation and characterisation**

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## Equipment Supplier

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### Catalysed foam preparation and characterisation

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## Equipment Supplier

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Appendix 2

Darcian ($k_1$) and non-Darcian ($k_2$) permeability constants obtained by curve fitting collected data to the Forchheimer equation allowing for the compressibility of air and their respective correlation coefficients for alumina foams ($\mu = 1.827 \times 10^{-5}$ Pa s and $\rho = 1.3$ kg m$^{-3}$)

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<tr>
<th>Foam sample #</th>
<th>$k_1 \times 10^{-10}$ (m$^2$)</th>
<th>$k_2 \times 10^{-4}$ (m)</th>
<th>$r^2$</th>
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