Safety aspects of the effects of hydrogen sulphide concentrations in natural gas

Further work

Prepared by WS Atkins Consultants Ltd for the Health and Safety Executive

CONTRACT RESEARCH REPORT 287/2000
Safety aspects of the effects of hydrogen sulphide concentrations in natural gas

Further work

John Mather
WS Atkins Consultants Ltd
Woodcote Grove
Ashley Road
EPSOM
KT18 5BW

This report presents the results of a further study conducted by WS Atkins Consultants on behalf of the Health and Safety Executive (HSE) concerning safety aspects of the effects of hydrogen sulphide concentrations in natural gas. The work develops that previously conducted by WS Atkins and presented in an Interim Report. This report is not, at the request of the HSE, a comprehensive review of the sulphidation issue in GB, but presents the results of the further work in the context of those from the initial study. The Terms of Reference for the study required the provision of factual information regarding impacts of hydrogen sulphide in gas, but excluded providing policy advice. This document does not therefore contain specific recommendations to the HSE concerning their future course of action.

The existing legacy of widespread black dust problems will remain in the short and medium term even if the specification for hydrogen sulphide concentrations in the gas supply is revised. This is the result of a large number of properties with casing containing unstable deposits requiring stabilisation and existing black dust deposits. To remediate this problem, awareness of the issue within the gas industry needs to be improved together with knowledge and availability of appropriate remediation techniques. In addition, some modifications to appliance design, notably discontinuing the use of copper containing gas carrying components within new appliances, should be considered.

Finally, whatever the ultimate decision of the HSE concerning the course of action to be pursued regarding sulphidation, there is clearly a need for prompt decision making to bring an end to the present uncertainty affecting the industry.

This report and the work it describes were funded by the Health and Safety Executive. Its contents, including any opinions and/or conclusions expressed, are those of the author alone and do not necessarily reflect HSE policy.
EXECUTIVE SUMMARY

This report presents the results of a further study conducted by WS Atkins Consultants on behalf of the Health and Safety Executive (HSE) concerning safety aspects of the effects of hydrogen sulphide concentrations in natural gas. The work develops that previously conducted by WS Atkins and presented in an Interim Report. This report is not, at the request of the HSE, a comprehensive review of the sulphidation issue in GB, but presents the results of the further work in the context of those from the initial study. The Terms of Reference for the study required the provision of factual information regarding impacts of hydrogen sulphide in gas, but excluded providing policy advice. This document does not therefore contain specific recommendations to the HSE concerning their future course of action.

In this version of the report the origin and basis of all commercially sensitive information has been removed to protect the suppliers. Consequently, the detailed basis for some of the findings are not entirely transparent. A previous Confidential Draft Report has been produced for the HSE and the consultants findings and approach have therefore been extensively independently reviewed.

Hydrogen sulphide in gas in concentrations in excess of 0.4 mg m$^{-2}$ reacts with copper carcassing or copper components within appliances in a sulphidation reaction resulting in formation of unstable deposits of copper sulphide. This scale subsequently detaches from the copper surface and can be transported into a gas appliance. Within gas fires the black dust deposit predominantly collects in multi-port injectors and can lead to poor combustion. In combination with inadequate fluing, these combustion products could spill into the room containing the appliance, with potentially hazardous consequences. Twenty two local authorities reported experiencing sulphidation problems. Of these 9 per cent reported at least one incident of soot formation above gas fire radiants with householders experiencing headaches nausea, while 4.5 per cent reported at least one incident of soot formation above gas fire radiants alone. However, 14 per cent reported at least one incident of householders experiencing headaches and nausea without signs of soot formation above gas fire radiants. No information has been obtained from premises where gas fires are unaffected by sulphidation to enable comparison with the data gathered for this report.

Within central heating boilers black dust deposits can collect in pilot assemblies leading to nuisance shut-down, or within the control valve. Substantial black dust deposits have been observed within gas valves leading to appliance malfunction. Seventy three per cent of the authorities experiencing sulphidation problems reported at least one incident of an appliance with a contaminated valve, with
32 per cent reporting at least once incident where there were small amounts of gas let-by. Of those, one authority reported at least one incident of a gas odour, while another authority reported at least one incident of noisy ignition. There have been two reported incidents of explosions attributed to gas leaking through safety valves contaminated with solid material, one resulted in a minor injury. In both, the solid materials contained a proportion of copper sulphide scale.

Undergassing of appliances, as a result of substantial deposits of black dust within gas pipes, has been reported from a number of areas. This problem is particularly common where on-line filters have been fitted and are not serviced sufficiently regularly. Undergassing of appliances results in inefficient combustion and instability of the flame leading to the appliance going out. On appliances without either pilot or flame failure safeguards, principally some fires and cookers, this could lead to gas leaks. Uniform corrosion of copper carcassing does not result in a significant risk of pipe failure, but isolated incidents of pitting to the carcassing wall due to presence of corrosive substances within the pipework could lead to formation of pin-holes in extreme circumstances.

HSE would consider that sulphidation would have significant safety implications if it lead to incidents reported under the Reporting of Injuries, Diseases and Dangerous Occurrence Regulations (1995) (RIDDOR). No reliable data are available from which to assess the number of serious incidents arising from black dust contamination of appliances. However, HSE have advised WS Atkins that there have been no fatal or non-fatal incidents reported under the RIDDOR, which can be attributed to sulphidation. Similarly, HSE have advised that there have been no reports of dangerous gas appliances caused by sulphidation reported under RIDDOR. Therefore, the hazard from sulphidation does not appear to have significant safety implications as defined by HSE.

Evidence from local authority surveys suggests that approximately 39,000 properties in GB are currently affected by sulphidation. These affected properties are concentrated in Scotland, Northern and North Western England, North Wales and northern parts of the East and West Midlands (Figure 1). These areas receive gas with the highest hydrogen sulphide concentrations from the St Fergus and Barrow terminals.
The winter average hydrogen sulphide concentration of the gas supplied to a region principally determines its corrosiveness towards copper. Winter average hydrogen sulphide concentrations from the St Fergus terminal have increased since gas was first delivered from the terminal, are presently estimated to be 3.0 mg m$^{-3}$ and are projected to continue to rise. Winter average hydrogen sulphide concentrations from the new Teesside terminal are currently about 1.5 mg m$^{-3}$. The other terminal supplying gas with a significant hydrogen sulphide concentration is Barrow, currently about 3.5 mg m$^{-3}$. Examination of monitoring data from network entry points strongly suggests quality assurance and control procedures are inadequate and the reliability of the data is therefore uncertain.

The emphasis of monitoring hydrogen sulphide at Network Entry Points requires that regional estimates of concentration must be principally based upon extrapolating from terminal feeder data using information on the origin of gas supplied to the region, this introduces unavoidable uncertainty into the assessment. The relationship between regional incidences of properties affected by sulphidation and hydrogen sulphide concentrations (Figure 2) nevertheless clearly demonstrates that below about 1.0 mg m$^{-3}$ hydrogen sulphide sulphidation incidences are extremely low, less than 0.05 per cent. In those regions receiving
St Fergus gas or St Fergus and Barrow gas with a hydrogen sulphide content of above 2.0 mg m⁻³ sulphidation incidences are much more common, up to 0.75 per cent of properties.

![Graph showing the relationship between percentage of affected properties and winter hydrogen sulphide concentration](image)

**Figure 2 - Hydrogen sulphide concentration and incidences of sulphidation**

Figure 2 assumes both a linear relationship between 1.0 and 3.0 mg m⁻³ hydrogen sulphide ($R^2 = 0.95$) and also that the linear relationship will continue above this concentration. Assuming this to be correct the graph suggests that were the 5.0 mg m⁻³ specification to be attained between 1 and 1.5 per cent of properties in regions receiving gas of this specification would be affected.

Future hydrogen sulphide concentrations in different regions of GB will be dependent upon:

- the origin of the gas supplied to each region which will be a function of: the proportion of production from different terminals, origin of gas exported via the Interconnector, and the future gas market in GB, and

- the hydrogen sulphide concentration of the gas at the National Transmission System (NTS) Entry Point, which is affected by: the hydrogen sulphide content of the gas received by the terminal, and treatment undertaken.

Future regional hydrogen sulphide concentrations are therefore particularly uncertain to predict. High, Medium and Low scenarios for future hydrogen sulphide concentrations from terminal feeders have been applied to derive anticipated ranges of likely regional concentrations in 2005. Both estimates of future terminal feeder and regional hydrogen sulphide concentrations are based upon a
range of assumptions detailed in the main body of the report. High, Medium and Low scenarios for the growth in the number of properties in GB in 2005 affected by sulphidation have been derived (Figure 3) using the future estimated regional hydrogen sulphide concentrations and linear concentration/effect relationship. These estimates contain significant uncertainty since they are based upon a large number of assumptions, but provide a best estimate of how the problem is likely to develop.

![Graph showing estimated number of properties affected by hydrogen sulphide concentration scenario](image)

**Figure 3 - 2005 estimated incidence of sulphidation in GB**

An estimated 39,000 properties are currently affected by sulphidation. By 2005 the most optimistic scenario suggests this will have increased by about 20 per cent to 50,000 properties, the biggest increases being in the East and West Midlands. The Medium Scenario, which is considered the most likely, suggests by 2005 about 70,000 properties will be affected; the High Scenario estimate is for approaching 100,000 affected properties. These estimates are more optimistic than those in the Interim Report which estimated in excess of 120,000 affected properties by 2002. If gas significantly more sour than at present is supplied to southern England substantial, existing, stable copper sulphide deposits will flake from the surface of the pipe creating a large quantity of black dust to contaminate appliances and a significant increase in the proportion and number of affected properties. This is not considered likely before 2005 since there is usually a three year lag between an increase in hydrogen sulphide levels and on-set of the flaking, but is quite possible after this date based on long-term gas production forecasts.

Sulphidation is currently widespread and could become significantly worse in the future. The sulphide flake has the capacity to effect shutoff valves, mainly through blockage, but it may cause them to leak. Although there are potentially severe consequences associated with the leakage of
natural gas, there have been no incidents, reported under RIDDOR, directly attributable to sulphide flake. The incident frequency and therefore the risk can be considered negligible. It is for HSE to decide if mitigation measure should be applied to reduce risks at any time. The available evidence nevertheless strongly suggests a reduction in the hydrogen sulphide specification will reduce the number of properties affected by sulphidation, whilst with increasing hydrogen sulphide levels the problem will become increasingly widespread and severe. The suggestion that amine gas treatment systems whilst reducing hydrogen sulphide concentrations may enhance polysulphide levels and accelerate the sulphidation of copper is not considered at all likely.

To be confident that hydrogen sulphide reacting with copper will only produce stable copper sulphide deposits a maximum hydrogen sulphide concentration of 0.4 mg m$^{-3}$ is required. However, there is significant evidence that at a maximum hydrogen sulphide concentration of 1.0 mg m$^{-3}$ the number of affected properties, and consequently the contamination of appliances would be significantly reduced. Assuming the linear relationship between sulphidation incidences and hydrogen sulphide concentration, Figure 4 shows how a change in the hydrogen sulphide specification is estimated to alter the number of affected properties. This assumes a change in the specification does not have a significant effect upon future gas supply to GB, which is considered reasonable as the cost of hydrogen sulphide removal is not significant compared with other costs of extraction, transport, treatment and distribution.
Figure 4 - Estimated effect of a change in the hydrogen sulphide specification upon number of properties in GB affected by sulphidation in 2005

Reducing the hydrogen sulphide gas specification to 1.0 mg m\(^{-3}\) or below will significantly reduce the numbers of properties affected by sulphidation. A survey of gas terminal operators indicates a 1.0 mg m\(^{-3}\) specification is attainable at all terminals and that Southern Basin terminals would be only marginally affected. Additional treatment facilities would be required at St Fergus, Barrow and possibly Teesside terminal; but the associated cost to these terminals per m\(^3\) of gas supplied is very small.

The existing legacy of widespread black dust problems will remain in the short and medium term even if the specification is revised. This is the result of the large number of properties with carcassing containing unstable deposits requiring stabilisation and existing black dust deposits. To remediate this problem, awareness of the issue within the gas industry needs to be improved together with knowledge and availability of appropriate remediation techniques. In addition, some modifications to appliance design, notably discontinuing the use of copper containing gas carrying components within new appliances, should be considered. Finally, whatever the ultimate decision of the HSE concerning the course of action to be pursued regarding sulphidation, there is clearly a need for prompt decision making to bring an end to the present uncertainty affecting the industry.
CONTENTS

EXECUTIVE SUMMARY i

CONTENTS ix

1 INTRODUCTION 1-1

Summary of previous findings 1-1
This study 1-3

2 EFFECTS OF SULPHIDATION UPON DOMESTIC APPLIANCES 2-1

Introduction 2-1
Updated survey of sulphidation knowledge in the British gas industry 2-4
Conclusions 2-10

3 REGIONAL INCIDENCES OF AFFECTED APPLIANCES 3-1

Introduction 3-1
Methodology 3-3
Local authority survey skills 3-6
Conclusions 3-12

4 HYDROGEN SULPHIDE CONCENTRATIONS IN BRITISH GAS 4-1

Introduction 4-1
Hydrogen sulphide concentrations in GB 4-2
Regional hydrogen sulphide concentrations 4-5
Future hydrogen sulphide from terminal feeders 4-11
Future production profiles from British terminals 4-15
Future regional hydrogen sulphide concentrations 4-20

5 COPPER SULPHIDE PRODUCTION AND FLAKING 5-1

Introduction 5-1
Role of polysulphides in sulphidation chemistry 5-1
Copper sulphide deposit stability 5-9

6 CONCLUSIONS 6-1

Safety implications of sulphidation of domestic appliances 6-1
Implications of sulphidation chemistry and flaking rates 6-4
Current and future projected incidences of sulphidation in GB 6-6
Gas hydrogen sulphide specification 6-13

7 REFERENCES 7-1

APPENDICES

Appendix A Executive Summary - Interim Report
Appendix B Organisations Contacted
Appendix C Survey Questionnaire and Results
1. INTRODUCTION

1.1 This report presents the results of a further study by WS Atkins Consultants on behalf of the Health and Safety Executive (HSE) concerning safety aspects of the effects of hydrogen sulphide concentrations in natural gas. The study develops that previously undertaken by WS Atkins and contained within the published Interim Report (HSE, 1998) the Executive Summary to which is contained in Appendix A.

SUMMARY OF PREVIOUS FINDINGS

1.2 The Interim Report identified that hydrogen sulphide, present as an impurity within natural gas, reacts with copper carcassing and components within domestic gas appliances. This sulphidation reaction produces a black copper sulphide film or scale which can subsequently flake from the surface of the copper. These flakes can become entrained in the gas stream and be transported into an appliance where some deposit as black dust and can cause the appliance to malfunction. The Interim Report identified deposition of copper sulphide flakes occurring principally at two sites within appliances, on:

- multi-port injectors in gas fires, and
- gas valve seatings in central heating boilers.

1.3 The Interim Report concluded deposition of copper sulphide within multi-port injectors may cause reduced output from the appliance and incomplete combustion but is unlikely to create a hazardous situation providing there is adequate venting of the combustion products. The study also estimated approximately 21,000 domestic properties to be affected by black dust in Great Britain (GB) and that blockages to burner jets account for over 90 per cent of these. The study also concluded deposition on the seating of gas valves may cause the valve diaphragm to form an incomplete seal resulting in let-by of gas and a potential risk of explosion.
1.4 The Interim Report also concluded hydrogen sulphide in gas may contribute towards damage to other components of gas appliances such as crazing to glass fronted fires and corrosion of flues through contributing to production of sulphur oxides. The extent and safety implications of these primary effects of hydrogen sulphide in natural gas were not considered significant. Failure of copper pipe through sulphidation corrosion was considered highly unlikely due to the relatively slow corrosion rate compared to the carcassing thickness. The principal safety concern of hydrogen sulphide in gas highlighted in the Initial Report was therefore production of copper sulphide and subsequent deposition upon gas valve seating resulting in let-by of gas at valves and the potential risk for explosion.

1.5 The existing specification for hydrogen sulphide in natural gas was established in the Gas Quality Regulations, 1972 at 3.3 ppmv (5 mg m$^3$); and historically, concentrations of hydrogen sulphide in natural gas were an order of magnitude below this specification. The study identified that in recent years hydrogen sulphide concentrations have been increasing and, particularly during the winter, in some regions, are now less than a factor of two below the limit. The report concluded that at higher hydrogen sulphide concentrations the rate of copper sulphide production and flaking is increased and that areas receiving gas with a higher hydrogen sulphide concentration experience more widespread problems due to sulphidation.

1.6 The interim findings demonstrated a clear relationship between hydrogen sulphide concentrations and incidents of properties affected by sulphidation and highlighted that hydrogen sulphide in gas may have significant safety implications. Furthermore, they demonstrated that the numbers of properties affected by hydrogen sulphide in gas, which are already substantial, were predicted to increase significantly by 2003. Therefore the safety implications may be exacerbated. Furthermore, they also demonstrated that a reduction in the hydrogen sulphide specification for natural gas from the current concentration of 5 mg m$^3$ to below 1.5 mg m$^3$ (1 ppmv) would reduce the number of incidences of properties affected by copper sulphide deposits to a very low level, which would significantly reduce the risk of a serious accident. The data upon which this conclusion was based contained significant uncertainties that some of the further work presented in this report is designed to reduce.
1.7 Deposition of copper sulphide within gas appliances clearly presents a major nuisance to gas consumers with frequently affected appliances. However, in order for the HSE to be justified in taking measures to address the cause of the nuisance, the problem must be demonstrated to be one that affects personal safety. A significant revision of the hydrogen sulphide specification would have implications for gas and terminal operators in some instances requiring investment in additional plant to supply gas within a reduced specification. It is therefore important that any revision is based upon the most comprehensive information available.

1.8 The aim of the work presented in this report is to provide the decision relevant information with which the HSE can determine whether, and if appropriate the measures required, to control incidences of sulphidation affecting domestic gas appliances in GB. This report therefore extends and complements the findings of the initial study. The report is divided into seven sections and a number of appendices:

Section 1 this Introduction, has provided the background to the study and overview in the context of the previous Interim Report,

Section 2 Effects of sulphidation upon domestic gas appliances, presents updated information on the manner in which appliances are affected and safety implications,

Section 3 Sulphidation incidence in GB presents improved estimates of the numbers of appliances in GB affected by sulphidation,

Section 4 presents further information regarding current and future gas hydrogen sulphide concentrations in GB,

Section 5 includes details of the role of polysulphides in catalysis of the sulphidation reaction,

Section 6 presents the report Conclusions and recommendations, and

Section 7 References.

1.9 This report is not, at the request of the HSE, a comprehensive review of the sulphidation issue in GB. Rather it presents the results of the further work in the context of those from the initial study. This enables a direct assessment of the improved understanding to be obtained but does not provide a comprehensive text of the current knowledge. Knowledge of the findings of the Interim Report is therefore
assumed, although principal conclusions are summarised where relevant as an aide-memoir.

1.10 This report does not include information with commercial implications provided in confidence by organisations. In some instances the bases of some of the findings are therefore not entirely transparent. The HSE have been made aware of the origin and basis for all the findings through a previous Confidential Draft Report and are satisfied as to the appropriateness and origin of all the information utilised in producing this text.
2. EFFECTS OF SULPHIDATION UPON DOMESTIC APPLIANCES

INTRODUCTION

2.1 This section provides updated information concerning the effects of hydrogen sulphide and copper sulphide deposits upon domestic gas appliances in order to obtain a more thorough understanding of their safety implications. The information was obtained from a telephone survey of informed gas industry and other sources. At the end of the section the conclusions which can be drawn from the findings of the surveys and assessments are presented and those at variance with the conclusions of the Interim Report are highlighted.

Interim Report conclusions

2.2 The Interim Report contained detailed information regarding the manner in which domestic gas appliances are affected by sulphidation and the likely safety implications. It identified that gas appliances are affected by the presence of hydrogen sulphide in gas either by corrosion of components, or the secondary deposition of the copper sulphide produced by copper corrosion. There are five possible ways in which appliances can be affected, all of which may have potential safety implications:

- partial or complete blockage of components within the burner by copper sulphide deposits. This causes possible incomplete combustion of the gas and the generation of the products of incomplete combustion (carbon monoxide and unburned gas). This is likely to result in serious safety effects if combined with inadequate flue arrangements;

- deposition of copper sulphide on gas valve-seatings causing possible leakage of gas with the potential for explosion and subsequent fire. This is potentially the most serious problem, although most modern appliances are designed to fail safe;
corrosion of glass-fronted fire fronts possibly affecting their structural integrity, considered to be mostly an aesthetic concern. Hydrogen sulphide only contributes a small proportion of the sulphur load to generate the corrosive sulphur oxides believed in part to be responsible;

corrosion of flues or draft-diverters affecting their operation, to which hydrogen sulphide is a contributor. This may cause a reduction in the efficiency of the components and causes problems when combined with an inefficient appliance. Compared with the other sulphur containing compounds, the contribution of hydrogen sulphide to the resulting acid flue products is small;

corrosion of copper piping resulting in failure of the pipe and release of gas. This is not considered likely.

2.3 The Interim Report also identified the susceptibility of gas appliances to the effects of copper sulphide deposits to be due to four main factors:

- the output of the appliance; the greater the output the greater the capacity to entrain copper sulphide particles in the gas stream. Fires with back boiler units are therefore particularly susceptible;

- the orientation and size of the inlet pipe for gas delivery into the appliance; wide diameter tubes and vertical delivery reduces the capacity of the gas to transport particles. Floor mounted boilers and fires are therefore more readily affected than cookers;

- the size of injector or burner units; multi-port injectors with a narrow bore block more readily; and

- the presence of double wall copper flashed Bundy Tubing within the appliance, particularly at high temperature, enabling intra-appliance copper sulphide production. There is substantial evidence detailed in the Interim Report that gas fires using this tubing are more severely affected.

2.4 UK regulations require that appliances should not become unsafe as a result of a single component failure. Older appliances do however have less safety devices and are therefore at potentially greater risk. The Interim Report identified one accident
resulting in injury caused by a central heating boiler gas valve failing which let-by gas, due to deposition of solid material on the seating. Occurrences of failing valves, due to blockage, are however much more frequent and the Interim Report detailed one thorough investigation which identified the cause to be copper sulphide deposits.

2.5 One incident of pipe failure due to corrosion has been reported in the USA, although the cause and details are unknown. The Interim Report concluded the possibility of pipe failure due to sulphidation is small, but in the long term not insignificant, if some regions of GB continue to receive increasingly high concentrations of hydrogen sulphide.

2.6 With respect to appliance design the Interim Report identified double walled copper flashed Bundy Tubing used within appliances as a ready site for copper sulphide generation due to the elevated temperature of the copper. Furthermore the report recommended alternative tubing should be considered by manufacturers for new appliances as a matter of urgency and identified single walled nickel coated tubing as offering a particularly attractive alternative. For existing appliances the report recommended where manufacturers were experiencing repeated problems they should consider replacing copper flashed tube with a non-reactive tubing.

2.7 The Interim Report identified that a number of possible techniques exist for remedying the effects of copper sulphide deposits in appliances. All of these approaches have advantages and disadvantages. None of these approaches affect copper sulphide deposits generated inside the appliance. Direct effects of hydrogen sulphide corrosion in gas appliances are unlikely to cause major safety problems. The secondary deposition of copper sulphide flakes within gas valves present more serious safety implications due to the potential for let-by of gas. Modern appliances with leaking gas valves should fail safe, but if a second fault is present may not. Older appliances contain a lower level of safety devices. Overall the Interim Report concluded that copper sulphide deposits within gas appliances caused by the reaction between hydrogen sulphide in gas and copper carrier piping may have significant safety implications for gas appliances.
Introduction

2.8 In order to improve and update knowledge of the nature in which gas appliances are affected by sulphidation, a telephone survey was conducted with representatives from the British gas industry plus other informed sources. The individuals contacted were those identified during work undertaken to produce the Interim Report as being particularly well informed regarding the sulphidation issue. Individuals and organisations contacted as part of the survey are listed in Appendix B. The objectives of the survey were to gather information regarding:

- changes in the severity and nature of the sulphidation problem in different parts of GB since the initial survey was undertaken in October / November 1995,

- incidents involving the let-by of gas from gas control valves, and any accidents arising from the resulting gas leak, and

- any alterations made to products or working practices as a result of problems from sulphidation.

2.9 The survey was carried out by telephone because a standard questionnaire could not cover the wide range of potential issues raised in the previous survey and to facilitate targeting of questions in order to obtain the specific detailed information sought. In order to ensure all relevant issues were addressed, and to structure the discussions, an outline questionnaire and proforma were developed. The survey was undertaken in October and November 1996, approximately one year after initial survey. This had the advantage that changes over the period of a year could be evaluated. However, in common with the original study, an October survey poses problems in obtaining an accurate measure of the severity of the sulphidation problem in different regions. This is since gas appliance usage had been low in the 6 months prior to the survey and consequently the number of affected appliances, awareness and concern are also low.
Copper sulphide contamination of gas fires

2.10 The updated gas industry survey supported the findings of the Interim Report that the most commonly reported effects of copper sulphide are blockages to multi-port injectors in gas fires. One major gas fire manufacturer also reported pre-pilot gauze filters becoming blocked on their appliances. Reports of poor combustion in gas fires were illustrated by engineers observing a yellow flame, reduced heat output and popping sound flame where injectors were contaminated with black dust. Concerns were raised that where an appliance is undergassed the heat output and buoyancy of the combustion products will also be reduced which may result in spillage of the combustion products, particularly if fluing is inadequate. Although large numbers of incidents of reduced output from injectors in gas fires were identified by the survey, no safety incidents were reported. This suggests although some carbon monoxide may have been produced the amounts are generally small and the existing fluing arrangements have, in all reported incidences, been adequate.

Copper sulphide contamination of boilers

2.11 Where central heating boilers are affected, problems have resulted from copper sulphide contamination within gas valves or within the pilot system of the appliance. Where pilot lights have become contaminated the shape of the flame became distorted resulting in cooling of the thermocouple and nuisance shutdown of the appliance.

2.12 One extreme example of a central heating boiler valve contaminated and malfunctioning, because of a blockage, as a result of black dust deposits was reported in Glasgow. On one occasion the engineer cleaned the valve but was called back to the house 2 days later for the same fault and again found the valve to be full of black dust. The component was cleaned again, replaced and the appliance left to operate for 20 minutes after which time the valve was checked and found to be full once again! The engineer subsequently contacted CORGI who referred him to WS Atkins. The rate with which deposits are collecting in the carcassing is exceptional but reports of the frequent need to remove black dust deposits from applications have been provided from North Wales. Furthermore, the report demonstrates beyond question deposits of black dust can rapidly enter gas valves in significant quantities and affect the operation of the appliance. A report from a CORGI Field Inspector in Cumbria (Northern Gas Region) has also demonstrated that a significant quantity of copper sulphide may be present in an appliance’s supply pipes.
2.13 An explosion at a warehouse in Paisley, Scotland has been reported which has been attributed to black dust containing copper sulphide contaminating a safety valve. The incident, which was investigated by the HSE Field Operations Division (FOD), occurred when the deposits prevented adequate sealing of the diaphragm allowing let-by of gas into the combustion chamber, this subsequently ignited on light-up causing the explosion. Quantitative analysis of the black deposits was not carried out, however, HSE have informed WS Atkins that qualitative analysis showed that copper and sulphur were minor constituents and were present as the smaller particles. The major constituents and larger particles were composed of aluminium, silicon, iron, oxygen, carbon and calcium. Evidence from gas service engineers in the region suggest that valves in the area are commonly being replaced and on-line filters require servicing every few weeks.

**Pressure drop associated with copper sulphide blockage of carcassing**

2.14 Where gas supply pipes have been severely affected by sulphidation, the build up of copper sulphide may cause a significant drop in the gas pressure as it passes through the pipe. In North Wales, a gas engineer reported a drop in gas pressure from 8 inches to 1 inch over a 15 foot stretch of copper supply pipe. This level of pressure loss could result in appliances being undergassed and failing to operate correctly. If this were to result in fluctuations in gas pressure a potentially dangerous situation could arise where the gas pressure drops so low that it cannot support a flame (in a fire or oven). When the pressure subsequently increases, gas would be able flow through the appliance unignited.

2.15 A case of gas pressure fluctuation as a result of black dust contamination has been reported in Glasgow by the Gas Consumers Council. In this case an on-line filter (fitted to a gas fire with frequently affected injectors) became blocked with copper sulphide dust which reduced the gas flow to the appliance. When the residence’s gas boiler ignited the gas demand reduced the gas pressure to the extent that the fire’s flame was severely diminished and the residence’s gas oven became unusable. When the boiler was switched off the gas pressure increased again. Although no incidence of gas flowing unignited (due to a drop in pressure extinguishing the flame) through an appliance has been reported at this property, there is clearly a risk of this occurring, especially as gas fires and cookers are not fitted with the same safety valves to prevent release of unignited gas that are used in boilers. A similar report by another engineer suggests low gas pressure as a result of the build up of copper sulphide in carcassing, or behind on-line filters, can make appliances difficult to light. If the user fails to
notice that the appliance has not lit then there is again a risk of gas leakage and subsequent explosion.

**Carcassing failure due to corrosion**

2.16 The Interim Report concluded that carcassing failure due to corrosion was considered unlikely in the short to medium term, but acknowledged a general lack of reliable data to be confident of this. Further work by British Gas Research and Technology (1997) undertaken as part of this study provides further evidence that under almost all circumstances the corrosion will not result in significant loss of carcassing wall thickness. British Gas Research and Technology have examined carcassing throughout GB. Based upon their extensive observations they conclude that even at the maximum hydrogen sulphide content of gas (5 mg m⁻³) over 100 years would be required for 25 per cent loss of wall thickness. This calculation is based upon the assumption that the corrosion occurs in a uniform manner across the surface of the pipe.

2.17 British Gas Research and Technology have identified occasional incidents where pitting has occurred to the surface of the carcassing resulting in uneven corrosion. In these circumstances the copper loss in isolated spots within the carcassing has been more significant and therefore potentially could result in failure of the pipe integrity. British Gas Research and Technology believe a further survey of pipework, which has not been undertaken since 1984 would be advisable to assess the extent and nature of copper carcassing corrosion.

**Other effects of hydrogen sulphide in natural gas**

2.18 In addition to the common hydrogen sulphide related problems in gas fires and boilers, other less common occurrences have been reported which may also be associated with the primary or secondary effects of hydrogen sulphide in gas and could have safety implications. A report has been received that some crazed glass is now so severely damaged that its structural integrity is compromised and that it could potentially shatter. Although hydrogen sulphide contributes to the acidic sulphur load in flue gas products and therefore to the acid corrosion of glass fronted fires and flues, there are other naturally occurring organic sulphides and the odorant, added to the gas, that contribute more.
2.19 Another incident involving exceptional deposits of a black dust, but within mild steel carcassing, have been reported by a service engineer in Glasgow. The engineer was initially called to the property to replace the mild steel carcassing which had become blocked with tea-leaf sized flakes of a graphite like substance. The nature of the substance is not known but mild steel readily reacts with hydrogen sulphide in gas to produce iron sulphide. This incident suggests mild steel carcassing will be affected in a similar manner to copper, as would be anticipated from the chemistry. The engineer has now fitted a filter which requires replacing every 3 weeks to prevent creating an unacceptable pressure drop on the appliance.

2.20 A hitherto unreported potential effect of hydrogen sulphide in natural gas is on three way isolating cock valves. In Easington District Council the valve plugs have been affected by a contaminant in the gas supply. The plugs are nylon and have been reported as stiffening after installation. The stiffened plugs may fail to seal correctly and allow a let-by of gas when the appliance is disconnected. This has occurred in at least ten cases in Easington and the cock valve suppliers have since replaced them with metal plugged valves. Cock valves are used to isolate an appliance from the mains gas supply for maintenance, this means that gas service agents have always been present when gas leaks have occurred, the situation is however potentially very hazardous. To date no evidence has been identified to demonstrate that hydrogen sulphide or copper sulphide is responsible for the effects seen on the cock valves. Easington is, however, a region with a proven history of sulphidation related problems, and those gas engineers who have examined the failed valves feel that attack from hydrogen sulphide or copper sulphide could be responsible. This evidence is nevertheless circumstantial.

Remediation

2.21 The telephone survey of representatives of the gas industry indicated that the responses of those affected by sulphidation were little changed since the previous year. The industry did however appear to be more aware of the sulphidation issue and that there are potential safety implications, a factor that had not been appreciated by many companies and local authorities at the time of the first study. The increase in awareness is believed to be principally as a result of the work undertaken by WS Atkins on behalf of the HSE.

2.22 British Gas Service no longer fit on-line filters to appliances without charge and as a result local authorities, service companies and private residents are now bearing the
financial cost of having them installed and maintained (around £50 per appliance). Other gas service companies and some local authorities are refusing to fit on-line filters to affected appliances because of concerns regarding the undergassing of appliances should the filters become blocked and because they believe they should not be liable for the cost. One service company report that filters installed in the past which are no longer being regularly serviced are now becoming blocked resulting in the undergassing of appliances. This is particularly a problem within private residences.

2.23 Other remediation techniques attempted during the past year include replacing the copper carcassing. This has been successful to date, indicating that in these cases the copper sulphide is formed in the carcassing rather than within the appliance (this is supported by evidence from one major gas fire manufacturer whose appliances are still experiencing problems even though they contain no copper). Replacement of carcassing is not considered a cost-effective solution by most homeowners or local authorities. Research into the technique for coating the internal surface of copper carcassing to prevent flaking has been discontinued by British Gas Service. The research has, however, been left in a state such that it can be rapidly reactivated if research funding can be identified. ICI Katalco have investigated the potential of installing a small absorber within the domestic gas supply to remove hydrogen sulphide from gas as it enters properties. The approach was not however considered viable.

2.24 Several appliance manufacturers have investigated the possibility of removing copper from their appliances and tubing suppliers report receiving several enquiries concerning the appropriateness of alternative tubing. One gas fire and boiler manufacturer has also investigated the possibility of fitting filters before control valves in order to improve their performance. None of the manufacturers contacted suggested they would be making any major appliance changes until clearer guidance was available. Responsibility for appliance design resides with the Department of Trade and Industry (DTI). Recommendations or requirements for appliance design modifications will therefore not be issued by the HSE.

2.25 Overall, the survey of gas industry response to sulphidation occurrences showed that awareness of the problem is increasing, but that as yet few companies are prepared to commit to any design changes without further guidance. Many companies expect this guidance to be issued by HSE although the DTI have the formal responsibility for
appliance design. This confusion needs to be rectified in the future by better communication.

CONCLUSIONS

2.26 Overall the findings of this further work are similar to the conclusions of the Interim Report. This confirms that blockages to multi-port injectors in gas fires are still the most widespread problem associated with sulphidation. Concerns have also been raised that undergassing of the appliance will result in the dual problem of incomplete combustion and reduced heat producing a less buoyant exhaust gas and less effective fluing. Where these occur on an appliance, without adequate fluing, the combination of factors could result in spillage of combustion products.

2.27 The further work reaffirms that central heating boiler valves do become contaminated with black dust. It has also shown that there are rare instances where significant amounts of black dust can accumulate in a valve over very short periods, causing it to fail by blockage. The explosion in Paisley indicates gas let-by, caused by valve contamination, is a safety issue. However, what has not been established, is whether copper sulphide has, or can, cause sufficient let-by of gas to produce a significant risk. British Gas Research and Technology are currently investigating the potential and risk of valve contamination on behalf of the HSE. Their findings will be reported separately.

2.28 This further work has also identified a number of incidents in which large quantities of deposits within carcassing have caused substantial pressure drops in gas supply. This could lead to undergassing of an appliance, and as a consequence the burner flame could extinguish. For those appliances not fitted with flame failure protection, there is a potential for gas leakage and risk of subsequent explosion. Although it is possible that the deposits may have originated from another source, for example the distribution main, analyses of deposits in a number of premises indicate that it is more likely for the deposits to be copper sulphide, formed from copper installation pipe. Again, British Gas Research and Technology are investigating the potential risks associated with low supply pressures.

2.29 New problems, possibly associated with sulphidation, have also been identified. The Interim Report indicated high levels of acid flue gases, to which hydrogen sulphide contribute, may be responsible for crazing to glass fire fronts, but that the problems were aesthetic. New information obtained as part of this further work suggests the
effects may be sufficiently severe to cause the structural integrity of the glass to be affected. Hydrogen sulphide however only contributes to the acid flue gases which are probably responsible. The other new phenomena possibly associated with sulphidation is damage to three-way isolating cock valves but sulphidation has not been demonstrated as the certain cause.

2.30 It is not possible from the information within the HSE Gas Safety Statistics to determine whether increasing quantities of hydrogen sulphide in natural gas are resulting in additional incidences of carbon monoxide poisoning or explosions and fires. The majority of dangerous situations arise as a result of human error in the installation or modification of appliances, but a significant proportion (26 per cent) are not accounted for in this way. Generally, the evidence from the telephone survey supports the overall conclusion from the Interim Report that copper sulphide deposits within gas appliances may have significant safety implications for gas appliances.
3. REGIONAL INCIDENCES OF AFFECTED APPLIANCES

INTRODUCTION

3.1 This section provides a comprehensive update of the number, distribution and nature of sulphidation incidents affecting domestic properties within GB. The results have been combined with those of regional hydrogen sulphide concentrations (presented in Section 4) to derive in the Conclusions (Section 6), more confident estimates of the effect of gas hydrogen sulphide concentrations upon the proportion of properties affected by sulphidation.

3.2 The Interim Report presented detailed information on the number, distribution and type of incidents of sulphidation affecting domestic properties. From this it was possible to determine a tentative relationship between regional hydrogen sulphide concentrations and the proportion of affected properties. The methodology adopted did however have a number of limitations most notably that:

- information was only available from District Councils;

- the numbers of gas appliances in each region were not known and consequently it was not possible to estimate accurately the proportion of properties or appliances affected; and

- in developing estimates of the total number of affected properties it was assumed public and private housing were equally affected within each region, with a limited basis for this assumption.

3.3 In order to overcome the limitations of the methodology adopted in the Interim Report, this further work has obtained additional data from:

- a survey of Metropolitan Authorities and London Boroughs not included within the previous survey of District Councils (Appendix B);
• the British Gas Household Gas Survey, which provides details of numbers and types of domestic gas appliances in different gas regions; and

• a telephone survey of informed sources to determine the ratio of private and publicly owned properties affected in each gas region.

**Interim Report conclusions**

3.4 The Interim Report included a detailed investigation of the regional distribution of sulphidation occurrences in gas, principally using data obtained by the Association of District Councils (ADC) in their 1995 members survey. Seventy-five per cent (251 of 333) of the District Councils in England and Wales responded; and of these 48 (19 per cent) reported that they were experiencing some incidents of appliance contamination with black dust, or some other effect related to corrosion caused by hydrogen sulphide. The national coverage of this survey was extensive and substantial amounts of data relating to the prevalence of sulphidation were obtained.

3.5 The principal results of the Interim Report were that the appliance types most severely affected by copper sulphide flakes are fires, through blockage of multi-port injectors and to a lesser extent central heating boilers by failure of gas control valves which let-by gas. Corrosion of exhaust flues is much less commonly reported than copper sulphide contamination, and is most often attributed to high indoor chlorofluorocarbon concentrations. However, due to the nature and location of the corrosion, incidents are probably significantly underreported (or wrongly attributed). Cases of high sulphur levels being found in prematurely corroded flues, were identified but hydrogen sulphide in domestic natural gas is only a small contributor to sulphur-containing acid flue products.

3.6 The Interim Report estimated approximately 19,000 properties are affected nationally. The most severely affected regions being in Scotland, the North and North West of England and North Wales. The number of incidences in the West Midlands is growing rapidly highlighting the southerly trend in the incidents of new occurrences. The study also suggested about 650 central heating boiler valves per year may be affected although there was a high degree of uncertainty in this estimate. The most common response to the problem was to fit an on-line filter, which has been shown to be effective in many cases. Other methods such as cleaning or replacing the affected components have been less effective.
The study also found that the distribution of occurrences within a district council area is often inhomogeneous with either specific regions being more severely affected than others, or a random distribution of incidents among similar residences. The report suggested the unevenness of distribution in some areas may be linked to relatively subtle differences in the gas supply system, or in the way in which the gas supply or appliance was installed.

**METHODOLOGY**

**Survey of Metropolitan Authorities and London Boroughs**

This study has supplemented data on incidences of sulphidation obtained by the ADC, and presented in the Interim Report, with additional survey data obtained from Metropolitan Authorities and London Boroughs. The survey was conducted by WS Atkins with the assistance of the Association of Metropolitan Authorities (AMA). A copy of the questionnaire issued is contained in Appendix C. The objective of extending the available dataset and developing the methodology was to improve the confidence in estimates of the number of properties affected by sulphidation. This improved dataset was then used to derive a more confident relationship between regional occurrences of sulphidation and regional hydrogen sulphide concentrations and predictions of the likely growth in affected premises (Section 6). The survey was conducted during the first quarter of 1997, prior to the reorganisation of local government. The target for the survey was the 69 members of the AMA. Information was sought concerning whether the authority was:

- aware of the black dust problem and cause;
- whether, and if so when problems were first identified;
- the type of appliance and component affected;
- whether, the nature of any effects affected the householders safety; and
- details of servicing implications and approaches adopted to remediate the problem.

The survey of Metropolitan Authorities obtained a response rate of 64 percent (44 of 69) of which 23 (52 per cent) were positive. The survey was restricted to England and
Wales, the new data from Metropolitan Authorities covering a more restricted geographical spread than that of District Councils. The survey did, however, cover areas in which there were significant gaps from the original survey, notably the gas regions of: East and West Midlands (Birmingham conurbation); North West (South Yorkshire, Manchester and Liverpool); North East (urban areas of West Yorkshire and northern areas of Tyneside); and North Thames (London).

British Gas Household Gas Survey

3.10 In order to obtain improved estimates of the number of households in gas regions with specific gas appliances, information from the British Gas Household Gas Survey was utilised. The questionnaire survey, last conducted in 1990, comprised a substantial sample of approximately 35,000 residences and is the definitive information source on gas appliances in households within GB. Data are available at a regional and district level on the number of households with different appliance types including:

- central heating systems;
- space heaters (both number of households and total number);
- cooking appliances; and
- gas water heating appliances.

3.11 The previous study, in the absence of alternative data, had relied upon several assumptions concerning numbers of gas users and appliances in each region. The new data supplied by British Gas provided accurate statistics and numbers of households with different types of appliances and assisted in provision of more reliable estimates of the proportion and actual numbers of properties affected by sulphidation problems.

Incidents amongst private and publicly owned properties

3.12 In order to determine the total number of affected properties in GB from survey data conducted for publicly owned housing only, it is necessary to make some assumption concerning the ratio of public to privately owned properties likely to be affected. The Interim Report assumed private and public properties within the same region to be equally affected by sulphidation, but limited data supported this. To test the assumption representatives from the gas industry and local authorities known to be
affected by sulphidation were canvassed for their opinions. This was thought to be the most effective strategy given the problems and cost of attempting a comprehensive quantitative survey. Appendix A lists those companies and organisations contacted.

3.13 All the appliance manufacturers and service companies contacted with experience of both the public and private sector reported properties in both sectors to be affected. Contacts with regional offices of the Gas Consumers Council (GCC) also provided evidence of private properties being affected by sulphidation in the North Wales region in significant numbers. Each individual or organisation contacted also confirmed greater experience of incidents in publicly owned appliances than privately owned ones. The contacts were not able to confirm whether the apparent difference in the proportion of affected properties is actual or a result of different levels of identification or reporting through more frequent servicing of privately owned properties.

3.14 Significant differences between the servicing schedules of appliances used in the public and private sectors may cause differences in either reporting and/or prevalence of sulphidation related incidents. It is a legal requirement for appliances in rented properties to be serviced annually but very few privately owned properties are serviced this often. Private property householders are liable for the maintenance costs, consequently they will be much less likely to report an apparently minor problem such as a partially blocked injector. The difference in servicing schedules may result in different levels of identified incidences. Regular servicing is likely to detect early signs of sulphidation. More, but less severe occurrences are therefore likely to be detected during annual services. However, this can be complicated by the fact that more frequent servicing may also create extra disturbance to the appliance and its pipework which may result in an increased amount of copper sulphide being dislodged and entrained within the appliance. The reduced servicing frequency of appliances in private properties may also result in an appliance performance deteriorating undetected until a dangerous fault develops. A smaller number, of more severe faults, may therefore be detected in private properties.

3.15 As there is no reason to expect that public and private properties in each region are affected differently, and the higher number of reported incidents in public properties may be due to frequency of servicing, this report has assumed private and council properties in each region are equally affected by sulphidation in order to generate an estimate of the number of properties affected in GB. There is however uncertainty in this assumption.
3.16 In the survey of Metropolitan Authorities and London Boroughs conducted as part of this study, 52 per cent of respondents reported problems with black dust (Appendix C) compared with 19 per cent of District Councils in the original survey. This significant increase in positive responses is partially as a result of the northern location of a higher proportion of the authorities surveyed and would therefore be anticipated.

3.17 The growth in the number of authorities reporting incidents of black dust affecting properties is shown in Figure 3.1. This demonstrates that the increase in the numbers of authorities reporting problems in the original ADC survey has been repeated in the survey of Metropolitan Authorities with a sharp rise since 1991. The trend exhibited is consistent for both data sets and over time and indicates the problem to be increasingly widespread. Part of this increase may also be due to the raised awareness of the problem, prompting correct diagnosis.

**The nature of occurrences**

3.18 In the previous section, and Interim Report, it was ascertained that the two main appliance groups affected by sulphidation are gas fires and central heating boilers, approximately 90 per cent of problems being estimated to be associated with fires. In this further study information on the relative rate of problems associated with each of these appliance types was requested in addition to the total numbers of properties affected. Most positively responding authorities reported that both fires and boilers were affected by black dust, but were unable to supply reliable quantitative information on the numbers of each. It is not therefore possible to generate reliable predictions of the proportion of appliance types (fires and boilers) affected based upon the data provided. Although authorities were generally not aware of numbers of different types of appliances displaying faults within the property normally records were maintained of total properties affected. It has therefore been possible to estimate the number of affected households.
Figure 3.1 - Number of authorities reporting incidents of Sulphidation

![Graph showing number of authorities reporting problem from 1985 to 1996.]

Note: An assumption has been made that for District Councils in 1996 the increase in the number of councils experiencing sulphidation is the same as for the previous year.

**Regional distribution of sulphidation**

3.19 The previous study highlighted a strong north-south divide in sulphidation occurrences, most notably in Wales, where sulphidation in the North affected a far greater proportion of properties than in the South. Figure 3.2 illustrates the estimated number of potentially affected properties using data from the ADC survey of District Councils, survey of Metropolitan Authorities conducted for this work, and with the results of both surveys combined.

3.20 The District Council data presented in Figure 3.2 have been adjusted from the results presented in the Interim Report to take into account the number of gas users in each region using the information from the British Gas Household Gas Survey. The Interim Report estimated 19,000 properties to be affected in England and Wales. Using data from the ADC survey combined with the British Gas Household Gas Survey data gave an estimate for total affected properties in England and Wales of 25,000. This increase is purely as a result of the improved methodology employed. Combining the results of both ADC and Metropolitan Authority surveys gives a new estimate for the total number of affected properties in England and Wales of 32,000
properties. Eliminating the effects of the improved methodology this represents an increase of about 28 per cent over the estimate made in the previous study. Figure 3.3 illustrates the estimated properties affected per million residences. This gives an indication of the worst affected areas independent of population. The survey of Metropolitan Authorities produced generally higher estimates of the proportion of properties affected than District Councils within the same region. The results of both surveys nevertheless show the broad pattern of a North-South divide in sulphidation affected properties.

Figure 3.2 - Number of potentially affected properties.

Note: Differences in the estimated number and proportion of affected properties between the two surveys, within the same region, may be due to a number of reasons.
3.21 The Metropolitan Authority survey was conducted a year later and consequently more properties may now becoming affected. Also, awareness of sulphidation may now be greater than a year ago and also more widespread in Metropolitan Authorities because of the larger number of owned and therefore affected properties.

3.22 In some areas inhomogeneity in the origin of the gas supplied to the region may also produce inconsistencies. In the East and West Midlands Metropolitan Authorities are predominantly located in the north of the regions which receive more sour gas than southern areas where there are greater proportions of smaller District Councils. The effect of this inhomogeneity is that sulphidation occurrences in the region are not uniform and this is reflected in the survey results (inhomogeneity in gas supply is discussed further in Section 4).

3.23 In some regions, the small sample of councils in the ADC survey also contributes to the variability of results. For example, the population of the North West overwhelmingly reside in Metropolitan Authorities and estimates of affected properties based upon the survey of District Councils therefore contained considerable uncertainty as the sample was small and unrepresentative. This highlights the importance of conducting the additional survey as part of this study in order to expand the size of the sample and reliability of the estimates. The overall results of the
combined survey are therefore significantly more robust than the results of either of the two individual surveys.

Secondary symptoms of sulphidation

3.24 In addition to providing data concerning the number of affected properties in each authority, the survey of Metropolitan Authorities included a number of questions concerning secondary symptoms of the effects of black dust. These questions were specifically designed to assess the possible safety implications of black dust. The information provided by local authorities was not as robust or comprehensive as that provided on numbers of affected properties (which were used to derive the total number of incidents in GB). The information on secondary effects could not therefore be used to quantify the number or proportion of appliances or properties affected in each gas region. The data do however indicate the presence of a significant number of authorities reporting appliance faults, caused by sulphidation, which is a cause for concern. However, none of the authorities reported that there had been any incidents where the occupier’s safety had been put at risk. Table 3.1 presents a summary of the results which are shown in Appendix C. Caution is needed in the interpretation of the data, as the results do not take into account occasions where although sulphidation has occurred these symptoms occur as a result of other problems, such as a defective appliance etc. The authority may also be responding positively where only one incident, of the type referred to, has occurred. The results do however provide further evidence of the nature and severity of the current problems.

3.25 Uneven fire flames can be an indication that there is a restriction in either the gas or air supply to the burner, or both. A restriction of the gas supply, alone, could result in the formation of greater concentration of carbon monoxide in the combustion products, due to the lower flame temperature. This should not be a problem provided there are adequate flue and ventilation provisions. HSE have informed WS Atkins that carbon formation will not occur solely from the restriction of the gas supply, because of the amount of excess air available (this was not known at the time of the formulation of the questionnaire). Further, the presence of soot is indicative of other, or additional, problems associated with an inadequate air supply to the burner and/or an inadequate flue, and excessive carbon monoxide formation due to spillage of combustion products. The reporting by 14 per cent of authorities of the presence of soot above the radiants is therefore of concern. The main effects of sulphidation is well demonstrated by the fact that 82 per cent of authorities reported uneven flames.
Nine per cent of authorities reported incidents of soot formation above gas fire radiants with householders experiencing headaches and nausea, while 4.5 per cent reported incidents of soot formation above gas fire radiants alone. However, 14 per cent of authorities reported incidents of householders experiencing headaches and nausea without signs of soot formation above gas fire radiants. No information has, however, been obtained from premises where gas fires are unaffected by sulphidation to enable comparison with the data gathered here. Be that as it may, coincidental spillage of combustion products is required for the effects of sulphidation to be a hazard. All authorities reporting householders experiencing headaches and nausea are in regions which receive gas with a high concentration of hydrogen sulphide.

Table 3.1 - Occurrence of faults as a result of black dust in authorities

<table>
<thead>
<tr>
<th>Fault</th>
<th>Number of authorities experiencing symptom</th>
<th>Percentage of Metropolitan Authorities (44) experiencing symptom</th>
<th>Percentage of authorities (22) with sulphidation problems experiencing symptom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uneven flames in burners</td>
<td>18</td>
<td>41 %</td>
<td>82 %</td>
</tr>
<tr>
<td>Sooting above radiants</td>
<td>3</td>
<td>7 %</td>
<td>14 %</td>
</tr>
<tr>
<td>Customers experiencing headaches or nausea</td>
<td>5</td>
<td>11 %</td>
<td>23 %</td>
</tr>
<tr>
<td>Accumulation in boiler control valves</td>
<td>16</td>
<td>36 %</td>
<td>73 %</td>
</tr>
<tr>
<td>Excess noise from boiler</td>
<td>7</td>
<td>16 %</td>
<td>32 %</td>
</tr>
<tr>
<td>Smell of gas in a property</td>
<td>1</td>
<td>2 %</td>
<td>4.5 %</td>
</tr>
<tr>
<td>Dust causing gas to leak past boiler valves</td>
<td>7</td>
<td>16 %</td>
<td>32 %</td>
</tr>
</tbody>
</table>

NB: The table indicates the number and proportion of authorities experiencing at least one occurrence of these types of symptom

Seventy three per cent of authorities with sulphidation affected properties report experiencing problems with boiler valves contaminated with black dust. This is a
very high percentage and provides very strong evidence that black dust is indeed entering gas control valves leading to faults. Dust within a valve is not in itself a safety issue unless that valve subsequently allows gas to leak as a result. Thirty two per cent of authorities however also report "banging" from a boiler contaminated with black dust when lit. Only one authority reported a gas odour. British Gas Research and Technology are currently conducting research to assess the risk of valve failure as a result of black dust contamination. Evidence from service companies and component manufacturers in this, and the Interim Report, suggests such leaks do occur and can occasionally be significant.

CONCLUSIONS

3.28 The work conducted as part of this study generally supports the results and conclusions presented in the Interim Report. In particular, effects which can be contributed to sulphidation are much more prevalent in Scotland, Northern and North West England, North Wales and some parts of the West Midlands than in the south of England. The main differences between the results of the two surveys are that sulphidation appears to be generally a greater problem in Metropolitan Authorities than in District Councils for the reasons discussed in this section. The further work supported the findings of the Interim Report that the number of authorities affected by sulphidation in GB is continuing to increase.

3.29 The Interim Report estimated 19,000 properties in England and Wales to be affected by sulphidation with at least another 2,000 properties in Scotland. Using an improved methodology to determine the number of gas users in each region (in particular data from the British Gas Domestic Gas Survey); the original estimate was conservative and probably about 25,000 properties in England and Wales were affected. The results of the survey of Metropolitan Authorities (combined with those of the survey of District Councils) indicates an estimated 32,000 properties in England and Wales are affected with sulphidation problems. The further work therefore suggests a significantly greater number of properties to be affected than originally estimated. The regional estimates of the proportion of affected properties are combined with regional gas concentrations, where appropriate, in Section 6 to assess the relationship between hydrogen sulphide levels in gas and sulphidation incidences.

3.30 It was not possible using the data supplied by the local authorities to estimate reliably the number of fires, central heating boilers and other types of appliances affected. Evidence from the survey did however indicate that multi-port injectors in gas fires
are the most widely affected component followed by control valves in central heating boilers. The survey also showed there may be significant safety implications arising from copper sulphide contamination of the appliance. Of the 22 authorities reporting a sulphidation problem 82 per cent stated the appliances showed signs of uneven flames in burners, 9 per cent reported soot formation above gas fire radiants with householders experiencing headaches and nausea, 4.5 per cent reported soot formation above gas fire radiants alone and 14 per cent reported householders experiencing headaches and nausea without signs of soot formation above fire radiants. No information was obtained from premises where gas fires are unaffected by sulphidation to enable comparison with the data gathered for this report. Concerning boiler valves, 73 per cent of authorities with a sulphidation problem had found copper sulphide deposits within the valve, 32 per cent reported excess noise from boilers, 32 per cent had instances of small amounts of gas let-by and 4.5 per cent reported a gas odour. Overall, the survey showed that the number of properties affected by sulphidation are even more numerous than suggested by the Interim Report and the numbers of properties continue to increase.
4. HYDROGEN SULPHIDE CONCENTRATIONS IN BRITISH GAS

INTRODUCTION

4.1 The Interim Report identified that very sparse information is available on current hydrogen sulphide concentrations and trends in GB. Data are only available from TransCo measured at Network Entry Points and a few multi-pipeline junctions and compressor stations. Consequently, estimates of regional concentrations of hydrogen sulphide in gas inevitably contain significant uncertainties. Information contained within this section updates and improves upon the work undertaken in the initial study in order to improve confidence in the relationship derived between regional incidences of sulphidation in domestic premises and hydrogen sulphide concentrations and projections of the anticipated growth of the problem. The work undertaken has involved three principal tasks, the results of which are presented in the following subsections, which:

(i) update and expand the available information on hydrogen sulphide concentrations for 1996;

(ii) calculate improved estimates of current hydrogen sulphide concentrations in natural gas supplied to different regions of GB; and

(iii) develop more confident predictions of future hydrogen sulphide concentrations in natural gas supplied to different regions of GB.

4.2 In order to prevent the release of commercially sensitive information into the public domain it has been necessary to exclude from this document some of the data upon which specific assumptions have been derived. This is a regrettable, but inevitable, outcome of undertaking work of this nature. All of the raw data upon which the assumptions were based were made available to the HSE in a previous confidential draft report and have therefore been independently reviewed.
HYDROGEN SULPHIDE CONCENTRATIONS IN GB

Principal findings from the Interim Report

4.3 The Interim Report included: an investigation of annual average trends in hydrogen sulphide concentrations within GB; estimates of regional concentrations; and predictions of future concentrations from terminal feeders in some gas regions, where the region was wholly or principally supplied from one terminal. This identified that there are no sources of hydrogen sulphide within the National Transmission System (NTS), all the hydrogen sulphide in gas originating in the fields and being dependent upon the nature of the field and the extraction technique employed. Monitoring of hydrogen sulphide is therefore conducted predominantly at Network Entry Points (terminal feeders and liquid natural gas (LNG) storage facilities) to ensure gas entering the NTS is within specification. Some other measurements are conducted at compressor stations and multi-pipeline junctions. The concentration of hydrogen sulphide in gas entering the NTS at the terminals is therefore dependent upon the relative levels of hydrogen sulphide and proportion of production from each of the fields supplying the terminal and the extent to which treatment is conducted at the terminal.

4.4 The Interim Report also presented data on annual average concentrations from measurement stations, this showed gas from St Fergus and Barrow to have significantly higher levels of hydrogen sulphide than that originating from other terminals. Since 1986, the annual average concentration of hydrogen sulphide in gas from the St Fergus terminal has increased from about 0.5 to 2.0 mg m\(^{-3}\). The hydrogen sulphide content of gas from the Barrow terminal over the same period has varied between 2.5 and 4.8 mg m\(^{-3}\). The sourness of gas from the co-mingled Easington and Dimlington terminals has remained very low since 1990, whilst that from the Bacton and Theddlethorpe terminals has increased but generally the concentration of hydrogen sulphide has remained below 1.0 mg m\(^{-3}\).

Hydrogen sulphide trends

4.5 In summer domestic gas demand is only about 12 per cent of that experienced during winter peak demand conditions and use of gas fires and central heating boilers, the appliances identified as being the most susceptible to black dust, are significantly reduced. Throughput of gas to these appliances is therefore is significantly lower in summer than in the winter and the reduced throughput will result in the gas supplied
remaining within the carcassing for a significant period. During periods when appliances are not in use this time the available hydrogen sulphide in the gas will diffuse onto the surface of the pipe and either react with, or be absorbed into the copper sulphide layer (British Gas Research and Technology, 1997). The effect will therefore be a decrease in the hydrogen sulphide concentration locally within the pipe. The reduced flow of gas will also decrease the rate of copper sulphide deposition.

4.6 The effect of a longer residence period in the pipes and reduced flow in summer will be that gas with the same initial hydrogen sulphide concentrations is likely to have a significantly reduced capacity to corrode pipework and hence generate copper sulphide. In summer, the rate of sulphidation will therefore be reduced and the annual average rate of sulphidation will be dominated by gas use during the winter. Winter gas hydrogen sulphide concentration is therefore a better indicator of the gas corrosiveness and capacity to generate copper sulphide than the annual average value. The Interim report assessed trends in, and the relationship between regional annual average concentrations of hydrogen sulphide and sulphidation incidences. This further study has employed the winter average value as a better indicator of gas corrosiveness.

4.7 If the hydrogen sulphide concentration of the gas is relatively constant throughout the year the winter and annual average concentrations of hydrogen sulphide are similar. The Interim Report however demonstrated this is not always the case - due to fields being shut-down or placed on minimal output during the low demand summer period. The Interim Report identified production and the sourness of gas from the Barrow terminal to be higher in winter. Similarly, at Bacton the average ratio of winter to annual average concentration is 1.26 ± 0.50.

4.8 Trends in winter average hydrogen sulphide concentrations are shown in Figure 4.1. It shows the winter average trend is similar to that observed using annual average concentrations in the Interim Report. Data for the 1996/97 compared with the previous year shows that winter concentrations have at:

- **Easington**, remained constant at about 0.1 mg m⁻³;
- **Bacton**, increased slightly to 0.5 mg m⁻³;
- **Theddlethorpe**, continued to increase to 0.7 mg m⁻³; and
St Fergus, fallen very slightly to 2.4 mg m$^3$.

Figure 4.1 - Trends in winter mean hydrogen sulphide concentrations

4.9 It has not been possible to obtain data for the Barrow terminal for 1995/96 or 1996/97. Supply of gas from Teesside has now started and over the winters of 1996 and 1997 hydrogen sulphide levels averaged about 2.3 mg m$^3$. This indicates that the concentration of hydrogen sulphide in gas from this terminal is likely to be of a similar order to that from St Fergus.

Data quality

4.10 In order to assess the quality of the hydrogen sulphide monitoring data an assessment of the continuous (1 hour) hydrogen sulphide concentrations measured at different terminal feeders was undertaken. The review identified that the data contained:

- long gaps without measurements;
- periods of spurious measurements; and
- occasions at which the measured concentrations attained, but did not exceed the 5.00 mg m$^3$ limit, a highly unlikely occurrence.
4.11 The data had clearly not been quality assured and serious doubts therefore exist concerning the reliability of the measurements. The conclusions to the Interim report raised concerns over data quality of hydrogen sulphide measurements and these findings support those concerns. This is discussed further in Section 6, the Conclusions to this report.

REGIONAL HYDROGEN SULPHIDE CONCENTRATIONS

4.12 In order to evaluate the relationship between hydrogen sulphide concentration in gas and incidences of sulphidation, the Interim Report examined the relationship between regional incidences of sulphidation and regional hydrogen sulphide concentrations. The paucity of information concerning regional hydrogen sulphide concentrations requires regional concentrations to be determined by extrapolating the terminal feeder data and identifying the origin of gas supplied to different regions. The Interim Report utilised qualitative information from TransCo on the origin of gas supplied to different regions to estimate current regional concentrations. This report employs quantitative information from TransCo to improve the confidence of these estimates. These data are commercially sensitive and the following sections therefore outline gas supply to each region without disclosing commercial information. Future supply and the basis for the significant uncertainties in the regional estimates are discussed in a following subsection. Figure 4.2 shows a map of the NTS to assist with the explanation.

Scotland

4.13 Scotland receives gas exclusively from St Fergus with the rare exception of when stored gas from the Glenmavis LNG facility tops up supply. The winter average hydrogen sulphide concentration of gas in the region is therefore that of St Fergus gas, 2.5 mg m$^{-1}$. 
Northern

4.14 Northern region receives gas overwhelmingly from St Fergus. The offtake at Cowpen Bay now receives Teesside gas and some parts in the very south eastern corner of Northern Region will, in the future, receive gas from a combination of Teesside and St Fergus. The Rough storage facility also periodically supplies gas to the region. Overall it is reasonable to assume at present the concentration of hydrogen sulphide in this region is the same as that from St Fergus and Teesside a winter average 2.5 mg m$^{-3}$.

North West

4.15 During the winter the North West receives gas originating from a combination of the Barrow and St Fergus terminals which are co-mingled at Lupton where monitoring is conducted. Continuous monitoring data from winter 1995/96 show concentrations at Lupton to be about 3 mg m$^{-3}$ which is considered representative of gas throughout this region.

North East

4.16 Gas supply to the North East is from St Fergus, Easington, Rough (which is filled from St Fergus) and recently Teesside. Three 70 bar pipelines transport gas to and through the region, in the pipeline which runs along the east coast the gas "washes" up and down depending upon the output from southern basin terminals. The two more westerly pipelines transport gas exclusively south from St Fergus and Teesside. The complex pattern of distribution makes it impossible to produce a representative regional winter hydrogen sulphide concentration since levels will vary significantly in the region both spatially and temporally.

East Midlands

4.17 The East Midlands receives gas from St Fergus and Barrow to the north, and Bacton, Theddlethorpe and Easington to the east. The principal east and west coast gas lines converge at the Peterborough compressor and the different parts of the region therefore receive gas from different areas at different times, generalisation of the gas supply is therefore not possible. The northern and western areas of the region receive gas from Barrow and St Fergus, as for North West region. Southern and eastern areas of the East Midlands area receive gas from all terminals at different times of the year,
it is therefore not appropriate to derive an overall winter average hydrogen sulphide concentration for the entire region.

**West Midlands**

4.18 The West Midlands is another region supplied from a number of different terminals but the pattern of supply is less complex than for the East Midlands. Northern and central parts of the West Midlands are predominately supplied with gas from Barrow and St Fergus. Areas of the West Midlands to the south of the Churchover compressor station also receive gas from Theddlethorpe and a little from Bacton and Easington. As a general rule the area to the north of the M40 represents the dividing line, this means the heavily populated West Midlands conurbation: Birmingham, Wolverhampton and Walsall receive the more sour gas (TransCo, 1997). In view of the inhomogeneous gas supply to the region it is not possible to derive an overall winter average concentration for gas supplied to the region.

**North Wales**

4.19 North Wales receives gas from St Fergus and Barrow from a take-off at Audley. The region therefore at present receives gas with a winter average hydrogen sulphide content of about 3.0 mg m\(^3\), the same as that in the North West region.

**South Wales**

4.20 South Wales receives the same gas as that received to the south of the Churchover compressor station in southern area of the West Midlands region. This originates from Theddlethorpe and St Fergus and Barrow with a little from Bacton and Easington (British Gas Research and Technology, 1997). During the winter the contribution of St Fergus and Barrow gas is quite low when southern basin terminals operate at a much higher load factor. Assuming a fifth of the supply from Lupton and the remainder from Southern Basin terminals in equal proportions, the current level of hydrogen sulphide in gas supplied to South Wales would be about 1.0 mg m\(^3\) as a best estimate winter average and would certainly lie within the range 0.3 and 1.5 mg m\(^3\).
Eastern

4.21 Eastern region predominately receives gas from Bacton, particularly during the winter. The hydrogen sulphide content in the gas will therefore be about 0.5 mg m\(^{-3}\) at present. A little gas can be received from the Easington and Theddlethorpe terminals from central take-offs at Royston and Whitwell, but this will not significantly affect the hydrogen sulphide concentration in winter which is likely to range between 0.3 and 0.75 mg m\(^{-3}\).

North Thames

4.22 North Thames region predominately receives gas from Bacton. St Fergus gas does penetrate this far south via the east coast, but not significantly during the winter. Similarly gas from Theddlethorpe and Easington is also received, but generally in relatively small proportions. Overall the winter hydrogen sulphide concentration is likely to be similar to that in Eastern region, about 0.5 mg m\(^{-3}\).

South Eastern

4.23 As with North Thames, gas to the South Eastern region is predominately supplied from Bacton with other contributions mainly from Theddlethorpe and Easington. At present, the winter hydrogen sulphide concentration in the gas will therefore be approximately 0.5 mg m\(^{-3}\).

Southern

4.24 In winter Southern region receives gas from Theddlethorpe with significant contributions from Bacton and Easington in approximately equal contributions. St Fergus gas is also supplied, but only during the summer. The proportion of supply from each of the Southern Basin terminals is variable but the current average hydrogen sulphide content in winter is likely to be in the range 0.7 ± 0.2 mg m\(^{-3}\).

South West

4.25 The South West region receives gas from two pipelines, one from Wormington and the other from the Aylesbury compressor station (Figure 4.2) with the two pipelines joining at Ilchester. Analysis of the gas supply data suggests gas supplied to the part of the South West prior to the Ilchester junction is likely to contain about 1 mg m\(^{-3}\)
hydrogen sulphide. This is similar to the estimate for South Wales (1.0 mg m\(^{-3}\)) which is also supplied from Wormington. The Kenn take-off in the heart of the South West down stream of the Ilchester pipeline junction receives similar proportions of gas to Wormington. The South West region as a whole can therefore be estimated, currently, to receive gas with a winter hydrogen sulphide concentration of about 1.0 mg m\(^{-3}\).

4.26 Based upon the previous subsections Table 4.1 summarises the estimates of regional hydrogen sulphide concentrations for GB.

<table>
<thead>
<tr>
<th>Region</th>
<th>Winter average (mg m(^{-3}))</th>
<th>Range (mg m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scotland</td>
<td>2.5</td>
<td>2.3 - 2.8</td>
</tr>
<tr>
<td>Northern</td>
<td>2.5</td>
<td>2.3 - 2.8</td>
</tr>
<tr>
<td>North West</td>
<td>3.0</td>
<td>2.8 - 3.5</td>
</tr>
<tr>
<td>West Midlands</td>
<td>Not Applicable</td>
<td>1.0 - 3.5</td>
</tr>
<tr>
<td>East Midlands</td>
<td>Not Applicable</td>
<td>0.5 - 3.5</td>
</tr>
<tr>
<td>North East</td>
<td>Not Applicable</td>
<td>0.2 - 2.8</td>
</tr>
<tr>
<td>North Wales</td>
<td>3.0</td>
<td>2.8 - 3.5</td>
</tr>
<tr>
<td>South Wales</td>
<td>1.0</td>
<td>0.8 - 1.3</td>
</tr>
<tr>
<td>South Eastern</td>
<td>0.5</td>
<td>0.4 - 0.6</td>
</tr>
<tr>
<td>Southern</td>
<td>0.7</td>
<td>0.5 - 0.9</td>
</tr>
<tr>
<td>Eastern</td>
<td>0.5</td>
<td>0.4 - 0.6</td>
</tr>
<tr>
<td>South West</td>
<td>1.0</td>
<td>0.8 - 1.3</td>
</tr>
<tr>
<td>North Thames</td>
<td>0.5</td>
<td>0.4 - 0.6</td>
</tr>
</tbody>
</table>

Not applicable since average concentrations vary significantly either spatially and/or temporally in winter
FUTURE HYDROGEN SULPHIDE CONCENTRATIONS FROM TERMINAL FEEDERS

4.27 The Interim Report utilised historic trends in hydrogen sulphide concentrations to project future hydrogen sulphide concentrations from terminal feeders. These were used to estimate the mass of hydrogen sulphide likely to enter the NTS in future years for different supply scenarios. The results of this assessment (presented in Figure 0.4, Appendix A) had a number of inherent limitations and involved significant uncertainties, but was the most reliable approach possible given the available data. The objective of this subsection is to produce more reliable projections of future hydrogen sulphide concentrations from terminal feeders.

4.28 Gas production for the UK market is constantly changing as new reserves are identified and developed and exhausted, and uneconomic fields are closed. This changing supply also affects the concentration of hydrogen sulphide in the domestic gas supply because fields have very different hydrogen sulphide concentrations and some terminals treat the gas.

4.29 The approach adopted to assess future hydrogen sulphide concentrations from terminal feeders has been to utilise a range of information sources to examine future trends in gas production from terminal feeders and their hydrogen sulphide content. These information sources included Wood Mackenzie North Sea Service (Wood Mackenzie, 1996) and a survey of gas operators undertaken by WS Atkins and information of treatment facilities obtained by the HSE. Much of this information is commercially sensitive and consequently in presenting our projections it has been necessary to only provide a summary of the findings. This reduces the transparency of the assessment but is unavoidable. Table 4.2 presents a summary of the present hydrogen sulphide concentrations in gas supplied from the different UK terminals and gives an estimate of the likely changes in the concentration in the future. The table includes a best estimate and range of values which represent a High, Medium and Low scenario.
Table 4.2 - Present and possible future hydrogen sulphide concentrations in gas supplied from UK terminals

<table>
<thead>
<tr>
<th>Terminal</th>
<th>Present concentrations (mg m(^{-3}))</th>
<th>2005 predicted range (mg m(^{-3}))</th>
<th>2005 anticipated concentration (mg m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacton</td>
<td>0.5</td>
<td>0.1 - 1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Barrow</td>
<td>1.5 - 3</td>
<td>3.5 - 4.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Easington /Dimlington</td>
<td>0.05</td>
<td>0.05 - 0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>St Fergus</td>
<td>2.5</td>
<td>3.1 - 4.2</td>
<td>3.6</td>
</tr>
<tr>
<td>Teedlethorpe</td>
<td>0.3 - 1.28</td>
<td>0.5 - 1.25</td>
<td>1.0</td>
</tr>
<tr>
<td>Teesside</td>
<td>3.6</td>
<td>1.25 - 2.75</td>
<td>1.5</td>
</tr>
</tbody>
</table>

4.30 Table 4.2 is based upon a large number of assumptions, key amongst which are:

- that the proportion of supply in 2005 from each pipeline is that anticipated by Wood Mackenzie for contracted and possible contracts;

- there will be no new construction of treatment facilities at any of the Bacton receiving terminals;

- future supply to the Bacton Amoco and Esso/Shell terminals will be gas as sweet as that currently received;

- gas supplied from the Bacton Phillips terminal will be maintained at present hydrogen sulphide levels and may decrease as the proportion of sweet gas increases;

- supply and treatment of gas from Barrow, will remain largely unchanged until 2005;

- no additional treatment facilities will be installed at the Easington and Dimlington terminals and concentration of hydrogen sulphide in gas supplied will remain at present levels;
the hydrogen sulphide content of the gas supplied through the St Fergus Mobil SAGE, terminal will remain at current levels after the expansion of terminal facilities to receive gas from the Britannia field;

hydrogen sulphide levels in gas from the St Fergus Shell terminal (receiving gas from the Fulmar and Frigg pipelines) are anticipated to increase, possibly up to the level of the present specification although the contribution to overall production from St Fergus will fall;

the hydrogen sulphide concentrations at the St Fergus Total terminal (receiving gas from the Frigg pipeline), will remain at present levels in the short-term but will increase subsequently possibly up to the level of the present specification;

by 2005 the proportion of production at St Fergus from the Fulmar, Frigg, Sage and Flags systems will be 6, 36, 38 and 20 per cent respectively.

no additional treatment facilities will be employed at the Theddlethorpe terminal and the future concentrations of hydrogen sulphide will remain unchanged;

once gas treatment facilities are installed and in operation at Teesside, levels of hydrogen sulphide in outlet gas will decline to 1.5 mg m\(^3\). But, if this equipment is not used on a continuous basis levels could increase up to 2.75 mg m\(^3\).

4.31 Table 4.2 indicates that the most significant changes in the hydrogen sulphide concentration of gas entering the NTS from different terminals will be seen at St Fergus where the concentration is anticipated to increase, possibly significantly. Figure 4.3 shows past hydrogen sulphide concentrations and projections based upon the best estimate. Figure 4.4 shows the projected range of concentrations for St Fergus, Barrow and Teesside, those terminals with significantly the highest concentrations of hydrogen sulphide.
Figure 4.3 - Historic and projected future hydrogen sulphide terminal feeder concentrations

Figure 4.4 - High, medium and low hydrogen sulphide projections from terminal feeders
4.32 As a consequence of the wide range of hydrogen sulphide concentrations in gas from GB terminal feeders, the sourness of gas received by different regions of GB is dependent upon the origin of the gas supplied. This is dependent upon the relative level of production from each terminal which varies both seasonally, and over longer time periods as fields supplying the terminals come on-stream and subsequently become exhausted. In order to evaluate future regional trends in hydrogen sulphide concentrations it is therefore necessary to also consider long term trends in gas production.

4.33 The Interim Report presented information on annual production trends based upon TransCo's 1995 10 year Statement (TransCo, 1996). This subsection updates this information using 1996 data (TransCo, 1997) using winter time data, consistent with the revised average winter time hydrogen sulphide concentration employed. The section also considers the possible effect of the Interconnector. Deregulation of the gas supply industry, the rapid increase in gas generating capacity and the introduction of gas export via the Interconnector have resulted in large uncertainty concerning future gas supply. Any conclusions drawn by this section therefore must be considered as tentative.

4.34 TransCo predictions of future gas supply to the year 2004/05 have been used with information derived earlier in the section regarding future hydrogen sulphide concentrations to predict the quantity of hydrogen sulphide entering the NTS and to determine how this is likely to alter as supply patterns and hydrogen sulphide concentrations change. Figure 4.5 shows the predicted maximum beach deliveries by terminal and Figure 4.6 the proportion of the total supply by terminal. Two scenarios shown in the figures are:

- St Fergus Expansion (E) - where there are no network restrictions on gas flow, and

- Minimum Investment Case (C) where peak day St Fergus and Teesside flow rates are restricted to 109 Mm$^3$ and 34 Mm$^3$ respectively.
4.35 The two scenarios do not diverge until after 1997/98. The winter maximum is not the ideal supply scenario as it is not representative of conditions throughout the winter but was adopted since no information was available on an average winter day concentrations. Under winter average conditions compared to winter maximum it is
likely that production from Teesside, Barrow and St Fergus combined would be higher, so this represents a conservative assumption.

4.36 The data show that the proportion of supply from St Fergus, Barrow and Teesside is projected to increase from 45 to about 60 per cent between 1995/96 and 2004/05 for either scenario. Most of this increase is as a result of increased Teesside production but will result in a lower proportion of production from sweeter Southern Basin terminals. The result will be that regions in southern England which receive gas from southern basin terminals will receive a much high proportion of their winter supply from terminals with significantly higher hydrogen sulphide concentrations. Thames region already receives summer gas from St Fergus (TransCo, 1996) but since gas fires and boilers are likely to be in relatively sparse use during the summer the risk of sulphidation is significantly reduced. Northern parts of the West and East Midlands also receive St Fergus gas.

4.37 Utilising projections of future hydrogen sulphide concentrations (medium scenario) together with those of future production profiles, Figure 4.7 shows the anticipated change in the daily quantity of hydrogen sulphide entering the NTS and Figure 4.8 the proportion of hydrogen sulphide supply. Figure 4.7 demonstrates that the amount of hydrogen sulphide entering the NTS during winter periods is anticipated to increase by 24 per cent between 1995/96 and 2004/05. Most of this increase will result from changes in the production and hydrogen sulphide concentrations at St Fergus and increased production at Teesside. Figure 4.8 demonstrates half the hydrogen sulphide entering GB will originate from St Fergus and about a third from Barrow. Gas from these two terminals have significantly higher hydrogen sulphide concentrations than gas from other GB terminals and are overwhelmingly the cause of sulphidation in GB.
Figure 4.7 - Winter hydrogen sulphide supply

Figure 4.8 - Proportion of winter hydrogen sulphide supply

4.38 Figure 4.9 shows the anticipated mass of hydrogen sulphide entering the NTS for a winter day for the three scenarios of future hydrogen sulphide concentration discussed
in a previous subsection. The figure demonstrates a potentially wide range for the 
mass of hydrogen sulphide entering the NTS by 2004 of between 570 to 900 kg with 
the best estimate put at 700 kg. In the event of the high projection being followed it is 
anticipated that high incidences of sulphidation will occur in those regions receiving 
St Fergus and Barrow gas.

**Figure 4.9 - Mass of hydrogen sulphide entering the NTS for low, medium and high 
projections of hydrogen sulphide concentration**

![Graph showing mass of hydrogen sulphide entering the NTS for low, medium and high projections of hydrogen sulphide concentration.](image)

**Interconnector**

4.39 In the short to medium term the future origin of gas received by different regions will 
also be affected by the proportion of supply from each terminal being exported 
through the Interconnector. The Interconnector is planned to come into operation in 
October 1998 and has a capacity of 20,000 Mm$^3$ year$^{-1}$. The Interconnector will run 
from the Bacton terminal. Details of the entry facilities are currently being finalised, 
however the base case includes:
• the possibility for both import and export from October 1998;

• that TransCo will be able to supply gas from Bacton or other UK terminals; and

• that non NTS pipelines will be connected to the Interconnector at Bacton.

4.40 It is anticipated the Interconnector will export gas almost exclusively until about 2010 - with imports only likely during peak winter periods. Beyond 2010 it is anticipated the Interconnector will be a net importer of gas. TransCo anticipate that Teesside and St Fergus are likely to be the long-term supply points for UK Continental Shelf and Norwegian gas, and are planning NTS developments to accommodate the increased supply from the northern North Sea as the southern terminals move into decline.

4.41 The rate at which the increased supply from St Fergus and Teesside to southern England occurs will depend in part upon the extent to which new and existing fields supplying Bacton flow directly into the Interconnector rather than supplying the NTS and southern England. The extent to which this is realised will significantly affect the origin and hence hydrogen sulphide content of the gas supplied to Southern England. Since no firm commitments to export gas have at present been made the relative importance of this scenario is not known. If a significant proportion of gas from Bacton is exported, there will be a significant increase in hydrogen sulphide concentration in southern England. If export continues during winter this scenario will have a particularly significant effect upon incidences of sulphidation in those regions currently supplied with Bacton gas.

FUTURE REGIONAL HYDROGEN SULPHIDE CONCENTRATIONS

4.42 Future hydrogen sulphide concentrations in different gas regions will be dependent upon:

• the hydrogen sulphide concentration of gas at the NTS Entry Point, which is in turn dependent upon the hydrogen sulphide content of the gas received by the terminal and extent of treatment undertaken;

• the proportion of supply from each terminal, which will in part depend upon the development of the gas market;
• the destination of gas supplied from the new Teesside terminal which is unclear; and

• the volume and origin of gas exported by the Interconnector which is unknown.

4.43 Predictions of future hydrogen sulphide concentrations in most regions therefore inevitably contain significant uncertainties. Those regions currently supplied from St Fergus and Barrow are likely to continue to be, it is therefore possible to estimate concentrations of hydrogen sulphide to 2005 in Scotland, Northern England, North Wales and North West England from extrapolating from terminal feeder projections. Estimates for future hydrogen sulphide concentrations in other regions depend upon whether they continue to receive gas from the same origin as at present and this is far from certain. Table 4.3 presents estimates of future regional hydrogen sulphide concentrations in 2005 based upon estimates for terminal feeders. The reliability of estimates is dependent upon whether the assumptions made are correct. In addition assumptions made in estimating future feeder concentrations, described earlier in Section 4 are important. Table 4.3 presents the best estimates of future hydrogen sulphide concentrations in 2005. There is considerable, unavoidable uncertainty in these estimates but the range of concentrations proposed are considered realistic. These predictions are used in Section 6 to indicate how the current sulphidation problem in GB is likely to develop in the future and the likely impact of revisions in the hydrogen sulphide specification.
Table 4.3 - Regional winter hydrogen sulphide concentrations (mg m⁻³)

<table>
<thead>
<tr>
<th>Region</th>
<th>Present concentration</th>
<th>2005 estimate</th>
<th>Principal assumption (Uncertainty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scotland</td>
<td>2.3 - 2.8</td>
<td>3.1 - 4.2</td>
<td>• Continues to be supplied from St Fergus (Low)</td>
</tr>
<tr>
<td>Northern</td>
<td>2.3 - 2.8</td>
<td>3.1 - 4.2</td>
<td>• Continues to be supplied from St Fergus (Low)</td>
</tr>
<tr>
<td>North West</td>
<td>2.8 - 3.5</td>
<td>3.2 - 4.4</td>
<td>• Continues to be supplied from St Fergus and Barrow (Low)</td>
</tr>
<tr>
<td>West Midlands</td>
<td>0.8 - 3.5</td>
<td>3.2 - 4.4</td>
<td>• Entire region supplied from St Fergus and Barrow (High)</td>
</tr>
<tr>
<td>East Midlands</td>
<td>0.2 - 2.8</td>
<td>2.0 - 3.5</td>
<td>• Region predominately supplied from St Fergus and Teesside (High)</td>
</tr>
<tr>
<td>North Wales</td>
<td>2.8 - 3.5</td>
<td>3.2 - 4.4</td>
<td>• Continues to be supplied from St Fergus and Barrow (Low)</td>
</tr>
<tr>
<td>South Wales</td>
<td>0.8 - 1.3</td>
<td>0.8 - 1.5</td>
<td>• Same origin of supplies as at present (High)</td>
</tr>
<tr>
<td>South East</td>
<td>0.4 - 0.6</td>
<td>0.3 - 1.0</td>
<td>• Same origin of supplies as at present (Moderate)</td>
</tr>
<tr>
<td>Southern</td>
<td>0.5 - 0.9</td>
<td>0.8 - 1.5</td>
<td>• Same origin of supplies as at present (Moderate)</td>
</tr>
<tr>
<td>Eastern</td>
<td>0.4 - 0.6</td>
<td>0.5 - 1.0</td>
<td>• Same origin of supplies as at present (Moderate)</td>
</tr>
<tr>
<td>North East</td>
<td>0.2 - 2.8</td>
<td>2.0 - 3.5</td>
<td>• Supplied from Teesside and St Fergus predominately (Moderate)</td>
</tr>
<tr>
<td>South West</td>
<td>0.8 - 1.3</td>
<td>0.8 - 1.5</td>
<td>• Same origin of supplies as at present (Moderate)</td>
</tr>
<tr>
<td>North Thames</td>
<td>0.4 - 0.6</td>
<td>0.5 - 1.0</td>
<td>• Same origin of supplies as at present (Moderate)</td>
</tr>
</tbody>
</table>
5. COPPER SULPHIDE PRODUCTION AND FLAKING

INTRODUCTION

5.1 The Interim Report provided a detailed assessment of the reaction between copper and hydrogen sulphide and subsequent flaking of the deposits. This provided evidence that within natural gas in the presence of trace oxygen copper (I) sulphide is produced. The reaction is known to proceed at hydrogen sulphide concentrations as low as 0.075 mg m\(^{-3}\) and is accelerated in the presence of trace quantities of water:

\[
4\text{Cu}_\text{(s)} + 2\text{H}_2\text{S}_\text{(g)} + \text{O}_2(\text{g}) \rightarrow 2\text{Cu}_2\text{S}_\text{(s)} + 2\text{H}_2\text{O}_\text{(l)}
\]

5.2 This section elaborates upon two issues identified in the Interim Report as particularly significant in the production and subsequent flaking of copper sulphide:

(i) the role of polysulphides in catalysing the sulphidation reaction between copper metal and hydrogen sulphide under the conditions present in the GB domestic gas supply; and

(ii) factors affecting the flaking rate of copper sulphide deposits.

ROLE OF POLYSULPHIDES IN SULPHIDATION CHEMISTRY

5.3 The mechanism proposed for the production of copper sulphide involves a polysulphide intermediate generated by the reaction of mercaptans, oxygen and hydrogen sulphide in a liquid media. It has been suggested that this mechanism may be more rapid than the simple oxygen catalysed reaction by up to an order of magnitude. The hypothesis for a polysulphide mechanism of copper sulphidation was developed following investigation of sulphidation rates in gas supplied from three operating companies in the USA (Lyle, 1993a). This study suggested gas streams treated with amines to remove hydrogen sulphide concentrations may be more corrosive towards copper than gas streams with similar hydrogen sulphide concentrations which have not been treated, or have been treated using other
procedures. A possible implication of this observation, and the proposed polysulphide mechanism hypothesis, if correct, is that some techniques to remove hydrogen sulphide from gas may result in an increase in concentrations of reactive polysulphides which under certain conditions could accelerate the sulphidation reaction. In these circumstances consideration would have to be given as to whether, or how, it is appropriate to reduce hydrogen sulphide concentrations in gas in order to reduce occurrences of sulphidation.

5.4 The Interim Report was unable to identify any research which had measured concentrations of polysulphides in gas, calculated the rate determining step for the reaction, or demonstrated at the concentrations of hydrogen sulphide and oxygen present in the GB gas supply that the polysulphide reaction mechanism for sulphidation occurs. It is however clearly very important to evaluate comprehensively the possible mechanism for polysulphide production and the contribution of this mechanism to copper sulphidation under conditions present within the GB gas distribution and supply networks.

5.5 The presence of polysulphides in natural gas was originally postulated by McGrath and Prebble (1972) who proposed that mercaptans in natural gas could give rise to polysulphides in the presence of free sulphur and a base. In addition, they suggested that free sulphur may occur as a product of the oxidation of trace amounts of hydrogen sulphide by trace amounts of molecular oxygen in the presence of rust, present at some locations within steel transmission piping. The proposed reaction mechanism is shown below (Lyle, 1993a):

- \[ 2R-SH_{(g)} + H_2S_{(g)} + O_{2(g)} \rightarrow RSSR_{(g)} + S_{(g)} + 2H_2O_{(l)} \]
- \[ 2H_2S_{(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} + 2S_{(g)} \]
- \[ nS_{(s)} + RSSR_{(g)} \rightarrow RS_{n+2}R_{(aq)} \]
- \[ 2Cu_{(s)} + RS_{n+2}R_{(aq)} \rightarrow Cu_2S_{(s)} + RS_{n+1}R_{(aq)} \]

5.6 Gas treatment systems to remove hydrogen sulphide may provide the base by use of alkaline wash liquors, such as ethanolamine. This is the basis for the hypothesis that gas treatment to remove hydrogen sulphide may increase concentrations of polysulphides and accelerate the sulphidation reaction.
5.7 Natural gas supplies in GB typically contain 0.5 to 2.5 ppmv of naturally occurring mercaptans, usually methyl ethyl sulphide. A mix of one of the least easily oxidisable mercaptans, tertiary butyl mercaptan, one of the most easily oxidisable mercaptans, ethyl mercaptan, and diethyl sulphide is added to the gas supplies at a maximum concentration of 5 ppmv. The contractual limit for total sulphur in GB gas supplies is 30 ppmv, but the concentration of total sulphur is typically in the range 4 to 7 ppmv, of which mercaptans form a large part. Mercaptans are therefore present in significant concentrations within natural gas supplies in GB and could therefore be involved in a second sulphidation reaction mechanism.

5.8 British Gas Research and Technology (1997) noted that concentrations of mercaptans in gas supplied to GB are higher in gas from the Theddlethorpe and Bacton terminals than St Fergus. It would therefore be anticipated that if the polysulphide mechanism were a significant cause of sulphidation that more severe problems would be arising in areas supplied with gas from Bacton and Theddlethorpe than is the case. It is however also noted that if there is a critical concentration of hydrogen sulphide in the gas required to trigger the breakdown of the mercaptans it is possible that this critical level is not exceeded in Bacton and Theddlethorpe gas but is exceeded in gas from St Fergus.

5.9 McGrath and Prebble (1972) also postulated that, although the behaviour of organic monosulphides at pressures of 70 bar was unknown, reactions to produce polysulphides would be favoured by high pressures. However they qualified this with the statement that the corrosion consequences of the possible formation of polysulphides in high pressure systems were not likely to be serious as the concentrations of polysulphides in the gas would be very low.

5.10 Laboratory studies on the corrosion of copper by ethyl mercaptan were undertaken by Pyrburn et al. (1978). These studies, which involved the ASTM 1838 Copper Corrosion Test, included investigation of propane containing ethyl mercaptan alone, in the presence of hydrogen sulphide and in the presence of elemental sulphur. For ethyl mercaptan alone, concentrations of up to 100 ppm (assumed to be expressed by volume) did not cause failure of the copper strip in the test procedure. In the presence of hydrogen sulphide, ethyl mercaptan displayed an inhibitive effect, whilst in the presence of elemental sulphur it enhanced corrosion. However it should be noted that, whilst the employed concentrations of hydrogen sulphide (1 to 10 ppm w/w as sulphur) are representative of concentrations in natural gas supplies in GB, the
employed concentrations of ethyl mercaptan (30 to 100 ppm assumed to be expressed by volume) are greater than those in natural gas supplies in GB.

5.11 Work undertaken by Lyle (1993a) included a literature review which revealed that polysulphides, which are formed by reactions between hydrogen sulphide, mercaptans and oxygen, were significantly more corrosive to copper than any of these three individual species alone. An intermediate stage in the formation of polysulphides is the oxidation of mercaptans to disulphides. Therefore the presence of polysulphides in natural gases containing substantial amounts of low molecular weight mercaptans (e.g. methyl, ethyl or propyl mercaptans) was suggested to be more likely than in gases containing typical odourants (e.g. tertiary butyl mercaptans).

5.12 Experimental investigations within this work (Lyle, 1993a) produced a relationship for the corrosion rate. This relationship indicated that if hydrogen sulphide and oxygen concentrations were low, an increase in the mercaptan concentration would reduce the corrosion rate. Whilst at high concentrations of hydrogen sulphide and oxygen, the relationship indicated that an increase in the mercaptan concentration would produce an increase in the copper corrosion rate by means of an interactive effect. However, these results were strictly applicable only to the employed ranges of constituent concentrations. For hydrogen sulphide, mercaptans and carbon dioxide the ranges were substantially higher than concentrations representative of natural gases. In addition methyl mercaptan was used as the odourant in these investigations and this is not present in high concentrations within natural gas.

5.13 A programme of research work with the aim of investigating the previously developed relationship for the corrosion rate at constituent concentrations typical of natural gases was also undertaken (Lyle, 1993b). The experiments of the previous investigation were repeated. Employed concentrations for hydrogen sulphide were 0, 8 and 16 ppmv; for oxygen were 0, 0.25 and 0.5 volume percent; for carbon dioxide were 0, 0.75 and 1.5 volume percent; and for methyl mercaptan were 0, 10 and 20 ppmv. Methyl mercaptan was used as odourant for consistency with the previous investigations. For oxygen, carbon dioxide and mercaptan the employed concentrations are representative of natural gas supplies in GB, whilst for hydrogen sulphide concentrations of 8 and 16 ppmv are significantly greater than those permitted in natural gas supplies in GB.

5.14 The effect of methyl mercaptan in the research programme was found to be similar to its effect in the more severely contaminated gases in that increases in its concentration
led to decreases in the copper corrosion rate (Lyle, 1993b). No interactive effect between methyl mercaptan, hydrogen sulphide and oxygen was found. In the previous programme this interaction, which was consistent with the chemical reaction of these species to form polysulphides, resulted in increases in the copper corrosion rate. The lack of an interactive effect suggested that polysulphides may not be able to form in natural gases with hydrogen sulphide concentrations less than 16 ppmv and oxygen concentrations less than 0.5 volume percent. Therefore it was concluded that the effect of methyl mercaptan depends on the concentration of hydrogen sulphide. At low concentrations of hydrogen sulphide increases in methyl mercaptan concentrations reduce copper corrosion rates, whilst at high hydrogen sulphide concentrations increases increase copper corrosion rates.

5.15 A separate experiment was conducted to see whether the effect on the copper corrosion rate produced by typical odourant blends was the same as the effect produced by methyl mercaptan (Lyle 1993b). For this experiment the specimens were immersed in liquid water. Two blends of odourant were tested; 80% tertiary butyl mercaptan with 20% isopropyl mercaptan, and 80% tertiary butyl mercaptan with 20% dimethyl sulphide. The latter blend is more representative of odourants added to natural gas supplies in GB.

5.16 Two concentrations each of hydrogen sulphide (20 and 60 ppmv), oxygen (0.5 and 1.5 volume percent) and odourants (20 and 60 ppmv) were used in the tests in conjunction with carbon dioxide (1.5 volume percent). Therefore, except for the replacement of methyl mercaptan with the two odourant blends, the compositions of the eight basic gas streams were the same as for part of the previous investigations (Lyle, 1993a). For oxygen and carbon dioxide the employed concentrations are representative of natural gas supplies in GB, whilst for hydrogen sulphide and odourants the employed concentrations are much greater than those in natural gas supplies in GB. The mean corrosion rates of copper were generally lower for both odourant blends compared to methyl mercaptan but the results were found not to be statistically significant at the 5-per cent level. It was concluded that the substitution of the two odourant blends for the equivalent concentration of methyl mercaptan did not have a significant effect on the corrosion rate of copper.

5.17 The effect of the addition of monoethanolamine was also investigated (Lyle 1993b). This was accomplished in two ways. Firstly, a test specimen was exposed to an environment containing water plus 100 ppm of monoethanolamine that was saturated with a corrosive gas mixture containing 16 ppmv hydrogen sulphide, 15 ppmv methyl
mercaptan, 0.25 volume percent oxygen and 0.75 volume percent carbon dioxide. For monoethanolamine 100 ppm is typical of concentrations found in drip oils removed from operating pipelines. For oxygen and carbon dioxide the employed concentrations are representative of natural gas supplies in GB, whilst for hydrogen sulphide and odourants the employed concentrations are greater than those in natural gas supplies in GB. A small but statistically insignificant decrease in the copper corrosion rate was observed.

5.18 The second test for the effect of the addition of monoethanolamine involved the exposure of a specimen to a 20% monoethanolamine in high purity water environment that was saturated with high purity methane rather than the corrosive gas (Lyle, 1993b). This was to study corrosive effects due to monoethanolamine alone. The measured corrosion rate was only approximately 10% of the rate obtained in the water plus 100 ppm of monoethanolamine environment. This indicated that monoethanolamine alone does not cause significant corrosion of copper. This finding does not agree with the results of some earlier studies but this may be because the concentration of monoethanolamine used in these limited tests was too low to produce a significant effect.

5.19 Yan (1994) undertook a programme of work on the sulphidation of copper with the objective of understanding the factors, principally associated with the gas phase composition, which lead to sulphidation of copper at ambient temperature and pressure. Components added to methane as the base carrier gas formed the factors of a large factorial experiment, within which some factors were at several levels. The basic unit of level used in the factorial experiment was ppmv for hydrogen sulphide and oxygen, and dose (approximately 3 ppmv with respect to sulphur) for the odourant. Employed concentrations for hydrogen sulphide were 0 to 2 ppmv, for oxygen were 0 to 5 ppmv, and for odourant were 0 to 3 doses. These concentrations are representative of natural gas supplies in GB. Measurement of the rate of attack and investigation of the chemical composition of the surface deposit were provided by means of a photo-electron spectrometer.

5.20 This work concluded that in the presence of the other gases the influence of odourant on sulphidation was not as significant as the influence of hydrogen sulphide. Although sulphur existed on the surface of the copper, the odourant did not have a very high reactivity with copper. Evidence was provided that the odourant was probably chemisorbed onto the copper surface. Investigation of different odourants showed that ethyl mercaptan demonstrated the highest chemisorption ability.
compared with diethyl sulphide and tertiary butyl mercaptan. The employed concentration of odourant was between 0 and 6 ppmv, which is representative of natural gas supplies in GB. When oxygen at 5 ppmv was introduced into the system the main reaction product was found to be copper (I) oxide and the amount of chemisorbed odourant was very small.

5.21 Yan employed clean gases in a laboratory environment for his work. British Gas Research and Technology (1997) note that the absence of any interaction between complex sulphides and copper, may therefore be because there was either inadequate time for the polysulphides to fully form, or essential catalysts were not present. Nevertheless it is concluded that although polysulphide formation can occur, it is not thought to be a significant contribution to the rate of sulphide reaction that is found to occur in the present gas supplied to GB. It is also stated that probable future increases in hydrogen sulphide concentrations may increase both the rate of sulphidation originating from reaction with hydrogen sulphide and that with polysulphides.

Conclusions

5.22 Information concerning the role of polysulphides in the sulphidation of copper is sparse. However adequate studies have been conducted, and the results of these are sufficiently consistent to construct a reasonably confident assessment of the role of polysulphides in the production of copper (I) sulphide within domestic gas carrier piping. A summary of the principal research findings includes:

- Pyrburn et al. (1978) demonstrated that ethyl mercaptan in the presence of hydrogen sulphide at concentrations representative of natural gas supplies in GB displayed an inhibitive effect on corrosion;

- Lyle (1993b) concluded the effect of methyl mercaptan depended on the concentration of hydrogen sulphide. Furthermore that at hydrogen sulphide concentrations greater than, but more closely approaching, those representative of natural gas supplies in GB an increase in the methyl mercaptan concentration (which would promote a polysulphide reaction mechanism) produced a decrease in the copper corrosion rate;

- Lyle (1993b) in laboratory experiments also demonstrated that at hydrogen sulphide concentrations substantially greater than those representative of natural gas supplies in GB the substitution of odourant blends for methyl
mercaptan did not have a significant effect on the corrosion rate of copper. These same investigations indicated that the addition of monoethanolamine to gas mixtures containing hydrogen sulphides concentrations greater than those present in the natural gas supply in GB did not have an effect on the copper corrosion rate. The presence of monoethanolamine alone was found not to cause significant corrosion of copper.

- Yan (1994) concluded that the influence of odourant on sulphidation was not as great as the influence of hydrogen sulphide. Furthermore, evidence was provided that the odourant was probably chemisorbed onto the copper surface.

- British Gas Research and Technology (1997) concluded that if the polysulphide reaction was an important mechanism it was likely sulphidation occurrences in GB would be more widespread in areas supplied with gas originating from the Bacton and Theddlethorpe terminals since these contain gas with a higher mercaptan content than gas from the St Fergus terminal.

- British Gas Research and Technology (1997) also stated that although polysulphide formation can occur, it is unlikely to be a significant contribution to the rate of sulphide reaction within GB at present. However, future increases in hydrogen sulphide concentrations may increase the rate of sulphidation of copper by both the polysulphide mechanism and direct reaction with hydrogen sulphide and trace oxygen.

5.23 On the basis of the above evidence, it is concluded overall that:

- at the concentrations of hydrogen sulphide permitted in the natural gas supply in GB the polysulphide reaction mechanism, is not a significant route for copper sulphidation.

5.24 In addition, it appears that the presence of amines in the natural gas supply does not increase the rate of sulphidation.

5.25 The implication of this conclusion is that gas treatment techniques which reduce hydrogen sulphide concentrations will not lead to an increase in sulphidation through a secondary polysulphide intermediate. Furthermore, all other evidence of sulphidation in GB indicates that sulphidation occurrences will be reduced by a reduction in hydrogen sulphide concentrations.
The second important issue regarding copper sulphide production considered by this further work concerns the stability of the copper sulphide film produced by the reaction between copper and hydrogen sulphide. The Interim Report identified that the extent to which appliances are affected by sulphidation is dependent upon the rate at which deposits of copper sulphide flake from the surface of the pipes. Flakes grown at higher hydrogen sulphide concentrations form at higher rates and are less stable than flakes grown at lower rates, but the flake size is not significant. The Interim Report postulated this may be due to the higher proportion of faults in the crystalline structure during more rapid formation. The Interim Report also identified research which suggested the rate of gas flow also affects the rate at which flakes break away from copper surfaces with higher flow rates inducing higher flaking rates.

As part of this further work British Gas Research and Technology investigated the effect of hydrogen sulphide concentration upon the stability, hence flaking rate, of copper sulphide deposits (British Gas Research and Technology, 1997). This work drew upon their extensive experience obtained from both field and laboratory experiments on film growth rates to investigate three principal questions. The report is commercially confidential but findings provided valuable insight into the behaviour of copper sulphide films and how the black dust issue could be remediated, or develop in the future.

It is known through examination of domestic gas pipes in southern England that extensive deposits of stable copper sulphide have been slowly laid down by the reaction between low levels of hydrogen sulphide and copper. This demonstrates that in order to prevent copper sulphide flaking it is not necessary to remove all hydrogen sulphide from gas, rather only to reduce levels to below the concentration at which stable deposits form. British Gas Research and Technology concluded that from both field experience and laboratory research flaking begins to occur at about 0.3 - 0.4 mg m\(^3\) hydrogen sulphide. This supports the work undertaken in Section 4 which identified a small number of properties affected by black dust throughout GB, including those regions receiving relatively sweet gas from southern basin terminals. However, at these very low hydrogen sulphide concentrations, the number of affected appliances in properties is very small. The research also identified a three year lag period between receiving gas with a hydrogen sulphide content greater than 0.4 mg m\(^3\) and the onset of more widespread sulphidation problems.
5.29 In the future it is likely that areas of southern England, where substantial stable deposits of copper sulphide exist, will receive gas with a higher concentration of hydrogen sulphide (as production from southern basin terminals supplying sweet gas declines). British Gas Research and Technology (1997) concluded that the effect of these increasing concentrations upon the stable copper sulphide films will be to destabilise the existing film. This conflicts with the tentative findings of the Interim Report which surmised an unstable deposit would form above an essentially stable one and subsequent flaking would be at the interface of the two films. The British Gas Research and Technology report presents substantial evidence to demonstrate flaking occurs at the copper sulphide / copper surface interface. This finding suggests that the existing stable deposits of copper sulphide in southern England would become destabilised and begin flaking were they exposed to higher hydrogen sulphide concentrations in the future. The substantial deposits currently attached to pipework would therefore potentially become mobilised if exposed to significantly more sour gas and would be transported into appliances.

5.30 In Scotland, Northern England, North Wales and some parts of the West Midlands there are large deposits of currently unstable copper sulphide attached to copper carcassing. The British Gas Research and Technology research also assessed the likely impact upon these deposits of changes in the concentrations of hydrogen sulphide. British Gas Research and Technology have no direct experience of the effect of a decrease in hydrogen sulphide levels upon unstable copper sulphide deposits, conclusions regarding the likely effects are therefore based upon the general observed behaviour of film formation. This suggests the impacts could be highly variable and dependent upon the state of the existing pipework but that, in general, there would be an initial slow reduction in flaking which would gradually accelerate. The effect of a significant reduction in the hydrogen sulphide specification would therefore be a gradual remediation of the problem in currently affected areas although there would still be a substantial legacy of black dust within pipework to be addressed. In areas with existing flaking deposits which experience an increase in hydrogen sulphide concentration it is anticipated this would lead to flakes growing even more rapidly, flaking more rapidly and producing black dust at an accelerated rate thus worsening the problems affecting appliances.

5.31 The British Gas Research and Technology work also provides some further information as to why only some properties seem to be affected by sulphidation, even in heavily affected areas. This would appear to be the effect of three factors:
(i) in some properties new carcassing has not acquired a film thickness sufficient to initiate flaking;

(ii) the carcassing may be contaminated with some form of oil or glycol which stabilises the deposit; and/or

(iii) the flakes within the carcassing are not readily transported as the speed of gas flow is insufficient to transport the deposits into the appliance.

5.32 The findings provide a basis for why only some properties are affected and suggest that even were hydrogen sulphide levels to increase substantially there would probably always be some unaffected properties.
6. CONCLUSIONS

6.1 This section draws together the findings of this report and presents the overall conclusions. In particular the section provides an assessment of the appropriateness of the existing hydrogen sulphide specification in gas and examination of the need for any revision to the specification. The section also includes discussion of how the work conducted as part of this further study amends and/or supports the original conclusions of the Interim Report. The conclusions are presented in five subsections relating to:

- safety implications of sulphidation for domestic gas appliances;
- implications of sulphidation chemistry and flaking rates;
- current and future incidences of sulphidation in GB; and
- the gas hydrogen sulphide gas specification.

SAFETY IMPLICATIONS OF SULPHIDATION FOR DOMESTIC APPLIANCES

6.2 The Interim Report identified 5 mechanisms by which hydrogen sulphide in gas can directly and indirectly affect domestic gas appliances but concluded none of the effects of hydrogen sulphide upon appliances should in isolation result in development of a hazardous situation:

- incomplete combustion and inadequate fluing are potentially lethal in combination, but the former alone should not cause a major safety problem;
- let-by of gas from valves is highly undesirable, but on modern appliances should not result in a fire or explosion risk unless other components also fail;
- corrosion of glass fronted fires is principally an aesthetic problem;
• corrosion of flues reducing their efficiency (resulting from the presence of acid flue components to which hydrogen sulphide is a small contributor) is unlikely to result in serious safety consequences; and,

• failure of copper piping due to sulphidation corrosion is not considered at all likely.

6.3 The further work presented in this study broadly supports these conclusions but has identified a number of additional mechanisms by which high hydrogen sulphide concentrations or the secondary production of copper sulphide (black dust) can affect appliances. Most notable amongst these are reports of exceptional amounts of deposits in pipework significantly reducing gas flow and leading to undergassing of appliances. This has the potential to result in the appliance flame becoming unstable and going out. For appliances which have neither pilots nor flame failure safeguards, such as some cookers and gas fires, this will result in a release of gas. In properties in which on-line filters have been fitted and are not serviced with sufficient regularity this is a particular problem. There is also concern that undergassing of an appliance could affect the buoyancy of the combustion products. In combination with inadequate fluing those combustion products could spill into the room containing the appliance, with potentially hazardous consequences.

6.4 Where substantial quantities of deposits have been observed within carcassing a proportion of these may be originating from the local distribution system and are being transported into the property through the meter. The extent of carcassing contamination as a result of transport of materials from the local distribution system is not known. In the only extensive survey of pipework which has been undertaken (British Gas Research and Technology, 1997) the deposits were predominantly identified as copper sulphide and other analysis of deposits have similarly demonstrated the presence of copper. It is therefore concluded that where there is a rapid build-up of substantial deposits within carcassing this is unlikely to be only as a result of sulphidation of the copper. The overwhelming evidence however indicates a significant proportion of incidents of contaminated appliances are as a result of copper corrosion.

6.5 In the survey of local authorities conducted as part of this study a high proportion of the returned questionnaires that reported appliances affected by black dust also reported secondary symptoms, for example sooting, headaches etc. However, caution is needed in the interpretation of the local authority survey data as: no quantitative
results were obtained; no information from unaffected premises were obtained; and it
did not take into account incidents which may have been the result of other appliance
defects. The results do, however, provide further evidence of the nature and severity
of the current problems.

6.6 Twenty two local authorities reported experiencing sulphidation problems. Of these
eighty two per cent of authorities reported at least one incident of appliances burning
with an uneven flame. Nine per cent of the authorities experiencing sulphidation
problems reported at least one incident of soot formation above gas fire radiants with
householders experiencing headaches and nausea, while 4.5 per cent reported at least
one incident of soot formation above gas fire radiants alone. However, 14 per cent of
authorities reported at least one incident of householders experiencing headaches and
nausea without signs of soot formation above gas fire radiants. No information has,
however, been obtained from premises where gas fires are unaffected by sulphidation,
to enable comparison with data gathered here.

6.7 Seventy three per cent of local authorities in the survey also report experiencing at
least one incident with boiler control valves contaminated with black dust, with 32 per
cent reporting at least one incident where there was leakage of gas past the valve. Of
these, one authority reported at least one incident of the smell of gas, while another
authority reported at least one incident of excess noise from the boiler. This report
has discussed one incident of an explosion attributed to gas leaking through a safety
valve contaminated with solid material. The Interim Report discussed another which
resulted in a minor injury. In both, the solid materials contained a proportion of
copper sulphide scale.

6.8 The Interim Report concluded that copper sulphide deposits within gas appliances
may have significant safety implications for gas appliances. Since release of this
report the HSE have provided the following information: HSE would consider that
sulphidation would have significant safety implications if it lead to incidents reported
under the Reporting of Injuries, Diseases and Dangerous Occurrences Regulations
(RIDDOR) 1995. No reliable data are available from which to assess the number of
serious incidents arising from black dust contamination of appliances. However, HSE
have advised WS Atkins that there have been no reports of fatal or non-fatal incidents
reported under RIDDOR which can be attributed to sulphidation. Similarly, HSE
have advised that there have been no reports of dangerous gas appliances caused by
sulphidation reported under RIDDOR. Therefore, the hazard from sulphidation does
not appear to have significant safety implications as defined by HSE.
6.9 The level of risk required before measures should be adopted to mitigate the risk is clearly a matter of degree and interpretation, which are policy decisions for the HSE. The Terms of Reference for this report specifically exclude providing policy advice or recommendations to the HSE. This report, and the confidential previous draft, will nevertheless clearly contribute into this policy making process.

IMPLICATIONS OF SULPHIDATION CHEMISTRY AND FLAKING RATES

Polysulphide mechanism

6.10 The Interim Report included a detailed literature review of the reaction chemistry between copper and hydrogen sulphide and determined the principal factors in accelerating the rate of copper sulphide deposits and flaking. It highlighted the role of oxygen, water (either as an oxygen carrier or a reaction medium) and hydrogen sulphide as the principal reagents in the sulphidation reaction with minor roles for mercaptans and possibly carbon dioxide. The review also highlighted a suggested alternative mechanism for sulphidation, via a polysulphide intermediate, generated by the reaction of mercaptans, oxygen and hydrogen sulphide in a liquid medium.

6.11 The possible polysulphide mechanism is important as some techniques to remove hydrogen sulphide from gas may increase concentrations of reactive polysulphides. These could, under certain conditions, accelerate the sulphidation reaction. If the mechanism was proven some techniques to reduce hydrogen sulphide concentrations could therefore inadvertently worsen the copper corrosion. Section 5 concluded that despite sparse information concerning the role of polysulphides in the sulphidation reaction adequate studies producing sufficiently consistent conclusions are available to construct a reasonably confident assessment of the role of polysulphides in the production of copper (I) sulphide within domestic gas carrier piping. On the basis of the evidence it was concluded overall that: at the concentrations of hydrogen sulphide permitted in the natural gas supply in GB the polysulphide reaction mechanism, is not a significant route for copper sulphidation. In addition, it appears that the presence of amines in the natural gas supply does not increase the rate of sulphidation.

6.12 The implication of this conclusion is that gas treatment techniques which reduce hydrogen sulphide concentrations will not lead to an increase in sulphidation through a secondary polysulphide intermediate. Furthermore, all other evidence of sulphidation in GB indicates that sulphidation occurrences will be reduced by a reduction in hydrogen sulphide concentrations.
Section 5 included a review of the mechanism for copper sulphide flaking building upon information within the Interim Report. This identified that deposits of copper sulphide formed on copper pipework throughout GB including those areas which are not experiencing widespread problems with black dust and where substantial but stable deposits have been identified. Information from British Gas Research and Technology (1997) indicate that these stable deposits occur where the hydrogen sulphide concentration is less than about 0.4 mg m\(^3\). This is since under these conditions crystal growth is slow and the lattice contains few irregularities. The research also indicated that the existing stable deposits of copper sulphide in southern England grown under these conditions would become destabilised and begin flaking were they exposed to higher hydrogen sulphide concentrations in the future. The substantial deposits currently attached to pipework would therefore potentially become mobilised if exposed to more sour gas from the St Fergus, Teesside and Barrow terminals.

The research concluded that the impact upon flaking rates of reducing hydrogen sulphide concentration in areas in which deposits are presently flaking will be highly variable but, in general, there would be an initial slow reduction in flaking which would gradually accelerate. The effect of a significant reduction in the hydrogen sulphide specification would therefore be a gradual remediation of the problem in currently affected areas although there would still be a substantial legacy of black dust within pipework to be addressed. The research also indicated in areas with existing flaking deposits which experience an increase in hydrogen sulphide concentration it is anticipated this would lead to flakes growing even more rapidly, flaking more rapidly and producing black dust at an accelerated rate thus worsening the problems affecting appliances.
CURRENT AND FUTURE PROJECTED INCIDENCES OF SULPHIDATION IN GB

Sulphidation incidences

6.15 Both the work presented in this report, and the previous Interim Report, has included considerable research to evaluate the number of affected properties in GB and proportion of total properties in each region. The results of these surveys, together with estimates of regional hydrogen sulphide concentrations, has enabled assessment of how numbers of properties are affected by the hydrogen sulphide concentration in the received gas.

6.16 The Interim Report estimated in excess of 19,000 properties in England and Wales and 21,000 properties in GB as a whole are affected by sulphidation (assuming 2,000 affected properties in Scotland). This report has used information from the British Gas Domestic Gas Survey, a further survey of local authorities and other sources to provide more accurate figures for the number of properties affected. The further work estimates that approximately 33,000 properties are currently affected in England and Wales and a further 5,500 in Scotland (assuming Scotland is affected similarly to Northern Region - a reasonable assumption since both receive gas from St Fergus and hence with the same hydrogen sulphide content. The number of properties affected by sulphidation in GB is therefore estimated to be about 39,000. This represents approximately 0.2 per cent of gas supplied properties in GB, but this total masks considerable regional variations, as demonstrated in Table 6.1.

6.17 There has also been a considerable increase in the number of local authorities reporting problems with households affected by sulphidation both in the survey of District Councils presented in the Interim Report and the survey of Metropolitan Authorities and London Boroughs, the results of which are presented in Section 3. The increase in sulphidation incidences is reflected by an increase in hydrogen sulphide concentrations in gas received by some regions, discussed in the following section.
Table 6.1 - Regional estimates of sulphidation affected properties

<table>
<thead>
<tr>
<th>Region</th>
<th>Percentage premises affected</th>
<th>Potentially affected properties (thousands)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Western</td>
<td>0.7</td>
<td>20</td>
</tr>
<tr>
<td>Northern</td>
<td>0.5</td>
<td>4</td>
</tr>
<tr>
<td>North Eastern</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>North Wales</td>
<td>0.6</td>
<td>1</td>
</tr>
<tr>
<td>South Wales</td>
<td>&lt;0.1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>West Midlands</td>
<td>0.3</td>
<td>5</td>
</tr>
<tr>
<td>East Midlands</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>Eastern</td>
<td>&lt;0.1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>North Thames</td>
<td>&lt;0.1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>South Eastern</td>
<td>&lt;0.1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Southern</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>South Western</td>
<td>&lt;0.1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Scotland</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>Total</td>
<td>0.2</td>
<td>39</td>
</tr>
</tbody>
</table>

Regional hydrogen sulphide concentrations

6.18 Section 4 presents a detailed analysis of past and present hydrogen sulphide concentrations from terminal feeders and information on the proportion of supply to different gas take-offs in order to estimate current regional winter concentrations of hydrogen sulphide in gas. Winter average concentrations have been used since it was concluded wintertime hydrogen sulphide concentrations are the best indicators of the corrosiveness of the gas. The Interim Report used annual average values, Table 6.2 presents a comparison of the results.
Table 6.2: Regional hydrogen sulphide concentrations (mg m⁻³)

<table>
<thead>
<tr>
<th>Region</th>
<th>Winter average (best estimate)</th>
<th>Range</th>
<th>Annual average¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scotland</td>
<td>2.5</td>
<td>2.3 - 2.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Northern</td>
<td>2.5</td>
<td>2.3 - 2.8</td>
<td>2.1</td>
</tr>
<tr>
<td>North West</td>
<td>3.0</td>
<td>2.8 - 3.5</td>
<td>2.5</td>
</tr>
<tr>
<td>West Midlands</td>
<td>Large regional variation</td>
<td>0.8 - 3.5</td>
<td>2.5</td>
</tr>
<tr>
<td>East Midlands</td>
<td>Large regional variation</td>
<td>0.2 - 2.8</td>
<td>0.5</td>
</tr>
<tr>
<td>North Wales</td>
<td>3.0</td>
<td>2.8 - 3.5</td>
<td>2.5</td>
</tr>
<tr>
<td>South Wales</td>
<td>1.0</td>
<td>0.8 - 1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>South Eastern</td>
<td>0.5</td>
<td>0.4 - 0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Southern</td>
<td>0.7</td>
<td>0.5 - 0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Eastern</td>
<td>0.5</td>
<td>0.4 - 0.6</td>
<td>No data</td>
</tr>
<tr>
<td>North East</td>
<td>Large regional variations</td>
<td>0.2 - 2.8</td>
<td>0.2</td>
</tr>
<tr>
<td>South West</td>
<td>1.0</td>
<td>0.8 - 1.3</td>
<td>0.8</td>
</tr>
<tr>
<td>North Thames</td>
<td>0.5</td>
<td>0.4 - 0.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

¹ From Interim Report

6.19 The table demonstrates that, in most regions, the estimates presented in the Interim Report were close to, or within the range of, the estimates determined in the further work presented in this report. Regional variations in the sourness of gas exist in most regions and were identified in the Interim Report. The further work has however suggested that regional variations in the West and East Midlands and North East are so large it is not possible to produce a representative concentration for the region as a whole. This has implications for assessing the effect of sulphidation incidence and hydrogen sulphide concentrations in these regions.
Hydrogen sulphide monitoring

6.20 The hydrogen sulphide concentrations from terminals feeders, upon which the regional estimates are based, are monitored by TransCo at Network Entry Points. Continuous monitors are employed at locations at which hydrogen sulphide levels are appreciable. Spot measurements are used at entry points such as Easington when concentrations of hydrogen sulphide are very low. As part of this study a close examination was undertaken of continuous monitoring records supplied by TransCo. The data contained long gaps in the time series and numerous spurious measurements. Concentrations as high as 5.00 mg m\(^{-3}\) were shown but no exceedences of the specification. This is very surprising given the fact that measurements were reported to two decimal places.

6.21 The inconsistencies in the continuous data record strongly suggest the data are of poor quality and quality assurance and control procedures are inadequate. The reliability of measurements upon which a number of important conclusions of this study are based is therefore questionable. It has also not been possible to obtain recent data for Lupton or Teesside from TransCo. The Interim Report concluded that the current procedures, monitoring and information available to ensure the concentration of hydrogen sulphide in gas remains within specification are inadequate. The evidence of this report supports these conclusions and suggests procedures for monitoring and assessing hydrogen sulphide levels need to be reconsidered to ensure that not only out of specification gas does not enter the NTS but also adequate records are kept.

Regional sulphidation incidences and hydrogen sulphide concentrations

6.22 By combining information on regional incidences of properties affected by sulphidation and regional hydrogen sulphide concentrations (where gas supply to a region is reasonably homogeneous) it is possible to assess how the sourness of gas effects the number of properties affected by sulphidation, as shown in Figure 6.1.
6.23 Figure 6.1 demonstrates very clearly that:

- below 1.0 mg m\(^3\) hydrogen sulphide sulphidation incidences are extremely low, less than 0.05 per cent; and

- in those regions receiving St Fergus gas or St Fergus and Barrow gas with a hydrogen sulphide content of above 2.0 mg m\(^3\) sulphidation incidences are much more common, up to 0.75 per cent of properties.

6.24 Prior to 1991 relatively few authorities reported experiencing problems with black dust. At this time hydrogen sulphide concentrations in St Fergus gas were about 1.0 mg m\(^3\) but Barrow gas concentrations were much higher, about 3.5 mg m\(^3\). This supports the evidence that concentrations greater than 1.0 mg m\(^3\) have a significant corrosive effect.

6.25 Figure 6.1 does not provide any evidence of the nature of the relationship between sulphidation incidences at hydrogen sulphide concentrations between about 1.0 and 2.0 mg m\(^3\). Evidence from the Interim Report indicated an logarithmic relationship between sulphidation incidences and hydrogen sulphide concentration. However, this conclusion was based upon data from regions in which variations in the origin of the supplied gas confound the relationship. The new analysis presented in this report
suggests a linear relationship between incidences of sulphidation and gas sourness to be most likely although there is uncertainty in this conclusion. Understanding the relationship is important since it enables projection of how the sulphidation problem may develop in the future as shown in Figure 6.2.

**Figure 6.2 - Linear plot of hydrogen sulphide concentration and incidences of sulphidation**

![Graph showing linear relationship between hydrogen sulphide concentration and percentage of affected properties. The equation of the line is y = 362.1x + 0.6634 and R² = 0.9499.]

6.26 Figure 6.2 shows how sulphidation incidences will increase with hydrogen sulphide concentrations assuming a linear relationship. The R² value of 0.95 shows a strong linear relationship. The plot assumes both a linear relationship between 1.0 and 3.0 mg m⁻³ hydrogen sulphide but also that the linear relationship will continue above this concentration - this is highly uncertain. If the assumption is correct the figure suggests that were the 5.0 mg m⁻³ specification to be attained approximately 1 to 1.5 per cent of properties in each region would be affected. This is considerably less than the prediction in the conclusions of the Interim Report which was based upon a logarithmic relationship and concluded as a result of gas hydrogen sulphide concentration attaining the existing specification every property receiving gas of this sourness would be affected by sulphidation.
Using future estimated regional hydrogen sulphide concentrations for 2005 (Section 4) together with a linear hydrogen sulphide concentration/sulphidation incidences relationship the growth in the number of affected properties in GB has been estimated. Three scenarios have been produced High, Medium and Low reflecting the High, Medium and Low terminal feeder projections and possible changes in gas supply within GB. It is stressed that these estimates contain considerable uncertainty and are provided for illustrative purposes to suggest how the problem may develop, undue confidence should not be attached to them. The projected increases in occurrences to 2005 are shown in Figure 6.3.

Figure 6.3 shows the estimated 39,000 properties that are currently affected by sulphidation. By 2005 the most optimistic scenario suggests this will have increased by about 20 per cent to 50,000 properties, the biggest increases being in the East and West Midlands. The Medium Scenario is considered the most likely and suggests by 2005 about 70,000 properties will be affected. If the High Scenario is followed this is estimated to be approaching 100,000 properties affected nationally including increasing numbers in southern England. These estimates are based upon a large number of assumptions detailed throughout the report. The High Scenario is not a worse-case. A worse-case scenario would involve a significant increase in hydrogen sulphide from the St Fergus terminal and supply of gas from southern basin terminals predominately for export via the Interconnector. This would allow penetration of considerably more sour gas from Barrow, St Fergus and Teesside to regions in southern England during the winter. In the medium term, by 2005, this is not considered likely, although in the longer term it is possible.
6.29 These estimates are lower than those in the Interim Report which estimated in excess of 120,000 affected properties by 2002 and were based upon a logarithmic relationship between sulphidation incidences and hydrogen sulphide concentration.

**GAS HYDROGEN SULPHIDE SPECIFICATION**

6.30 This study together with the work presented in the Interim Report have provided a substantial body of information concerning the cause, nature, effects including safety implications, and potential growth of the sulphidation issue in GB. Furthermore, on the whole the results have been sufficiently consistent that it is possible to be reasonably confident of the conclusions drawn. Key findings of the two studies are that:

- black dust deposits within gas fire injectors and central heating boiler pilots and valves result from a reaction between hydrogen sulphide, trace oxygen and/or water and copper. This reaction is accelerated by the hydrogen sulphide content of the gas, temperature and high gas flow rates;
the proposed polysulphide mechanism for the reaction is not significant under conditions within domestic pipework and amine treatment processes to remove hydrogen sulphide will therefore not exacerbate the corrosion rate;

under ambient conditions stable deposits of copper sulphide appear to form at concentrations of hydrogen sulphide of about 0.35 mg m$^{-3}$. However, a very small percentage of properties receiving gas up to 1.0 mg m$^{-3}$ hydrogen sulphide experience problems with sulphidation;

areas receiving gas with an excess of about 2.0 mg m$^{-3}$ hydrogen sulphide experience much more widespread occurrences of affected properties;

hydrogen sulphide concentrations in gas from the St Fergus terminal are anticipated to continue to increase and in gas from Barrow terminal to remain high. This will accelerate the flaking rate of copper sulphide in areas of GB currently experiencing widespread sulphidation problems;

in the future more sour gas from St Fergus, Barrow and Teesside will probably supply most of the West and East Midlands and may penetrate into Southern England during the winter causing the substantial and widespread stable copper sulphide deposits in this area to begin to flake;

thirty-nine thousand properties are currently affected by sulphidation in GB. Furthermore by 2005 this is anticipated to have increased to between 50,000 and about 100,000 properties (best estimate 70,000) depending upon how gas supply and hydrogen sulphide concentrations change;

copper sulphide deposits within gas valves contribute to, and may cause, let-by of gas. In two incidents where explosions have resulted, copper sulphide formed minor proportions of the black deposits found in the gas valves; and

copper sulphide deposits within gas fire multi-port injectors result in poor combustion, with increased concentrations of carbon monoxide in the combustion products. If this is combined with an inadequate flue, where spillage of combustion products occur, then the hazard may be increased.

6.31 To summarise, the black dust problem is currently geographically widespread, affects an appreciable number of properties and is very likely to get significantly worse. The
greater the number of future affected properties the larger will be the number of incidents resulting from copper sulphide contamination of appliances.

6.32 If the HSE consider the risk from sulphidation to be significant, and propose to remediate the situation, there will need to be a significant reduction in the hydrogen sulphide specification of gas. In order to be confident hydrogen sulphide reacting with copper will only produce stable copper sulphide deposits a maximum specification of 0.4 mg m\(^{-3}\) hydrogen sulphide would be required. However, there is sufficient evidence to suggest that a specification of 1.0 mg m\(^{-3}\) would significantly reduce the number of affected properties and consequently the number of incidents. A specification of 2.0 mg m\(^{-3}\) will not significantly affect existing levels of sulphidation whilst a specification of greater than 2.0 mg m\(^{-3}\) will have a marginal effect upon current numbers of affected properties and small effect upon the projected future growth of the problem depending upon the level of the specification.

6.33 Assuming the linear relationship between sulphidation incidences and hydrogen sulphide concentration, Figure 6.4 shows how a change in the specification may alter the number of affected properties, assuming a change in the specification does not have a significant effect upon future gas supply to GB. Since the cost of hydrogen sulphide removal is not significant compared with other costs of extraction, transport, treatment and distribution this assumption is considered reasonable. These data are based upon how modifications to the specifications will affect the level of hydrogen sulphide in gas supplied to different parts of the UK. The graph is therefore not linear as the distribution of affected properties is not homogeneous.

6.34 Figure 6.4 suggests a specification of 2.5 mg m\(^{-3}\) would result in no further worsening of the sulphidation problem within GB (that is about 39,000 properties would be affected). This assumes gas of this specification is not supplied to southern England; and that terminals currently supplying gas with concentrations below this specification do not increase the sourness of the gas they supply by conducting less treatment, as would be possible at Teesside and Bacton.
6.35 If the HSE consider the severity of the existing sulphidation problem to be unacceptable, it will be necessary to reduce the hydrogen sulphide specification to below 2.5 mg m\(^{-3}\). To reduce sulphidation incidences to levels experienced in southern England a specification of below 1.0 mg m\(^{-3}\) is required. As part of a survey of gas terminal operators the HSE sought information regarding the implications of a reduction in specification to this level. The survey results suggest a reduction of the specification to 1.0 mg m\(^{-3}\) would largely unaffuct southern basin terminals but additional treatment facilities would be required at the St Fergus, Barrow and possibly Teesside terminals which currently supply the most sour gas to GB. Gas from St Fergus and Barrow is currently causing the major sulphidation problems in GB and it is these terminals which would bear the greatest financial cost, if removal of hydrogen sulphide were to occur at terminals, although the additional costs per m\(^3\) of gas supplied is small.

6.36 Overall the evidence suggests that a reduction in the hydrogen sulphide specification to 1.0 mg m\(^{-3}\) would prevent the current substantial problems from worsening and would eventually reduce the number of affected properties. A reduction of hydrogen sulphide concentration to this level would not prevent mobile sulphide scale from forming, this would require the specification to be reduced to about 0.4 mg m\(^{-3}\). Rather, a revised specification of 1.0 mg m\(^{-3}\) would significantly reduce the effects of
sulphidation. The costs involved in treating gas to attain this specification would be borne by the terminal operators.

6.37 Even with the proposed revision of the hydrogen sulphide specification there will be an existing legacy of the current widespread black dust problems in GB. Large numbers of properties contain unstable deposits which need to be stabilised or black dust within pipework to be removed. Awareness of the sulphidation problem within the gas industry needs to be improved together with knowledge of appropriate remediation techniques. In addressing future problems CORGI will undoubtedly have a significant role and should be consulted at an early opportunity to discuss how members can be made more aware of the issue. In addition, there is a clear need for a system to stabilise deposits in situ.

6.38 The results of this study, and those presented in the Interim Report, have explained the causes and implications of the black dust problem, and provided evidence of its anticipated growth. If the HSE consider the existing extensive problems represents hazards which are sufficient to warrant action, two specific measures should be particularly effective:

(i) a revision of the hydrogen sulphide specification for gas to 1.0 mg m$^{-3}$ or below; and

(ii) a change in the specification for gas appliances to prevent the use of copper flashed Bundy Tubing in new gas appliances.

6.39 The second of these measures would be enacted by the DTI which have responsibility in this area. This report has also highlighted concerns regarding the quality of hydrogen sulphide monitoring data and indicated current arrangements need to be reassessed. In addition, wider publicity throughout the gas industry of the causes, effects and safety implications of the black dust and remediation options is clearly advantageous, an issue this report should help in part to address. Finally, whatever the ultimate decision of the HSE concerning the course of action to be pursued regarding sulphidation, there is clearly a need for prompt decision making to bring an end to the present uncertainty affecting the industry.
7. REFERENCES

British Gas Research and Technology (1997)

Copper sulphide film formation on copper gas carcassing pipework, Confidential Report GRC/96/638, Loughborough

HSE (1996)

Executive summary: Safety aspects of the effects of hydrogen sulphide in natural gas, HSE, Bootle

HSE (1998)


HSE (1997)

Personal Communication

Lyle, F F (1993a)

An experimental evaluation of copper corrosion by constituents of natural gas. Gas Research Institute Report GRI-93/0122

Lyle, F F (1993b)

Gas composition effects on interior gas distribution systems. Gas Research Institute Report GRI-93/0418

McGrath, L and Prebble, K A (1972)


Pyburn, C, Cahill, F P and Lennox, R K (1978)

TransCo (1996)

Ten year statement, 1995, British Gas TransCo

Trans Co (1997)

Ten year statement, 1996, British Gas TransCo,

WS Atkins (1996)

Safety aspects of the effects of hydrogen sulphide concentrations in natural gas. Confidential report to the HSE.

Wood Mackenzie (1996)

North Sea oil and gas service, Pipelines and terminals, Wood Mackenzie Consultants Ltd, Edinburgh

Yan, H (1994)

Reaction of copper with low concentration of oxygen and sulphur compounds. Ph D Thesis, University of Surrey.
APPENDIX A

Executive Summary - Interim Report
Executive Summary

Summary

Principal findings

- This report assesses the safety implications for domestic appliances of hydrogen sulphide in natural gas; and in particular evaluates the appropriateness of the specification of hydrogen sulphide in natural gas.

- Hydrogen sulphide affects domestic appliances by either corrosion of piping, or components; or production of copper sulphide deposits. These deposits flake and are carried into the appliance where they can block burners causing incomplete combustion or can be deposited in gas valves causing leakage of gas. Neither of these effects should however in isolation result in a hazardous situation developing.

- Approximately 21,000 properties in Great Britain (GB) are estimated to be affected by the presence of hydrogen sulphide in gas. Over 90 per cent of these problems are estimated to be associated with blockage of burners and about five per cent with central heating boiler valve failure. Lack of awareness of the phenomenon may however mask the full extent of the problem.

- Those regions receiving gas with the highest hydrogen sulphide concentration in GB, the North West and North Wales (annual average 2.5 mg m⁻³), have the highest proportion of properties affected by sulphidation (about 0.7 per cent). By 2002, these regions and others are predicted to receive gas with a hydrogen sulphide concentration of about 3.5 mg m⁻³ resulting in an estimated 10 per cent of properties being affected. If in the future some regions receive gas up to the maximum hydrogen sulphide concentration of 5 mg m⁻³ virtually all properties receiving this gas are likely to be affected.

- The proportion of more sour gas jointly supplied by the St Fergus, Teesside and Barrow terminals will increase in the future. This will result in regions of Southern England, currently generally unaffected by sulphidation, being supplied with more sour gas which is likely to increase occurrences of sulphidation.

- Although the risk of a hazardous situation caused by copper sulphide deposits in gas appliances is small, the scale of the problem is such that the risk of a particular combination of circumstances resulting in a dangerous situation occurring may not be insignificant. It will also become greater in the future if the proportion of properties affected by sulphidation increases as projected.
Principal recommendations

In order to reduce the risk due to the presence of hydrogen sulphide in gas it is recommended that:

⇒ consideration should be given to reducing the hydrogen sulphide specification to between 1.0 to 1.5 mg m$^{-3}$, the precise level for which will be dependant upon the results of further work to be commissioned by the Health and Safety Executive (HSE);

⇒ the use of copper flashed carrier tubing in new appliances is discontinued subject to the satisfactory completion of tests to identify a replacement;

⇒ for existing appliances with copper flashed tubing frequently affected by copper sulphide deposits, consideration is given by manufacturers and service companies to replacement of gas carrier piping with non-copper flashed alternatives;

⇒ British Gas Service recommence development of their pipe treatment remediation technique; and,

⇒ recommendations for further work are supported by funding from the HSE.
Introduction

This report has been produced by WS Atkins Environment for the HSE to assess the safety implications for domestic appliances of hydrogen sulphide in natural gas. In particular, to ascertain the appropriateness of the maximum hydrogen sulphide specification for natural gas and to propose a revision to the specification if necessary.

Hydrogen sulphide is a naturally occurring impurity in natural gas the concentration of which is principally dependent upon the nature of the gas field. Hydrogen sulphide affects domestic appliances both through the primary corrosion of components; and production of copper sulphide by reaction (sulphidation) with copper carcassing and copper components within appliances. The rate of copper sulphide production and stability of the deposits are dependent upon a number of factors including:

⇒ the hydrogen sulphide concentration in the gas;
⇒ the presence of trace amounts of oxygen either naturally present in the gas, introduced in the blending of gas to attain acceptable gas quality, or dissolved in water present within the gas due to seepage into the mains or from water sealed gas holders;
⇒ the flow rate of the gas and presence of bends in the piping; and,
⇒ the temperature of the copper.

It has been shown that under ambient conditions sulphidation occurs at concentrations below 0.5 mg m\(^{-3}\), although copper sulphide deposits at these concentrations are generally stable due to their slow rate of formation. Unstable copper sulphide deposits flake from the surface of the pipe, become entrained in the gas stream and are carried into the appliance where they can affect the operation of a number of components in particular burners and gas valves. This report examines in detail the effects of hydrogen sulphide corrosion and deposition of copper sulphide within gas appliances including detailed assessment of:

⇒ the nature and extent of the effects of hydrogen sulphide concentrations upon domestic gas appliances in GB, and international knowledge and experience of the problem;
⇒ the status and trends in hydrogen sulphide concentrations in natural gas within GB, prediction of future concentrations and the likely impact upon the extent of properties affected by sulphidation;
⇒ the reaction between hydrogen sulphide and copper and important catalysts in the process; and,
⇒ the effects and safety implications of hydrogen sulphide in gas upon domestic appliances.

The conclusion to the report draws together the principal findings and produces recommendations:

⇒ to improve the safety of gas appliances affected by hydrogen sulphide;
⇒ regarding the appropriateness of the existing specification for hydrogen sulphide in gas and procedures to ensure this specification is met; and,
⇒ for further work to improve knowledge of the problem and enhance the confidence in the findings.
The information contained within this report is based upon that provided for a confidential report produced by WS Atkins Environment for the HSE. Consequently, some of the sources and detail of the information within this report have not been identified in order to avoid release of commercially sensitive information.

Effects of Hydrogen Sulphide Upon Gas Appliances

There are five categories of possible effects upon domestic appliances to which hydrogen sulphide in gas is a cause or contributory factor:

\[ \Rightarrow \text{partial or complete blockage by copper sulphide deposits of components within the burner, possibly causing incomplete combustion of the gas and generation of products of incomplete combustion (carbon monoxide and unburned gas);} \]
\[ \Rightarrow \text{deposition of copper sulphide on gas valve-seatings causing possible leakage of gas with the potential for explosion and subsequent fire;} \]
\[ \Rightarrow \text{corrosion of glass-fronted fires possibly affecting their structural integrity;} \]
\[ \Rightarrow \text{corrosion of flues or draft-diverters reducing the efficiency of their operation and potentially leading to a build-up of carbon monoxide and other products of incomplete combustion; and,} \]
\[ \Rightarrow \text{corrosion of copper piping resulting in failure of the pipe and release of gas.} \]

Approximately 21,000 properties in GB are estimated to be affected by the presence of hydrogen sulphide in gas. It is estimated over 90 per cent of these problems involve partial or complete blockage of burner jets causing incomplete combustion. Most of these blockages are of multi-port injectors in gas fires due to their small orifices. Fires fitted in combination with back boiler units are particularly susceptible due to the high gas flow through the appliance. Appliances containing copper flashed gas carrier are also widely affected due to the elevated temperature of the copper within the appliance accelerating the rate of production of copper sulphide.

Cookers are not generally affected by blocked burners since the burner unit has a much larger diameter than in fires and the rate at which gas enters the appliances is not generally sufficient to entrain the flakes in the gas stream. Where burners or multi-port injectors in appliances do become blocked the products of incomplete combustion should not be created in such high concentrations as to cause a serious safety problem, unless combined with inadequate fluing.

Deposition of copper sulphide on gas valves resulting in let-by of gas is believed to affect about 650 appliances nationally - although there is large uncertainty in this estimate. This is considered to be the most serious problem affecting gas appliances. However, on modern appliances leakage of gas should not result in a fire or explosive risk unless other components fail in combination. One accident has been reported due to gas valve failure resulting from solid material on the valve seating to which sulphidation was a contributory factor.
The production of copper sulphide flakes results in a thinning of the wall of the copper carcassing raising concerns regarding the possibility of corrosion leading to failure of the piping. This is not considered likely in view of the low rate of copper sulphide flaking compared to the thickness of the carcassing.

Corrosion of glass-fronted fires is principally an aesthetic problem as failure of the glass is considered unlikely. Corrosion of flues and draft diverters on warm air units are infrequent occurrences caused by acid flue products originating from a number of sources including nitrogen oxides, chlorofluorocarbons and sulphuric acid to which hydrogen sulphide in gas contributes only a small amount.

The primary effects of hydrogen sulphide and the secondary production of copper sulphide deposited within gas appliances are unlikely to result in development of a hazardous situation. The large number of occurrences however significantly affects the overall risk that a particular combination of factors will result in a serious incident. The overall risk given the scale of the problem nationally is therefore significant, and effects of hydrogen sulphide in gas therefore have significant safety implications, but do not currently represent a major safety issue for gas appliances.

Internationally problems due to sulphidation have been reported in Canada and the United States of America, including failure of a domestic copper gas pipe. Anecdotal reports of problems have occurred in other countries including France and Italy but information is difficult to obtain due to the general lack of understanding or knowledge of the problem. Use of copper carcassing is not widespread globally and this is likely to affect significantly the number of countries reporting problems. Hydrogen sulphide concentrations and specifications in Western Europe are broadly similar.

**Hydrogen Sulphide Concentrations and Sulphidation Incidents in Great Britain**

**Current hydrogen sulphide concentrations in natural gas and incidence of sulphidation**

The existing maximum specification for hydrogen sulphide in gas of 5 mg m$^{-3}$ (3.3 ppmv) was established in the Gas Quality Regulations, 1983. In the past, concentrations of hydrogen sulphide in natural gas supplied to GB have been approximately an order of magnitude below this concentration. However, in recent years more sour gas from the Barrow terminal supplied predominantly from the South Morecambe Bay field has come on-stream; and the hydrogen sulphide concentration in gas from the St Fergus terminal has steadily increased (Figure 1). North West England and North Wales now receive gas with an annual average concentration of hydrogen sulphide of 2.5 mg m$^{-3}$ and during periods of peak demand, receive gas with a hydrogen sulphide content of up to about 4 mg m$^{-3}$. 
Data on occurrences of sulphidation which have been derived from data provided by district councils in England and Wales, combined with regional hydrogen sulphide concentrations, demonstrate that those regions of GB which receive the most sour gas are also those which report the highest number of incidents of properties affected by sulphidation (Figure 2).

The distribution of affected properties shows a distinct north - south divide with the North of England, North West England, North Wales and Scotland (for which no quantitative data are available) experiencing the most widespread problems. These regions receive gas from St Fergus and Barrow terminals which supply more sour gas (Figure 1). The infrequent occurrence of sulphidation in district councils south of the Midlands is because these regions are predominantly supplied with sweeter gas from the Southern Basin terminals.

Within different gas regions the proportion of properties affected by sulphidation increases significantly when the concentration of hydrogen sulphide exceeds about 1.5 mg m$^{-3}$ (1.0 ppmv) (Figure 2). This suggests that although sulphidation occurs at concentrations below 0.5 mg m$^{-3}$, appliances are not widely affected until the annual average concentration of hydrogen sulphide in the gas is around 1.5 mg m$^{-3}$. 
Figure 2: Regional hydrogen sulphide concentration and sulphidation incidents

Source: Derived from data provided by TransCo, 1996b and a questionnaire survey originally issued by the Association of District Councils. Regions refer to former British Gas regions.

Future predicted hydrogen sulphide concentrations in natural gas and instances of sulphidation

The future extent of sulphidation occurrences in GB will be dependent upon the hydrogen sulphide concentration in gas from terminal feeders and the proportion of gas from each terminal, both of which are anticipated to alter significantly in the future. Predictions of future hydrogen sulphide concentrations in gas from terminal feeders have been based upon past trends (Figure 1) and therefore contain significant uncertainties. Conservative estimates suggest the hydrogen sulphide concentration in gas from the St Fergus terminal is likely to continue to increase at a rate of about 0.2 mg m\(^{-3}\) a\(^{-1}\). Under this scenario by 2002 the concentration of St Fergus gas is estimated to be 3.5 mg m\(^{-3}\). The hydrogen sulphide concentration of gas from the Barrow terminal is estimated to remain at about 3.5 mg m\(^{-3}\), the median annual average concentration at which the terminal has been operating since 1986, until 2002. Levels of hydrogen sulphide in gas from other terminals are anticipated to remain broadly at current concentrations. The level of hydrogen sulphide from the new Teesside terminal is predicted to be about 2.0 mg m\(^{-3}\). Based upon these predictions, by about 2002/03 gas within GB with the highest concentrations of hydrogen sulphide GB will be supplied from the St Fergus and Barrow terminals to Scotland, Northern England, North West England, North Wales and possibly other areas at about 3.5 mg m\(^{-3}\). From extrapolation of Figure 0.2 it is therefore possible to estimate the proportion of properties in these regions likely to be affected by sulphidation (Figure 3).
**Figure 3: Prediction of the effects of increasing hydrogen sulphide concentrations upon sulphidation incidents**

![Graph showing the prediction of effects of increasing hydrogen sulphide concentrations upon sulphidation incidents.](image)

Source: Derived from data provided by TransCo, 1995b and a questionnaire survey originally issued by the Association of District Councils, 1995

Currently in the most severely affected regions approximately 0.7 per cent of properties are believed to be affected by sulphidation. If, as predicted, concentrations of hydrogen sulphide in these regions increase to 3.5 mg m\(^{-3}\) this is likely to result in an approximate ten-fold increase in the proportion of affected properties. In Scotland, Northern and North Western England and North Wales there are at present over 12,000 premises affected by sulphidation. If the projection is correct, by 2002 this figure is likely to be well in excess of 120,000 properties nationally. With this scale of problem the probability of a hazardous situation developing is significantly greater. Figure 0.3 also shows that if the hydrogen sulphide concentration of gas was allowed to approach the existing specification of 5.0 mg m\(^{-3}\), the effect would be that almost every property in the regions receiving gas with this concentration of hydrogen sulphide would be affected.

The proportion of gas supplied to each gas region from different terminals also has a significant effect upon regional hydrogen sulphide concentrations in GB, due to the wide variations in the sourness of the gas supplied from each facility (Figure 1). In the future, the proportion of GB gas supplied from the St Fergus and Teesside terminals is projected to increase, and the proportion of production from the Southern Basin terminals which supply much sweeter gas will decline by an equivalent amount. The consequence of these changes will be that hydrogen sulphide concentrations in some regions currently supplied with gas predominantly from Southern Basin terminals will increase together with occurrences of sulphidation. This is demonstrated by Figure 4 which shows the past and projected increase in the mass of hydrogen sulphide entering the National Transmission System (NTS) for the Base Price Supply Case.
Safety Aspects of the Effects of Hydrogen Sulphide Concentrations
in Natural Gas - Report of Initial Findings

Under other supply scenarios the proportion of production from the St Fergus terminal increases above that projected for the Base Price Case. By 2003/04, under these scenarios the mass of hydrogen sulphide entering the NTS per year will be 170,000 kg resulting in a higher overall average hydrogen sulphide concentration within GB.

Projected increases in hydrogen sulphide concentrations and the proportion of production from St Fergus terminal are likely to result in a significant increase in the mass and concentration of hydrogen sulphide in gas throughout GB in the future. Furthermore, other effects upon future gas production such as deregulation of the gas supply market and demerger of British Gas may also result in higher hydrogen sulphide concentrations in gas. These predictions suggest that the current problems of sulphidation will become significantly greater and more widespread in the future unless measures are introduced to control the future level of hydrogen sulphide in gas.

**Figure 4: Past and predicted future mass of hydrogen sulphide entering the NTS**

![Graph showing past and predicted future mass of hydrogen sulphide entering the NTS]

a: mass based upon actual field production data and hydrogen sulphide concentrations in terminal feeders;  
b: mass based upon the estimated proportion of production from terminals and actual hydrogen sulphide concentrations in terminal feeders; and,

Source: Derived from data provided by TransCo, 1995b
Recommendations to Reduce the Risk to Appliances from Hydrogen Sulphide in Natural Gas

Revision of the hydrogen sulphide specification of natural gas

Although formation of copper sulphide deposits occurs at hydrogen sulphide concentrations below 0.5 mg m$^{-3}$ in ambient conditions, the pattern of regional occurrences of sulphidation and hydrogen sulphide concentrations in GB suggests that occurrences of appliances affected by sulphidation are very uncommon if the concentration of hydrogen sulphide in gas is below about 1.0 mg m$^{-3}$ (Figure 0.2). **In order to reduce significantly occurrences of sulphidation, a specification of hydrogen sulphide in gas of between 1.0 and 1.5 mg m$^{-3}$ (0.66 to 1.0 ppmv) is appropriate.** The uncertainties in the available data are such that it is not possible at this stage to define a more precise level for the specification and further research has been commissioned by the HSE to address this. There is however a good body of evidence to indicate that the value of the new specification should be in this range.

A revised specification for hydrogen sulphide in gas between 1.0 and 1.5 mg m$^{-3}$ will not prevent all occurrences of sulphidation but should significantly reduce the proportion of affected appliances to below 0.1 per cent of properties, significantly less than the 0.7 per cent currently reporting problems in the most affected regions; and the projected 10 per cent of properties if hydrogen sulphide concentrations increase to 3.5 mg m$^{-3}$ as predicted. With only about 0.1 per cent of properties affected the risk of a serious incident related to sulphidation will be significantly lower.

Amendments to appliance design and servicing

In order to reduce further the risk to appliances and consumers there are a number of additional amendments to appliance design and servicing, and remediation strategies to prevent occurrences which would further reduce incidences and risks.

The presence of copper flashed double walled Bundy tubing has been shown to be an important contributory factor in the extent to which particular designs of appliance are affected by copper sulphide flakes. Discussions with tubing manufacturers has demonstrated that single-walled nickel coated tubing is available and offers the advantages of the enhanced leak security without the accelerated production of copper sulphide. Alternatively single-walled tubing could be substituted if adequate protection against possible pin-hole leaks is adopted by manufacturers. Nickel coated tubing is not presently in use on gas appliances but, assuming the material is shown to be satisfactory, manufacturers are strongly recommended to use nickel coated single-walled Bundy tubing in all new appliances.

Replacement of copper with nickel coated single-walled Bundy tubing in appliances which are frequently affected by blockages of burner jets and gas valve damage should be considered by appliance manufacturers and service companies as a possible remediating solution in some instances.
One consequence of the widespread sulphidation affecting gas piping and appliances within Scotland, Northern and North West England, North Wales and the Midlands, is that there are large amounts of copper sulphide flakes (or deposits imminently about to flake) currently within copper carcassing throughout these regions. These flakes will continue to affect appliances in the future unless the loose flakes are removed and those flakes likely to become imminently detached are fixed to the surface of the pipes. The most effective long-term solution to this problem appears to be offered by the pipe-treatment technique developed by British Gas Service which has shown promising performance in field trials. British Gas Service have stated that they do not intend to test and develop this technique further. British Gas should consider reviewing this decision in light of the increasing incidences of sulphidation.

Use of on-line filters will continue to demonstrate an excellent short-term solution to many instances of appliance contamination caused by sulphidation of copper carcassing. Filters do not however address the cause of the problems but only the effect. In the long-term, reducing the hydrogen sulphide specification, the pipe-remediation system and amendments to appliance design and servicing offer the best solutions to prevent the increased risk due to hydrogen sulphide in gas.
APPENDIX B

Organisations Contacted
TELEPHONE SURVEY CONTACTS

Service Companies

Maclean and Nuttall, Robert Prettie & Co, Heating Spares and Services, Servowarm (Southern, Warrington, and Burton), Gas Firing Services, Butco Heating

Appliance Manufacturers

Baxi Heating, Hepworth Heating (Glow worm), Valor Heating, Johnson & Starley, Potterton Myson, Caradon Ideal, Halstead Boilers, and Vaillant,

Component Manufacturers

Honeywell, SIT and Bundy Tubing

Trade Association and other bodies

society British Gas Industries, CORGI, Association District Councils, Confederation Scottish Local Authorities, Association Metropolitan Authorities and Gas Consumers Council.

Local Authorities

Easington, Glasgow and Middlesbrough
<table>
<thead>
<tr>
<th>Gas region</th>
<th>Authority Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>East Midlands</td>
<td>Leeds</td>
</tr>
<tr>
<td>East Midlands</td>
<td>Sheffield</td>
</tr>
<tr>
<td>Eastern</td>
<td>Waltham Forest</td>
</tr>
<tr>
<td>North Eastern</td>
<td>Barnsley</td>
</tr>
<tr>
<td>North Eastern</td>
<td>Calderdale</td>
</tr>
<tr>
<td>North Eastern</td>
<td>Kirklees</td>
</tr>
<tr>
<td>North Eastern</td>
<td>Wakefield</td>
</tr>
<tr>
<td>North Thames</td>
<td>Corporation of London</td>
</tr>
<tr>
<td>North Thames</td>
<td>Croydon</td>
</tr>
<tr>
<td>North Thames</td>
<td>Ealing</td>
</tr>
<tr>
<td>North Thames</td>
<td>Hillingdon</td>
</tr>
<tr>
<td>North Thames</td>
<td>Hounslow</td>
</tr>
<tr>
<td>North Thames</td>
<td>Islington</td>
</tr>
<tr>
<td>North Thames</td>
<td>Kensington &amp; Chelsea</td>
</tr>
<tr>
<td>North Thames</td>
<td>Lambeth</td>
</tr>
<tr>
<td>North Thames</td>
<td>Lewisham</td>
</tr>
<tr>
<td>North Thames</td>
<td>Richmond upon Thames</td>
</tr>
<tr>
<td>North Thames</td>
<td>Tower Hamlets</td>
</tr>
<tr>
<td>North Thames</td>
<td>Wandsworth</td>
</tr>
<tr>
<td>North Thames</td>
<td>Westminster</td>
</tr>
<tr>
<td>North West</td>
<td>Bolton</td>
</tr>
<tr>
<td>North West</td>
<td>Bury</td>
</tr>
<tr>
<td>North West</td>
<td>Knowsley</td>
</tr>
<tr>
<td>North West</td>
<td>Manchester</td>
</tr>
<tr>
<td>Gas region</td>
<td>Authority Name</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>North West</td>
<td>Oldham</td>
</tr>
<tr>
<td>North West</td>
<td>Rochdale</td>
</tr>
<tr>
<td>North West</td>
<td>Salford</td>
</tr>
<tr>
<td>North West</td>
<td>Sefton</td>
</tr>
<tr>
<td>North West</td>
<td>St Helens</td>
</tr>
<tr>
<td>North West</td>
<td>Stockport</td>
</tr>
<tr>
<td>North West</td>
<td>Trafford</td>
</tr>
<tr>
<td>North West</td>
<td>Wigan</td>
</tr>
<tr>
<td>Northern</td>
<td>Newcastle upon Tyne</td>
</tr>
<tr>
<td>Northern</td>
<td>North Tyneside</td>
</tr>
<tr>
<td>Northern</td>
<td>South Tyneside</td>
</tr>
<tr>
<td>Northern</td>
<td>Sunderland</td>
</tr>
<tr>
<td>South Eastern</td>
<td>Bromley</td>
</tr>
<tr>
<td>South Western</td>
<td>South Gloucestershire</td>
</tr>
<tr>
<td>West Midlands</td>
<td>Birmingham</td>
</tr>
<tr>
<td>West Midlands</td>
<td>Dudley</td>
</tr>
<tr>
<td>West Midlands</td>
<td>Sandwell</td>
</tr>
<tr>
<td>West Midlands</td>
<td>Walsall</td>
</tr>
<tr>
<td>West Midlands</td>
<td>Wolverhampton</td>
</tr>
</tbody>
</table>
APPENDIX C

Survey Questionnaire and Results
Questionnaire on the effects of ‘Black Dust Deposits’ on Domestic Gas Appliances

Please circle the appropriate answer Y (yes), N (no) or DK (don't know) and add N° (number of properties, number of times each year, etc.)

1. Local Authority (LA) name:

2. Contact Name: Tel: ( )

3. How many properties are your LA responsible for? N°: DK

4. How many of these properties have: gas fires? N°: DK gas central heating boilers? No: DK

5. Was the LA aware of the black dust (BD) problem? Y / DK / N

6. Was the LA aware that the BD problem was the result of hydrogen sulphide in natural gas reacting with copper installation pipework Y / DK / N

7. Has the LA experienced problems with black dust? Y / DK / N

If Don’t Know or No, thank you for taking the time to look at this questionnaire, please return to - Chris Ling, WS Atkins Environment, Woodcote Grove, Ashley Road, Epsom Surrey, KT18 5BW.

8. For gas fires, has the BD produced different heights of flames on burner (uneven flames)? Y / DK / N N°:

If Don't Know or No, go to question 11.

9. Have occupiers complained of headaches and/or nausea? Y / DK / N N°:

10. Has there been any sign of excess sooting (spillage) above the radiants, within the flue path of the fire or on the wall above the fire? Y / DK / N N°:
11. For gas central heating boilers, has the BD:

(a) accumulated in control valves? Y / DK / N  N°:

(b) allowed gas to leak past the control valves? Y / DK / N  N°:

If Don’t Know or No to both 11 (a) and 11 (b) go to question 13.

12. Has the occupier complained of:

(a) the smell of gas? Y / DK / N  N°:

(b) excess noise (bangs) from the boiler? Y / DK / N  N°:

13. When were the problems with BD first noticed?

Year:  Month (if known):

14. Are some particular locations more affected than others? Y / DK / N

15. Over the last 12 months has the severity of the problem:

Decreased?

16. How many properties are affected by BD? N°:

17. On average, how many times each year are:

(a) properties visited for general maintenance? N°:

(b) properties visited to remove black dust? N°:

18. Have any of the following methods been used in an attempt to solve the problem:

(a) filters installed in gas supply before appliances? Y / DK / N  N°:

(b) pipework replacement? Y / DK / N  N°:

(c) internal coating of pipework? Y / DK / N  N°:

(d) others (please specify)? Y / DK / N  N°:

If yes to any part of question 18 go to question 19, otherwise go to question 21.

19. Following remedial actions, how many times each year on average are premises now visited where:

(a) filters were installed in the gas supply before appliances? N°:

(b) pipework was replaced? N°:
(c) pipework was internally coated? N°:

(d) another method was used? N°:

20. If filters have been installed, how many times each year do they need cleaning? N°:

21. Have there been any incidents where the occupiers safety has been put at risk? Y / DK / N N°:

22. Have any occupiers attempted to carry out remedial work themselves? Y / DK / N N°:

If Yes to questions 21 or 22, please attach information on the incident, or attempts at remedial work.

23. Would you be willing to provide additional information about any of your answers, if contacted? Y / N

Thank you for completing this questionnaire. Please return it to -

Chris Ling, WS Atkins Environment, Woodcote Grove, Ashley Road, Epsom, Surrey, KT18 5BW
<table>
<thead>
<tr>
<th>Gas region</th>
<th>Authority</th>
<th>Aware of problem</th>
<th>Experienced problem</th>
<th>Initial problems</th>
<th>Aware of reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>East Midlands</td>
<td>1</td>
<td>Yes</td>
<td>No</td>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td>East Midlands</td>
<td>2</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>Eastern</td>
<td>3</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>North Eastern</td>
<td>4</td>
<td>Yes</td>
<td>Yes</td>
<td>1995</td>
<td>Yes</td>
</tr>
<tr>
<td>North Eastern</td>
<td>5</td>
<td>Yes</td>
<td>Yes</td>
<td>1995</td>
<td>Yes</td>
</tr>
<tr>
<td>North Eastern</td>
<td>6</td>
<td>Yes</td>
<td>Yes</td>
<td>1994</td>
<td>Yes</td>
</tr>
<tr>
<td>North Eastern</td>
<td>7</td>
<td>Yes</td>
<td>Yes</td>
<td>1991</td>
<td>Yes</td>
</tr>
<tr>
<td>North Eastern</td>
<td>8</td>
<td>No</td>
<td>Yes</td>
<td>1995</td>
<td>No</td>
</tr>
<tr>
<td>North Thames</td>
<td>9</td>
<td>Yes</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>North Thames</td>
<td>10</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>North Thames</td>
<td>11</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>North Thames</td>
<td>12</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>North Thames</td>
<td>13</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>North Thames</td>
<td>14</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>North Thames</td>
<td>15</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>North Thames</td>
<td>16</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>North Thames</td>
<td>17</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>North Thames</td>
<td>18</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>North Thames</td>
<td>19</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>North Thames</td>
<td>20</td>
<td>Yes</td>
<td>Yes</td>
<td>1996</td>
<td>Yes</td>
</tr>
<tr>
<td>North Thames</td>
<td>21</td>
<td>Yes</td>
<td>No</td>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>22</td>
<td>Yes</td>
<td>Yes</td>
<td>1991</td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>23</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>Gas region</td>
<td>Authority</td>
<td>Aware of problem</td>
<td>Experienced problem</td>
<td>Initial problems</td>
<td>Aware of reason</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------</td>
<td>------------------</td>
<td>---------------------</td>
<td>------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>North West</td>
<td>24</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>25</td>
<td>Yes</td>
<td>Yes</td>
<td>1995</td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>26</td>
<td>Yes</td>
<td>Yes</td>
<td>1993</td>
<td>No</td>
</tr>
<tr>
<td>North West</td>
<td>27</td>
<td>Yes</td>
<td>Yes</td>
<td>1991</td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>28</td>
<td>Yes</td>
<td>Yes</td>
<td>1995</td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>29</td>
<td>Yes</td>
<td>Yes</td>
<td>1996</td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>30</td>
<td>Yes</td>
<td>Yes</td>
<td>1992</td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>31</td>
<td>Yes</td>
<td>Yes</td>
<td>1990</td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>32</td>
<td>Yes</td>
<td>Yes</td>
<td>1992</td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>33</td>
<td>Yes</td>
<td>No</td>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td>Northern</td>
<td>34</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>Northern</td>
<td>35</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>Northern</td>
<td>36</td>
<td>Yes</td>
<td>Yes</td>
<td>1994</td>
<td>Yes</td>
</tr>
<tr>
<td>Northern</td>
<td>37</td>
<td>Yes</td>
<td>Yes</td>
<td>1994</td>
<td>Yes</td>
</tr>
<tr>
<td>South Eastern</td>
<td>38</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>South Western</td>
<td>39</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>West Midlands</td>
<td>40</td>
<td>Yes</td>
<td>Yes</td>
<td>1990</td>
<td>Yes</td>
</tr>
<tr>
<td>West Midlands</td>
<td>41</td>
<td>No</td>
<td>No</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>West Midlands</td>
<td>42</td>
<td>Yes</td>
<td>Yes</td>
<td>1995</td>
<td>Yes</td>
</tr>
<tr>
<td>West Midlands</td>
<td>43</td>
<td>Yes</td>
<td>Yes</td>
<td>1996</td>
<td>Yes</td>
</tr>
<tr>
<td>West Midlands</td>
<td>44</td>
<td>Yes</td>
<td>Yes</td>
<td>1994</td>
<td>Yes</td>
</tr>
<tr>
<td>Gas region</td>
<td>Authority</td>
<td>Uneven flames on fires</td>
<td>Headaches / nausea</td>
<td>Excess sooting</td>
<td>Black Dust in boiler valves</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------</td>
<td>------------------------</td>
<td>--------------------</td>
<td>----------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>North Eastern</td>
<td>4</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>North Eastern</td>
<td>5</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>North Eastern</td>
<td>6</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>North Eastern</td>
<td>7</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>North Eastern</td>
<td>8</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>North Thames</td>
<td>20</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>North West</td>
<td>22</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>23</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>North West</td>
<td>25</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>26</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>27</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>28</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>North West</td>
<td>29</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>North West</td>
<td>30</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>North West</td>
<td>31</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>North West</td>
<td>32</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Northern</td>
<td>36</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Northern</td>
<td>37</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>West Midlands</td>
<td>40</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>West Midlands</td>
<td>42</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>West Midlands</td>
<td>43</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>West Midlands</td>
<td>44</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Gas region</td>
<td>Authority</td>
<td>Filters installed</td>
<td>Pipework replaced</td>
<td>Pipework coated</td>
<td>Other</td>
</tr>
<tr>
<td>----------------</td>
<td>-----------</td>
<td>-------------------</td>
<td>-------------------</td>
<td>----------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>North Eastern</td>
<td>4</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Compressed air</td>
</tr>
<tr>
<td>North Eastern</td>
<td>5</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North Eastern</td>
<td>6</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North Eastern</td>
<td>7</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North Eastern</td>
<td>8</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North Thames</td>
<td>20</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North West</td>
<td>22</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North West</td>
<td>23</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North West</td>
<td>25</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North West</td>
<td>26</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North West</td>
<td>27</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North West</td>
<td>28</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North West</td>
<td>29</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North West</td>
<td>30</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North West</td>
<td>31</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>North West</td>
<td>32</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Northern</td>
<td>36</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Northern</td>
<td>37</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>West Midlands</td>
<td>40</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>West Midlands</td>
<td>42</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Compressed air and filters</td>
</tr>
<tr>
<td>West Midlands</td>
<td>43</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>West Midlands</td>
<td>44</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Bundy Tubes replaced</td>
</tr>
</tbody>
</table>