Nent Haggs Mine Water Treatment Scheme -
Independent Review of Proposed Odour
Abatement

Report Reference: UC11596.03
February 2017
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Date: February 2017

Report Reference: UC11596.03

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Document History

<table>
<thead>
<tr>
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<tr>
<td>V1.0</td>
<td>Draft report issued</td>
<td>Richard Hooper</td>
<td>Jane Turrell</td>
<td>14 Jun 2016</td>
</tr>
<tr>
<td>V2.0</td>
<td>Final report issued - AAECOM comments</td>
<td>Richard Hooper</td>
<td>Jane Turrell</td>
<td>08 Feb 2017</td>
</tr>
<tr>
<td>V3.0</td>
<td>Final report reissued – Coal Authority comments</td>
<td>Richard Hooper</td>
<td>Jane Turrell</td>
<td>14 Feb 2017</td>
</tr>
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1. Introduction

The Coal Authority is in the process of submitting a planning application for a mine water treatment system (MWTS) at Nent Haggs. The Coal Authority asked WRc to carry out an independent review of the odour mitigation and abatement measures proposed for the Nent Haggs MWTS.

The objectives of this review were to:

- Check that the abatement measures are fit for purpose.
- Provide confidence to stakeholders that there would not be any odour nuisance issues should the mine water treatment system be installed.

This report provides a summary of WRc's technical review.
2. Background

It is proposed that the MWTS at Nent Haggs would use a passive Vertical Flow Pond (VFP) treatment system that consists of layers of an organic medium (compost/sludge/bark) and limestone, through which mine water drains under gravity to remove heavy metals, specifically zinc, from the mine water. Anaerobic conditions within the organic layer and an active microbial population lead to sulphate in the mine water being biologically reduced to hydrogen sulphide (H\textsubscript{2}S) which is present as dissolved sulphide. The sulphide precipitates as insoluble zinc sulphide. The system will contain residual dissolved H\textsubscript{2}S. The planning application includes a proposed odour abatement system to mitigate against the potential risk of odour emissions from residual H\textsubscript{2}S that could be released from the treated effluent as a result of agitation when it leaves the VFP treatment system, passes through a reedbed and over the final effluent cascade into the River Nent.

A similar VFP scheme at a Coal Authority site at Force Crag, in the Lake District, has been found to emit some H\textsubscript{2}S from the effluent as it discharges. The Force Crag site is located in a remote area and, therefore, no odour mitigation measures were required. The Coal Authority asked WRc to carry out an independent review of the odour mitigation and abatement measures proposed for the Nent Haggs MWTS because the site boundary would likely be within 100m of residences, a caravan park and public rights of way.
3. Documents covered in review

The following documents have been reviewed by WRc with a focus on salient points which are specifically relevant to the proposed odour abatement system:

- “Force Crag Mine water Treatment Facility – Air Quality Monitoring Survey” Ref: 60472598_00001 – April 2016, AECOM

- “Haggs Mine Water Treatment Scheme – Scoping Study and Remedial Options Appraisal” – June 2015, Ref: 47072599/MARP014, AECOM

- “Haggs Mine Water Treatment Scheme – Odour Control Options Appraisal” – March 2016, Ref: 47072599_MARP014, AECOM (Rev 0 LIB_20160407)

- “Outline Design Statement (TN02 Rev 4)”, April 2016, Technical Note: CA.2311.128_TN02, 14/4/16, AECOM

- “Haggs Mine Water Treatment Scheme – Environmental Statement – Volume I” – Chapter 4. Development Description – April 2016, AECOM


4. Review of documents

Details of the reviews of the eight documents listed in Section 3 and the main findings are summarised in the following sub-sections.

4.1 Review of Force Crag MWTS – Air Quality Monitoring Survey

Salient points identified in the report are discussed below.

Ambient H$_2$S concentrations were measured around the Force Crag mine water treatment system that has a VFP system similar to that proposed for the Nent Haggs MWTS. H$_2$S concentrations were measured at a comprehensive range of locations across the Force Crag MWTS using appropriate equipment.

There is evidence at the Force Crag VFP scheme that H$_2$S is liberated from the treatment system predominantly where effluent flows from the VFPs are turbulent (evidence of odours and elevated concentrations measured at some locations). These odours are primarily evident at the points at which water emerges from the VFPs into atmospheric conditions (e.g. open water cascading from flow control pipework [wet wells]) and at the entry and exit points of the aerobic wetland (between the VFP outlets and wetland inlet the water is contained within a pipe), which is consistent with H$_2$S degassing in turbulent aerated / oxygenated conditions. Odours are not measured in significant concentrations in the slow water-flow sections of the aerobic wetland at Force Crag. Monitoring undertaken by AECOM at Force Crag, indicates there are no significant fugitive emissions of H$_2$S occur via the pond water surfaces.

WRc comment:

H$_2$S concentrations were measured around the vertical flow pond (VFP) discharge point but not found around the rest of the VFP. Therefore, H$_2$S emissions appear to arise from the discharge of the effluent from the VFP due to the presence of residual H$_2$S in the mine water after it has passed through the VFP, this is in agreement with the conclusion specified by AECOM (Report Ref: 60472598_00001 – April 2016).

An appropriate range of gaseous species in addition to H$_2$S were measured using suitable methods. None of these odorous compounds were measured in the ambient air around the VFP, including the discharge point, above the odour threshold concentrations.

As the mine water originates underground and H$_2$S is generated within the VFP it is reasonable to expect that H$_2$S is the dominant odourant. However, if a VFP has just been commissioned with ‘fresh’ organic material this could lead to the transfer of other odorous chemicals into the VFP effluent that could add to the total odour emissions. Newcastle University reported that during commissioning and early operation at Force Crag there was no
evidence of other odorous compounds being reported above the typical level of detection by the human nose.

As the Nent Haggs MWTS will also have a VFP of the same type as Force Crag MWTS it is expected that the former will also have H₂S emissions arising from the discharge point of the VFP, the wetland and final effluent cascade into the River Nent if no abatement measures were installed. It is possible that for a period after commissioning, odorous chemical in addition to H₂S could be transferred to the VFP effluent that would increase the odour emission rate. AECOM report that there was no evidence of other odorous compounds during commissioning and early operation at Force Crag.

4.2 Review of Haggs MWTS – Scoping Study and Remedial Options Appraisal

Salient points identified in the report are discussed below.

The Nentsberry Haggs adit discharge rates show a wide variance, with flow values ranging from 2.5 to 17 litres/second. The flow variations were attributed to one or both of the following:

1. The flow logger was wrongly calibrated and was giving incorrect readings.

2. The occurrence of blockages or other changes in the structure of the adit.

Based on available flow and chemical quality data, the following estimated input parameters for the prospective Nentsberry Haggs mine water treatment works have been developed, based on 95th percentile values recorded from 2010-14: 16.2 litre/second.

AECOM recommended checks on the flow rates from the Haggs adit and these were carried out and reported in the “Outline Design Statement (TN02 Rev 4)”. In the Outline Design Statement it was stated that the mine water discharge from Haggs mine had been consistently recorded at approximately 5 litres/second during recent monitoring. However, AECOM’s review of longer term monitoring data confirmed that discharge flow rates of circa 15 litres/second have been typical until relatively recently. The balance of 10 litres/second is likely to be from mine water currently discharging from the Brownley Hill Low Level adit, which was diverted but will be reinstated to the Haggs adit portal in the near future.

Data from research work carried out by Newcastle University has been used to estimate an upper H₂S concentration of 15 mg/l that could be present in the effluent leaving the Nent Haggs MWTS VFP. This value was based on numerous laboratory, pilot and field scale studies undertaken on various North Penine mine waters by Newcastle University, a likely upper limit of 15 mg/l effluent H₂S concentration appears to be a reasonable design assumption.
Dissolved sulphide concentrations in the effluents from the VFPs at Force Crag MWTS have never been recorded at concentrations greater than 2mg/l. Consequently, this figure was used as a lower estimate of H_2S concentrations that could be present in the effluent leaving the Nent Haggs MWTS VFP.

The sulphate concentration in the Nent Haggs mine water is approximately 250 mg/l compared with the concentration in the Force Crag mine water of 30 mg/l.

The Haggs MWTS – Scoping Study and Remedial Options Appraisal report states that data from 22 laboratory, pilot and full scale VFP systems studies ‘suggests there is no relationship between the absolute influent sulphate concentration and the measured decrease in sulphate concentration – i.e. a higher mine water sulphate concentration does not equate to a proportionately higher amount of biological sulphur reduction and therefore higher amounts of sulphide generation.’

**WRc comment:**

Due to the relative molecular mass (rmm) of sulphate (SO_4) being 96 g/mol compared to 34 g/mol for hydrogen sulphide (H_2S), the conversion of 10 to 15mg/l sulphate to hydrogen sulphide should have been calculated as 3.5 to 5.3 mg/l H_2S rather than 10 to 15 mg/l. Therefore, the upper estimate of H_2S used for the technological and environmental assessment, based on the removal of sulphate within the VFPs should have been 5.3 mg/l.

It is possible that the higher sulphate concentration in the Nent Haggs mine water may result in a higher concentration of H_2S in the VFP effluent than that measured at Force Crag.

**WRc conclude from available data that the laboratory and pilot scale studies support the validity of the relationship between absolute influent sulphate and measured decrease in sulphate concentrations. WRc recommends that longer term measurements on a full-scale operation are undertaken to confirm whether changes to the influent sulphate concentration effect the directly measured sulphide concentration in the VFP effluent. Similar measurements at Force Crag could be completed to better understand this relationship on a well established VFP, although effluent sulphide are likely to also be influenced by influent metal concentrations which would be different between Force Crag and Nents Head.**

**WRc recommend that further work is needed to fully understand mechanisms for limiting sulphide generation in the VFP due to COD and/or BOD concentrations in the VFP influent stream. Initial laboratory and pilot scale testing by Newcastle University suggests there is no relationship between sulphide concentrations in the effluent and sulphate concentrations in the influent, but this is obviously a potentially important factor in the design of any new VFP systems.**
4.3 Review of Haggs MWTS - Odour Control Options Appraisal

Salient points identified in the report are discussed below.

4.3.1 Input data for appraisal

The Haggs Mine Water Treatment Scheme – Odour Control Options Appraisal restates that \( \text{H}_2\text{S} \) would be present in the VFP effluent and is expected to be released at points of turbulence.

AECOM has used the same values for the mine water flow to the MWTS (15 litres/second) and the higher and lower estimates for \( \text{H}_2\text{S} \) concentrations in the VFP treated effluent (2 and 15 mg/l) as those stated in the Haggs MWTS – Scoping Study and Remedial Options Appraisal document (see Section 4.2 above).

The AECOM report states that the biological sulphate reducing reactions are a result of a natural process and therefore may vary slightly with fluctuating conditions (e.g. temperature, pH, presence of nutrients, etc.). For the purposes of this evaluation, a precautionary principal has been adopted. The worst case scenario is that the presence of all excess sulphide (\( S^{2-} \)) is in the form of \( \text{H}_2\text{S} \). Although this is a very conservative approach, this scenario has been used for the evaluation.

**WRC comment:**

As explained in Section 4.2 the upper estimate of the \( \text{H}_2\text{S} \) concentration used for the technological and environmental assessment, based on the removal of sulphate within the VFPs should have been 5.3 mg/l rather than 15 mg/l.

WRC has checked the AECOM calculations made for the estimated daily production rates of \( \text{H}_2\text{S} \) from the estimates of the mine water flow rate and \( \text{H}_2\text{S} \) concentrations in the VFP effluent and found them to be numerically correct for the lower estimate of \( \text{H}_2\text{S} \) in the VFP effluent of 2mg/l. It is noted that this is a conservative approach as there is limited data for review and direct correlation to schemes where influent sulphate levels may be higher cannot be made.

4.3.2 Approach for assessment of odour abatement options

AECOM has identified and assessed a large range of options for removing \( \text{H}_2\text{S} \) from VFP treated mine water. A systematic approach was taken for the assessment of odour abatement options. An applicability matrix of odour control alternatives was drawn-up and assessed for the following aspects:

- Potential for applicability
- Pros
The assessment was carried out thoroughly and was well documented in the odour abatement appraisal report.

4.3.3 Outcome of the assessment of odour abatement options

The outcome of the assessment of odour abatement options was as follows.

Options shortlisted by AECOM:

- R1: Varied thickness of VFP compost.
- R4: Chemical dosing – hydrogen peroxide.
- R5: Chemical dosing – ozone.

Technology suitable for site but does not meet Coal Authority criteria. Therefore it was not shortlisted:

- R3: Engineering controls.

Options not shortlisted:

- R2: Maintaining elevated dissolved oxygen.
- R6: Chemical dosing – nitrate.
- R7: Chemical dosing – sodium hypochlorite.
- R8: Chemical dosing – sodium chlorite.
- R9: Chemical precipitation – ferrous chloride and ferric chloride.
- R10: Surface mediated redox – potassium permanganate.
- R11: Surface mediated precipitation – ferric oxides.

AECOM has identified both hydrogen peroxide and ozone as potential options for removing residual dissolved H₂S from VFP treated mine water.
WRc comment:

Hydrogen peroxide has been widely used in the water industry to remove H$_2$S from wastewater when cheaper options such as ferric dosing are not possible. The process is included in the UKWIR Report “Odour Control in Wastewater Treatment – A Technical Reference Document.” Ref No.01/WW/13/3. (Hobson, J., Yang, G. 2002) and a paper by Alken Murray Corp. Pollution Control (2016) called “Solving the Hydrogen Sulphide Problem.” The latter source states that hydrogen peroxide has been injected, upstream of the headworks or primary clarifiers, to react with hydrogen sulphide forming sulphur and water. Excess hydrogen peroxide decomposes to release oxygen and water, thereby increasing the dissolved oxygen in the stream.

Ozone has been used to remove H$_2$S from water as reported by Spartan Water Treatment (2016). There are pros and cons for both systems. Hydrogen peroxide dosing requires chemical deliveries and storage, whereas an ozone generator can use air as the source term and does not require any chemical deliveries or storage. However, an ozone generator would require a larger electrical power usage than hydrogen peroxide dosing.

WRc recommends that a process involving the dosing of both hydrogen peroxide and ozone should be assessed to see whether it would reduce the hydrogen peroxide dose needed and still be appropriate for the application.

AECOM have not included the design contact time for mixing hydrogen peroxide with the VFP treated mine water to remove dissolved H$_2$S in the outline design document. In addition they have not included the dimensions of the pipes between the VFPs and wetlands in order that the residence time can be calculated and assessed. Static mixers, which are commonly used after chemical dosing in the water industry to thoroughly mix chemicals with the receiving process stream, have not been mentioned in the AECOM outline design document. WRc acknowledge that these factors would be included in a detailed design scheme as part of an additional study.

The Odour Control Options Appraisal by AECOM has assumed a hydrogen peroxide to H$_2$S dosing ratio of 1.5 to 1 for the operation of the VFP when it has become established and the chemical oxygen demand (COD) has be estimated to be less than 10 mg/l. During the commissioning and establishment phases of the VFP when the COD concentration has been estimated to be 3,000 and 100mg/l, respectively, due to soluble organic material transferring from the biological media to the VFP effluent, it has been assumed that the hydrogen peroxide to H$_2$S dosing ratios would be 4 to 1 and 3 to 1, respectively. The UKWIR Technical Reference Document on odour control (Hobson, 2002) states that typical field applications of hydrogen peroxide require one to three kg of hydrogen peroxide per kg sulphide. WRc recommends that experimental trials are carried out to confirm whether the hydrogen peroxide dosing rates recommended by AECOM are appropriate, although they are within the same range as predicted in typical field trials.
Removal of hydrogen sulphide during commissioning and early stage operation may require greater dosing levels of hydrogen peroxide as leaching of natural organics from the compost material would be oxidised by hydrogen peroxide additions.

The estimate for the monthly volume of hydrogen peroxide chemical required for treating the Nent Haggs MWTS VFP would need to increase if additional experimental tests find that a greater dose of hydrogen peroxide would be required. If this were the case the number of deliveries and the size of the chemical storage area would need to increase.

4.4 Review of Haggs MWTS - Outline Design Statement (TN02 Rev 4)

Salient points identified in the report are discussed below.

The document mainly covers the points already addressed in Section 4.3 regarding the Haggs MWTS - Odour Control Options Appraisal document. However, it provides additional consideration on potential seasonal low temperature effects.

AECOM reported that as the mine water will be coming from underground, during winter conditions the temperature of the mine water is likely to be above ambient air temperatures and this is expected to prevent the MWTS from freezing up.

The document states that based on laboratory and field trial experience (particularly at Force Crag which is at a similar elevation and climate) a nominal hydraulic residence time of 18 hours is required (i.e. the length of time mine water is in contact with the compost media).

WRc comment:

WRc are in agreement with AECOM conclusion that mine water will be at a temperature above ambient air temperatures in winter months and therefore expected to prevent the MWTS from freezing up.

4.5 Review of Haggs MWTS – Odour Dispersion Modelling Report

Salient points identified in the report are discussed below.

AECOM have carried out odour dispersion modelling for the proposed Nent Haggs MWTS without odour abatement measures in place. The odour dispersion model has been set up using an advanced atmosphere dispersion model called ADMS (Advanced Dispersion Modelling Software) that is produced by Cambridge Environmental Research Consultants (CERC), and includes the locations of local sensitive receptors and appropriate meteorological data. Odour emission rates have been calculated correctly for high and low estimates of the H₂S concentration in the VFP effluent of 15 and 2 mg/l.
Modelling scenarios were carried out for different proportion of the H₂S being emitted from the inlet to the wetlands, the flow control structures and the final effluent cascade into the River Nent.

AECOM has predicted that if no odour abatement measures are put in place at the Nent Haggs MWTS the odour concentration at the local receptors would exceed the target odour concentration of 1.5 ou/m³ as an annual 98th percentile of hourly averages for both H₂S concentration estimates in the VFP effluent (2 and 15 mg/l).

WRc comment:

The calculations of odour emission rates use assumptions that are consistent with the other documents and assume that all the H₂S will be emitted. However, 5.3 mg/l should have been used instead of 15 mg/l as the upper estimate for H₂S in the VFP effluent (based on the reduction of sulphate measured across VFPs), as explained in Section 4.2.

As the final effluent cascade has the greatest turbulence WRc recommend that additional atmospheric dispersion modelling is carried out for different proportions of the H₂S being emitted from the cascade. This modelling allows for all possible fugitive emissions to be assessed and indicates a worst-case scenario if no engineering controls were installed.

4.6 Review of Haggs MWTS – Environmental Statement – Volume 1 – Chapter 4 – Development Description

Salient points identified in the report are discussed below.

An odour management plan has been developed to control odour levels during the operation of the Nent Haggs MWTS. See Section 4.8 for further details.

4.7 Review of Haggs MWTS – Environmental Statement – Volume 1 – Chapter 8 – Air Quality

Salient points identified in the report are discussed below.

AECOM have assumed that the dosing of hydrogen peroxide would remove all the H₂S from the VFP treated mine water. Therefore, AECOM conclude that the site having a ‘small source odour potential’. Consequently no odour dispersion modelling of the residual odour was carried out.

WRc Report P6830 “CP260 An investigation into the use of additives”, (Sivil et al, 2006) summarised a research project that tested the effectiveness of additives such as hydrogen peroxide on domestic settled sewage containing hydrogen sulphide. The initial settled sewage had a total dissolved sulphide concentration of 6.44 mg/l, the pH value of the settled sewage was 7.18 and the initial COD concentration was 650 mg/l. Bench scale tests using hydrogen
peroxide decreased the initial total dissolved sulphide concentration by 93.3% after 2 minutes and 99.0% after 10 minutes of mixing time. The experimental tests, therefore, found that the addition of hydrogen peroxide did not remove 100% of the dissolved sulphide under the conditions tested.

The UKWIR Technical Reference Document on odour control (Hobson, 2002) states that hydrogen peroxide is typically used up within 10 and 15 minutes of being dosed into wastewater. An article published by Alken Murray Corporation (2016) states that generally 90% of the reaction between hydrogen peroxide and hydrogen sulphide takes place within 10 to 15 minutes, with the balance reacting in an additional 20 to 30 minutes.

WRc comment:

The design contact time for the hydrogen peroxide with the VFP effluent is not specifically quantified in the outline design stage documents. In any final design specification the proposed length and diameter of the pipe between the VFP and the wetland would also need to be identified in order to calculate the contact time and consider whether it is of sufficient length.

WRc recommends that experimental tests are carried out to determine the effectiveness of hydrogen peroxide for removing H\textsubscript{2}S from VFP treated mine water and the dose and contact time needed. Such information can be used in a detailed design stage for the Nent Haggs installation.


Salient points identified in the report are discussed below.

A comprehensive odour management plan has been drawn up covering the aspects expected for operating and maintaining the odour control measures for the Nent Haggs MWTS.

A telemetry system has been proposed for monitoring the operational parameters.

WRc comment:

The H\textsubscript{2}S concentration in the VFP treated effluent is likely to change due to variations in operating conditions on a seasonal and possibly daily basis, such as the temperature and flow of the mine water being treated. Therefore, an automatic control system would be important to monitor the VFP effluent residual H\textsubscript{2}S concentration or the gaseous H\textsubscript{2}S concentration in a flow control structure and to adjust the hydrogen peroxide dose as needed.
5. Main findings and recommendations for future work

5.1 Monitoring at Force Crag MWTS

Appropriate monitoring methods have been carried out at Force Crag MWTS to determine that H$_2$S was present where effluent from the VFPs discharges and that no other gaseous species were measured above their odour threshold concentrations. This seems reasonable for a well-established MWTS (18 months old). Similar measurements could also be been made around a newly commissioned VFP, where odorous organic compounds from the new biological media may diffuse into the treated mine water and add to the odour emissions. It would be beneficial for such measurements to be made on an existing VFP, which could be used to simulate a range of potential treatment conditions. Newcastle University have reported to AECOM that there was no evidence of other odorous compounds during commissioning and early operation at Force Crag.

5.2 Estimate of H$_2$S in the VFP treated mine water at Nent Haggs MWTS

The University of Newcastle measured a considerably larger removal of sulphate across the VFPs at Force Crag MWTS compared to the concentration of sulphide that was present in the VFP effluent. This has resulted in a large discrepancy between two estimates made for the sulphide generation and used for the odour control option assessment of 2 and 15 mg/l.

Due to the relative molecular mass (rmm) of sulphate (SO$_4$) being 96 g/mol compared to 34 g/mol for hydrogen sulphide (H$_2$S), the conversion of 10 to 15mg/l sulphate to hydrogen sulphide should have been calculated as 3.5 to 5.3 mg/l H$_2$S rather than 10 to 15 mg/l. Therefore, the upper estimate of H$_2$S used for the technological and environmental assessment, based on the removal of sulphate within the VFPs should have been 5.3 mg/l.

WRc would like confirmation on the sample collection and analytical methods used by Newcastle University to measure the dissolved sulphide concentration in the VFP effluent at Force Crag which did not exceed 2 mg/l.

The sulphate concentration in the Nent Haggs mine water is approximately 250 mg/l compared with the concentration in the Force Crag mine water of 30 mg/l. Therefore, it is possible that the Nent Haggs mine water may result in a higher concentration of H$_2$S in the VFP effluent than that measured at Force Crag. An assessment by Newcastle University of laboratory, pilot and full scale VFPs indicated that there was no relationship between the influent sulphate concentration and the decrease in the sulphate concentration across the VFPs but the reason for this has not been established.
Flow information available for Force Crag MWTS could be used to confirm that the nominal hydraulic residence time for the VFPs is the same as the design hydraulic residence time for the VFPs proposed for the Nent Haggs MWTS of 18 hours. To further quantify odour conditions in a new VFP a laboratory or pilot scale systems could be used to simulate ambient air measurements could also be made around a new VFP to determine whether there are odorous materials that would diffuse in to the treated mine water and add to the odour emissions. The information obtained is used to estimate the residual hydrogen sulphide in the effluent from the VFPs for the Nent Haggs MWTS following hydrogen peroxide dosing.

WRc suggest that potential future work includes monitoring results are used to confirm whether or not changes in the sulphate concentration in the influent of a VFP effects the directly measured sulphide concentration in the VFP effluent.

- WRc does not possess information regarding the mine water flow rate to the Force Crag MWTS that would allow the nominal hydraulic residence time for the VFPs to be compared with the design nominal hydraulic residence time for the proposed VFPs at Nent Haggs MWTS of 18 hours. This design parameter will be a factor for the overall final scheme and should be modelled on the basis of a range of residence times.

This information can be used for the detailed design phase of the proposed Nent Haggs installation.

5.3 Assessment of potential options for removing H₂S from VFP effluent

AECOM created an odour dispersion model to predict the effects of odour emissions from H₂S in the effluent from a VFP if odour control measures were not included. The model predicts odour concentrations at the locations of local sensitive receptors that would exceed the Environment Agency odour concentration target of 1.5 ouE/m³ as 98th percentile of annual hourly averages. This confirmed that odour abatement measures would be required to remove H₂S from the VFP effluent.

Bearing in mind the points raised in Sections 5.1 and 5.2, the assessment of potential options for removing H₂S from the VFP treated mine water has been carried out thoroughly and has been well documented. Hydrogen peroxide and ozone were identified as the most appropriate options. Hydrogen peroxide has been used to remove H₂S from wastewater when cheaper options are not suitable and ozone has been used to remove H₂S from water.

WRc recommends that a process involving the dosing of both hydrogen peroxide and ozone should be assessed to see whether it would reduce the hydrogen peroxide dose needed and still be appropriate for the application.
5.4 Effectiveness of hydrogen peroxide for removing H₂S from mine water

AECOM has assumed 100% removal of H₂S from the VFP treated mine water from the dosing of hydrogen peroxide, and therefore predicts negligible effects from odour emissions on the local sensitive receptors. In addition, AECOM has not included in their outline design stage documents the design contact time for hydrogen peroxide to mix with the VFP treated mine water. In addition the dimensions of the pipes between the VFPs and the wetlands have not been provided for the residence time to be calculated and considered.

WRc have carried out experimental tests to assess the removal efficiency of hydrogen peroxide for H₂S in waste water treatment sewage. We found that hydrogen peroxide dosing could achieve a 99% removal after a contact time of 10 minutes. The UKWIR Technical Reference Document on odour control (Hobson, 2002) states that hydrogen peroxide is typically used up within 10 and 15 minutes of being dosed into wastewater. An article published by Alken Murray Corporation (2016) states that generally 90% of the reaction between hydrogen peroxide and hydrogen sulphide takes place within 10 to 15 minutes, with the balance reacting in an additional 20 to 30 minutes.

The Odour Control Options Appraisal by AECOM has assumed a hydrogen peroxide to H₂S dosing ratio of 1.5 to 1 for the operation of the VFP when it has become established and the chemical oxygen demand (COD) has been estimated to be less than 10 mg/l. During the commissioning and establishment phases of the VFP when the COD concentration has been estimated to be 3,000 and 100 mg/l, respectively, due to soluble organic material transferring from the biological media to the VFP effluent, it has been assumed that the hydrogen peroxide to H₂S dosing ratios would be 4 to 1 and 3 to 1, respectively. The UKWIR Technical Reference Document on odour control (Hobson, 2002) states that typical field applications of hydrogen peroxide require one to three kg of hydrogen peroxide per kg sulphide.

WRc and AECOM both recommend that experimental tests are carried out to determine the hydrogen peroxide dose, contact time and effectiveness for removing H₂S from effluent from mine water treated by a VFP and the residual H₂S concentration that would be achieved. A similar conclusion was noted in the AECOM reports. To inform final design plans WRc believe it would be beneficial to carry out further experimental tests using an established VFP and dosing with additional organic material to simulate higher COD/BOD in a newly commissioned VFP.

Static mixers, which are commonly used after chemical dosing in the water industry to thoroughly mix chemicals with the receiving process stream, have not mentioned in the AECOM outline design document. These considerations would be included at the detailed design phase.

The existing Force Crag MWTS in the Lakes District has VFPs similar to those proposed for Nent Haggs MWTS and is recommended for experimental tests on an established VFP. As a newly commissioned VFP at a MWTS is not expected to be currently available, it is
recommended that VFP effluent from a newly commissioned VFP is simulated by adding some soluble organic material, derived from biological media that would be used in a VFP, to samples of Force Crag MWTS VFP effluent to simulate an odour dosing trial on a newly commissioned VFP.

The estimate for the monthly volume of hydrogen peroxide chemical required for treating the Nent Haggs MWTS VFP would need to increase if the experimental tests find that a greater dose of hydrogen peroxide would be required. If this were the case the number of deliveries and the size of the chemical storage area would need to increase.

5.5 **Estimating and modelling the residual odour after odour control measures are installed**

Following the completion of the work recommended in Sections 5.1 and 5.3 it recommended that revised estimates are made for the H$_2$S and odour emission rates arising from residual H$_2$S concentrations in the VFP effluent following hydrogen peroxide dosing. The odour dispersion model previously set up by AECOM should then be updated with the revised odour emissions rates and run to predict the effects of H$_2$S emissions on the local sensitive receptors.

5.6 **Odour management plan**

A comprehensive odour management plan has been drawn up covering the aspects expected for operating and maintaining the odour control measures for the Nent Haggs MWTS.

A telemetry system has been proposed for monitoring the operational parameters. However, the H$_2$S concentration in the VFP treated effluent is likely to change due to variations in operating conditions on a seasonal and possibly daily basis, such as the temperature and flow of the mine water being treated. Therefore, an automatic control system would be important to monitor the VFP effluent residual H$_2$S concentration or the gaseous H$_2$S concentration in a flow control structure and to adjust the hydrogen peroxide dose as needed.
The main conclusions from the review are as follows:

- **Ambient gas monitoring around VFPs**: Appropriate monitoring methods have been carried out at Force Crag MWTS to determine that H\textsubscript{2}S was present where effluent from the VFPs discharges but no other gaseous species were measured above their odour threshold concentrations. This approach seems reasonable for a well-established MWTS (18 months old). Newcastle University have reported to AECOM that there was no evidence of other odorous compounds during commissioning and early operation at Force Crag.

- **Sulphide generation in VFPs**: The University of Newcastle measured a considerably larger removal of sulphate across the VFPs at Force Crag MWTS compared to the concentration of sulphide that was present in the VFP effluent. This has resulted in a large discrepancy between two estimates made for the sulphide generation and used for the odour control option assessment of 2 and 15 mg/l. Due to the relative molecular mass (rmm) of sulphate (SO\textsubscript{4}) being 96 g/mol compared to 34 g/mol for hydrogen sulphide (H\textsubscript{2}S), the conversion of 10 to 15 mg/l sulphate to hydrogen sulphide should have been calculated as 3.5 to 5.3 mg/l H\textsubscript{2}S rather than 10 to 15 mg/l. Therefore, the upper estimate of H\textsubscript{2}S used for the technological and environmental assessment, based on the removal of sulphate within the VFPs should have been 5.3 mg/l. WRc have been provided with sample collection and analytical techniques used by Newcastle University for on-site measurements. It is acknowledged that during field testing the practicalities of sampling bring uncertainties in results and there may be underestimates in concentrations of dissolved sulphide reported previously.

- **Sulphate concentration in influent mine water**: The sulphate concentration in the Nent Haggs mine water is approximately 250 mg/l compared with the concentration in the Force Crag mine water of 30 mg/l. Therefore, it is possible that the Nent Haggs mine water may result in a higher concentration of H\textsubscript{2}S in the VFP effluent than that measured at Force Crag. An assessment by Newcastle University of laboratory, pilot and full scale VFPs indicated that there was no relationship between the influent sulphate concentration and the decrease in the sulphate concentration across the VFPs but the reason for this has not been established.

- **Nominal hydraulic residence time of VFPs**: WRc does not possess information regarding the mine water flow rate to the Force Crag MWTS that would allow the nominal hydraulic residence time for the VFPs to be compared with the design nominal hydraulic residence time for the proposed VFPs at Nent Haggs MWTS of 18 hours. This design parameter will be a factor for the overall final scheme and should be modelled on the basis of a range of residence times.
• **Assessment of potential odour control options:** Bearing in mind the points raised above, the assessment of potential options for removing H\(_2\)S from the VFP treated mine water has been carried out thoroughly and has been well documented. AECOM noted that hydrogen peroxide and ozone were identified as the most appropriate options, WRc concurs that these options are suitable. Hydrogen peroxide has been used to remove H\(_2\)S from wastewater when cheaper options are not suitable and ozone has been used to remove H\(_2\)S from water. WRc recommends that a process involving the dosing of **both** hydrogen peroxide and ozone should be assessed to see whether it would reduce the hydrogen peroxide dose needed and still be appropriate for the application.

• **Effectiveness of hydrogen peroxide for removing H\(_2\)S:** AECOM have assumed 100% removal of H\(_2\)S from the VFP treated mine water from the dosing of hydrogen peroxide, and therefore predicts negligible effects from odour emissions on the local sensitive receptors. The performance of the H\(_2\)S removal process by hydrogen peroxide needs to be checked through experimental trials.

• **Contact time, dose and mixing of hydrogen peroxide with mine water:** In their outline design document AECOM have not included the contact time for hydrogen peroxide to mix with the VFP treated mine water. In addition the dimensions of the pipes between the VFPs and the wetlands have not been provided for the residence time to be calculated and considered. Ratios of hydrogen peroxide dose to H\(_2\)S have been estimated by AECOM for VFPs during commissioning, establishment and normal operational phases but require experimental verification. Static mixers, which are commonly used after chemical dosing in the water industry to thoroughly mix chemicals with the receiving process stream, have not been mentioned in the AECOM design document. These parameters will form part of the more comprehensive detailed design phase documents.

• **Odour management plan:** A comprehensive odour management plan has been drawn up covering the aspects expected for operating and maintaining the odour control measures for the Nent Haggs MWTS. However, an automatic control system would be important to monitor the VFP effluent residual H\(_2\)S concentration or the gaseous H\(_2\)S concentration in a flow control structure and to adjust the hydrogen peroxide dose as needed. AECOM recommended that dosing with peroxide was not a final decision, and that ozone dosing is a viable alternative.
7. Recommendations

WRc recommends that:

1. Experimental trials are carried out at Force Crag MWTS to determine the dose, contact time and effectiveness of hydrogen peroxide for removing H$_2$S from VFP treated mine water with and without additional COD that would arise from soluble organic material that would transfer to the VFP effluent during the commissioning and establishment phases of the VFPs. Use of ozone is another option for sulphide removal from the effluent, as also suggested by AECOM. [This recommendation was commissioned by the Coal Authority, carried out by WRc in September 2016 and summarised in WRc Report UC12271.1]

2. The experimental trials at Force Crag MWTS are also used to re-measure the sulphate concentrations in the mine water at the inlet and outlet to the VFPs and the proportion of the sulphate that is removed and converted to H$_2$S. [This recommendation was commissioned by the Coal Authority, carried out by WRc in September 2016 and summarised in WRc Report UC12271.1]

3. The information from the above experimental trials is used to compare the sulphate concentrations of the mine water entering the existing VFP at Force Crag MWTS with the mine water that would be treated at the proposed Nent Haggs MWTS. [This recommendation was commissioned by the Coal Authority, carried out by WRc in September 2016 and summarised in WRc Report UC12271.1]

4. Experimental data from Newcastle University is reviewed to assess if there is a mechanism for rate limiting sulphide generation in VFPs by either the COD and/or BOD concentration in the influent stream or COD and/or BOD that leaches out of the bio-bed during the commissioning, establishment and normal operating phases of a VFP. In addition it is recommended that any COD/BOD data for the influent mine water at Nent Haggs is also reviewed. Use flow information available for Force Crag MWTS to confirm that the nominal hydraulic residence time for the VFPs is the same as the design hydraulic residence time for the VFPs proposed for the Nent Haggs MWTS of 18 hours. Ambient air measurements are made around either a simulated VFP system or an existing system using BOD/COD dosing to determine whether there are odorous materials that would diffuse in to the treated mine water and add to the odour emissions. Information obtained from (1) to (3) is used to estimate the residual hydrogen sulphide in the effluent from the VFPs for the Nent Haggs MWTS following hydrogen peroxide dosing.

5. WRc conclude from available data that the laboratory and pilot scale studies support the validity of the relationship between absolute influent sulphate and measured
decrease in sulphate concentrations. Longer term measurements on a full-scale operation can confirm if changes to the influent sulphate concentration effect the directly measured sulphide concentration in the VFP effluent, although effluent sulphide will be influenced by influent metal concentrations.

6. Odour emission rates are predicted from the estimated residual hydrogen sulphide in the VFP effluent as it passes through the wetland and flow control structures and down the cascade into the River Nent.

7. Odour dispersion modelling is carried out to estimate the maximum predicted emissions of hydrogen sulphide that could be released from residual dissolved hydrogen sulphide in the treated water that would meet the odour concentration limits chosen for the proposed site boundary.

8. A process involving the dosing of both hydrogen peroxide and ozone should be assessed to see whether it would reduce the hydrogen peroxide dose needed and still be appropriate for the application.
8. References


Alken Murray Corp. Pollution Control, 2016. “Solving the Hydrogen Sulphide Problem.” Alken Murray Corp. Pollution Control, Virginia, USA (http://www.alken-murray.com/H2SREM5.HTM)
