WHY YOU SHOULDN'T ASSUME YOUR NON-HAZARDOUS FEEDSTOCK IS NON-HAZARDOUS: THE FORENSIC ANALYSIS OF A FILTER CAKE PRODUCED FROM THE MANUFACTURE OF FIREFIGHTING FOAM FROM HOOF AND HORN MEAL

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SUMMARY: Angus was informed by the regulator that they had to use the hazardous 07 07 10* code for the disposal of a non-hazardous filter cake generated from the hydrolysis of hoof and horn meal used to manufacture firefighting foam. This change in code tripled the waste disposal cost of the filter cake. However, if Angus could demonstrate that the filter cake did not have any hazardous properties, then Angus could apply to the Secretary of State for a decision, under Article 7 (3) of the Waste Framework Directive, that would allow the waste to be handled as a non-hazardous waste. The paper is a good (surprising) example of how one can't assume a waste is non-hazardous even though this might be a reasonable assumption. It is also a detective story, one that explains the journey a waste classifier needs to take to understand their waste and obtain a reasonable (as opposed to a worst case) classification. The paper describes how the metal species were identified and also explores the often confusing nature of different hydrocarbons tests (EPH/TPH) offered by the various laboratories and how understanding the differences can be used to better characterise and understand the nature of the unknown hydrocarbons in a waste.

1. INTRODUCTION

Angus produces approximately 1400 tonnes per annum of filter cake generated by the hydrolysis of hoof and horn meal for the manufacture of firefighting foam. The filter cake was originally classified as a non-hazardous entry (Chapter 6 Wastes from inorganic chemical processes; 06 13 99 Wastes not otherwise specified) and accepted for composting. However, following an audit, the

UK Environment Agency found that this code was incorrect as it had been selected from the wrong chapter of the List of Waste. Instead, the correct code should be from Chapter 7 Wastes from organic chemical processes: Section 07 07 wastes from the MFSU of fine chemicals and chemical products not otherwise specified: 07 07 10* other filter cakes and spent absorbents. Unfortunately this is a hazardous entry; there being no non-hazardous/ mirror entries for filter cakes in Chapter 7.

The consequence of this change to the coding was a threefold increase in Angus's disposal costs, from £280k (1405 tonnes) in 2016 to £733k (1365 tonnes) in 2017.

Logic would indicate that a filter cake produced from the simple hydrolysis of hoof and horn meal, with no hazardous substances added or created by the process, should generate a non-hazardous waste. To address this discrepancy, it was decided to:

1. Undertake a suitable chemical analysis and waste classification of the filter cake to confirm that it doesn't have any of the hazardous properties listed in Annex III of the Waste Framework Directive 2008/98/EC. The classification would follow the UK's WM3 technical guidance (EA 2015), the CLP (Regulation (EC) No. 1272/2008) and utilise the waste classification software HazWasteOnline™ (www.hazwasteonline.com).
2. Assuming that the filter cake does not display any of the hazardous properties listed in Annex III, the next step would be to appeal to the UK's Secretary of State for the Environment for a Regulation 9 decision (The Hazardous Waste (England and Wales) Regulations 2005; WFD Article 7 (3)) that will allow the waste to be treated as a non-hazardous waste and handled under The Waste (England and Wales) Regulations 2011.
3. With the Environment Agency's help, work with a recycler to arrange a variation to their environmental permit so that the filter cake can be recycled as a non-hazardous waste but under the hazardous List of Waste code 07 07 10*.

An initial worst waste classification of three samples of the filter cake analysed by a consultant declared the waste hazardous due to raised levels of hydrocarbons, iron and chromium. However, their worst case approach hadn't investigated the process that created the filter cake nor which hazardous substances might be present in the filter cake. The next task was therefore to better understand the composition of the filter cake and identify:

- The sources of the iron and the chromium and from that determine which compounds of iron and chromium are present in the filter cake and whether the concentrations of these compounds would make the filter cake hazardous.
- The type of hydrocarbons present in the filter cake and whether any of the hydrocarbons would make the waste hazardous.

2. THE PROCESS

A 4.5 tonne batch of hoof and horn meal is hydrolised with 1.3 tonnes of lime (calcium hydroxide) and 13 tonnes of water in an agitated reactor heated to about 95^{o}C. This process produces a solution of polypeptides created by the hydrolysis of the peptide bonds that link the fibrous structural proteins found in keratin, a key structural material that makes up horns, hooves and hair. There are also two side reactions that have to be managed;

1. cleavage of cystine bonds which yields free sulphide ions, and
2. hydrolysis of amide side groups to give ammonia.

After 8 hours, the hydrolysis is ended by cooling, followed by the injection of carbon dioxide to both a) reduce the pH from 12 to ~9 and b) to precipitate the calcium in the form of calcium carbonate. The free sulphide ions are dealt with by the addition of iron(II) sulphate which precipitates out some 50% of the sulphide ions; the remainder being gassed off along with ammonia.

This neutralised reaction slurry is then pumped to a filter press which, per batch, generates approximately 4 tonnes of hydrolised protein and 4 to 5 tonnes of filter cake. The filter cake varies in composition but is approximately 50% water, 40% calcium carbonate, 5% iron(II) sulphide and 5% unreacted meal.

3. REVIEW OF THE EARLIER TESTING AND CLASSIFICATION

In May 2015, Angus had a sample of the filter cake analysed for both solids and WAC. The solids analysis covered the BTEX, PAHs, TPH and 16 metals. The most significant results in this assessment found TPH at 1,900 mg/kg, chromium at 7,300 mg/kg and iron at 20,000 mg/kg. A follow-up analysis confirmed that the bulk of the chromium was in the form of chromium(III) with only a negligible amount in the form of chromium(VI).

Three new samples of the filter cake were analysed by a second laboratory using a similar test suite but utilising an EPH analysis rather than TPH. A consultant, commissioned to analyse these lab results using HazWasteOnline™ declared the filter cake hazardous due to high concentrations of chromium, iron and EPH.

The consultant had undertaken what we would call a worst case approach because they:

a) Had not investigated the source of the chromium or of the iron.
b) Had not justified the selection of the selected chromium species (chromium(III) oxide) and the iron species (iron(II) oxide) used in their classification.
c) Had not looked at whether HazWasteOnline's default (i.e. worst case) entry for either the chromium(III) oxide or the iron(II) oxide was reasonable for (a) the waste stream and (b) the particular properties of the selected metal compound in the filter cake.
d) Had assumed that the measured EPH was related entirely to petroleum based hydrocarbons. The EPH results had been entered into the HazWasteOnline™ entry "TPH (C_6-C_{40}) Petroleum Group", a determinand defined by the UK's environment agencies to assess unknown oils in a mixture. The hazard statements for this entry assume that the measured TPH is related to derivatives of petroleum whereas the hydrocarbons in this filter cake should be related to animal hydrocarbons.
e) Had not asked the laboratory for any interpretation of the EPH.
f) Had made no reference to the presence (in low concentrations) of PAHs and phenols

4. WASTE CLASSIFICATION SOFTWARE

HazWasteOnline™ is web-based software that is used by consultants, regulators, waste companies and industrials, mainly in the UK and Ireland but also in Europe, to classify wastes as either hazardous or non hazardous based on the waste's chemistry. The software utilises a classification engine that applies both the rules in the CLP and any additional rules added by national guidance and/or national legislation. HazWasteOnline™ contains 842 codes from the List of Waste and all ~4500 harmonised substances from Table 3 Annex VI of the CLP. It also contains more than 100 substances, defined by HazWasteOnline™, that are not in the CLP, including several of the standard PAHs and iron(II) oxide and chromium(III) oxide mentioned above.

It must be noted that for non harmonisd substances, HazWasteOnline™ has to err on the worst case side because it doesn't know which industry might need to use that substance in a classification and in which form (waste) that substance might be in. For example a drum of iron oxide powder would have irritant to eyes and airways type hazard statements while iron oxide in a soil would not. For the cases where the classifier can show that hazWasteOnline's worst case substance is unsuitable, the classifier can define their own user-defined substance for use in their classifications.

For work in the UK and Ireland, HazWasteOnline™ also has a number of substances defined in WM3; in particular, a substance called "TPH(C_6-C_{40}) Petroleum Group" which is to be used whenever a waste such as a soil or filter cake contains unknown oils. Effectively, an unknown oil is hazardous at 0.1% by HP7 carcinogenic and HP11 mutagenic, unless a) the laboratory confirms that it doesn't contain any diesel or petrol and b) the amount of the carcinogenic marker, benzo[a]pyrene is less than 0.01% w/w of the TPH; if this requirement is met, the carcinogenic/mutagenic outcome disappears and the next threshold is the ecotoxic threshold (H411) at 2.5%.

5. THE RE-ASSESSMENT

After reviewing the process that created the waste, the next step was to try and identify the most likely metal species to use in the classification. As laboratory tests only give us the total metal concentration for each metal (e.g. zinc) and unlike WAC (which only requires the assessment of the eluate for 12 metals), waste classification requires the classifier to use metal compound concentrations (e.g. zinc oxide).

Apart from chromium and iron, all other total metals concentrations in the filter cake were at minimal concentrations so the selection of a reasonable metal species for them was immaterial.

5.1 Assessment of chromium

The average concentration of chromium(III) in the three samples was 3,310 mg/kg (dry-weight). These concentrations were unexpected as nothing in the hydrolysis of hoof and horn meal could generate such significant quantities of chromium(III). Further investigation found that India is the world's third largest producer of leather and the tanning of animal hides uses chromium. When questioned, the UK supplier of the hoof and horn meal checked with their Indian supplier and confirmed that the product does contain cow hide from the Indian tanning industry.

Chromium(III) sulphate is used as a tanning agent in this industry to treat animal hide to produce a stretchable leather product for use in garments. Chromium(III) sulphate dissolves to give the hexaaqua-chromium(III) cation which under higher pH conditions undergoes a process called olation by which metal ions in the form of polymeric oxides are formed. These oxides react with the proteins in the animal hide to make a more durable material that is less susceptible to decomposition, i.e. leather.

Chromium(III) oxide was therefore used as a reasonable/worst case species for the form of chromium in the filter cake. [It should be noted that the original tanning agent, chromium(III) sulphate does not have any hazardous properties.]

Chromium(III) oxide (CAS 1308-38-9) is not a harmonised entry in the CLP Regulation. Examination of the ECHA databases and other sources (Table 1) found that many sources don't consider chromium(III) oxide to be hazardous. However some notifiers do, so on balance, a user-defined substance, with a conversion factor of 1.462 (total metal to metal compound concentration, based on molecular weight) was created with hazard statements: Acute Tox. 4 H302; Eye Irit. 2 H319; Skin Sens. 1 H317; Resp. Sens. 1 H334.

Data Source	Organisation	Findings (thresholds in %)
CLP Annex VI	Regulation 1272/2008/EC	Not a harmonised substance
Registered Substance Database	ECHA	Not classified
C&L Inventory Database	ECHA	Acute Tox. 4 H302 (25%); Eye Irit. 2 H319 (20%); Skin Sens. 1 H317 (10%); Resp Sens. 1 H334 (10%); Repro. 1B H360 (0.3%) * Classified: 696 notifiers Not classified: 590 notifiers
IARC	International Agency for Research on Cancer	No entry
Pesticides Properties Database	University of of Hertfordshire	No entry
REACH compliant Safety Data Sheet	Sigma Aldrich	Not considered hazardous

Table 1. Assessment of hazardous properties for chromium(III) oxide

* There were 179 notifiers who only registered Repro.1B H360 with no other hazard statements. No other notifiers registered H360. H360 was ignored as it is suspected that this notification must be for a particular composition of chromium(III) oxide and not likely to represent the hazardous properties of chromium(III) oxide.

5.2 Assessment of iron

During the production of the firefighting foam, free sulphide ions are produced which can in turn create hydrogen sulphide emissions. To minimise the production of this hazardous gas, iron(II) sulphate heptahydrate is added to the process to precipitate iron(II) sulphide.

Iron(II) sulphide is not a harmonised substance and therefore does not have an entry in Annex VI of the CLP. Examination of the ECHA databases and other sources (Table 2) found that iron(II) sulphide is not considered hazardous by any actor.

Data Source	Organisation	Findings
CLP Annex VI	Regulation 1272/2008/EC	No entry
Registered Substance Database	ECHA	Not classified
C&L Inventory Database	ECHA	Not classified
IARC	International Agency for Research on Cancer	No entry
Pesticide Property Database	University of Hertfordshire	No entry
REACH compliant Safety Data Sheet	Sigma Aldrich (2 different forms)	Not hazardous

Table 2. Assessment of hazardous properties for iron(II) sulphide

Examination of the sulphide levels in the laboratory results indicated that there wasn't enough sulphide to match (stoichiometric) the measured amount of iron with the amount of iron being a much closer match to the amount of total sulphate. The CLP entry, iron(II) sulphate heptahydrate

(CAS 7782-63-0) was used for the classifications, although neither the sulphate nor the sulphide would have made the waste hazardous.

5.3 Assessment of the Hydrocarbons

The original consultant had EPH(C_{10}-C_{40}) concentrations of ~6,500 mg/kg (dry-weight) with GRO(C_5-C_{10}) concentrations below detection. When classified using the TPH(C_6-C_{40}) Petroleum Group, this created a hazardous outcome due to HP7/HP11. No assessment as to the type of hydrocarbons present in the filter cake was undertaken nor was any attempt made to confirm whether any diesel was present.

The industrial process that generates the filter cake, through the hydrolysis of the hoof & horn meal, does not introduce any petroleum based hydrocarbons into the cake; no defoliants, emulsifiers or other potential oil based chemicals are used. It would therefore not be unreasonable to expect that all the hydrocarbons in the filter cake relate to animal hydrocarbons (fatty acids, cholesterols) and not to petroleum hydrocarbons.

In order to show that the filter cake contains (only) animal hydrocarbons, a more detailed set of tests were conducted to better identify the makeup and type of the hydrocarbons in the filter cake. To this end, the following tests were undertaken:

- **EPH** – this is the basic hydrocarbon test that extracts both the petroleum hydrocarbons and some more polar hydrocarbons such as fatty acids. The preparation method uses a mixture of n-heptane and acetone to extract the hydrocarbons from the filter cake. The resulting extract is passed through a Gas Chromatograph and Flame Ionisation Detector (GC-FID) and presented in a single chromatograph.
- **TPH-CWG** – this method utilises the same preparation method as the EPH above but then passes the extract through an alumina/silica filter to remove the fatty acids and also split the results into an aliphatic component and an aromatic component – the aliphatic component is realised using a non-polar solvent (n-heptane), while the aromatic component utilises a more polar solvent (acetone). Both are then passed through the GC-FID to create two separate chromatographs.
- **TIC** (Tentatively Identified Compounds) – Some of the original extract is passed through a Mass Spectrometer (GC-MS) rather than the flame ionisation detector (GC-FID). The MS breaks up individual molecules (i.e. equivalent to the peaks in the FID chromatograph) to identify specific hydrocarbons from their ions – the laboratories have a library of known ion spectra that is then used by a computer to identify specific organic compounds.
- **SVOC** (Semi Volatile Organic Compounds) – a standard list of organics including PAHs and phenols identified using their GC-MS signatures.

5.4 Results of the EPH, TPH-CWG & TIC analysis

The EPH interpretation for a new set of samples was “Fatty acids and naturally occurring compounds” with EPH (dry-weight) concentration of 6,711 and 6,353 mg/kg respectively (4,599 and 4,596 mg/kg after moisture correction). The TIC analysis identified significant concentrations of cholesterol (C_{27}) and C_{16} and C_{18} fatty acids including octadecanoic and hexadecanoic acid.

Figure 1 is an example of the chromatogram for one of the samples, showing peaks for a number of fatty acids subsequently identifed in the TIC analysis. (Note also the magnitude of the Y-axis scale when comparing with the chromatographs in the following figures.)

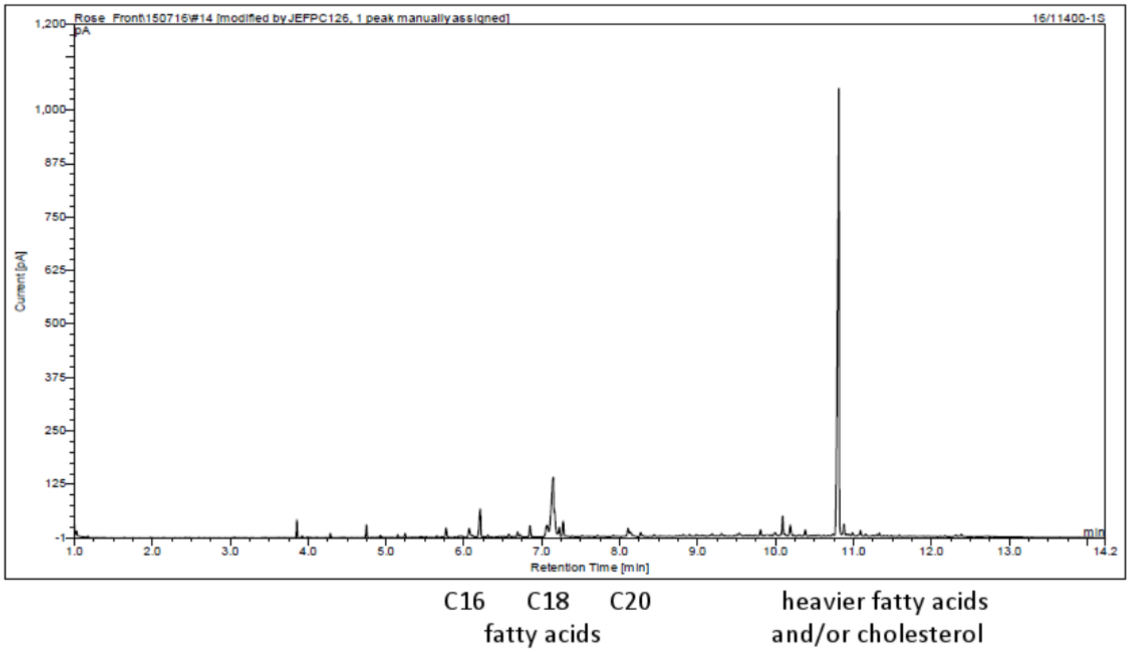

Figure 1. EPH Chromatogram

The TPH-CWG interpretation by the laboratory for both samples was degraded diesel, lubricating oil and possibly naturally occurring compounds, with total TPH-CWG dry-weight concentrations of 1,563 and 1,614 mg/kg (1,061 and 1,167 mg/kg after moisture correction). The chromatograms for one of the samples are shown in Figure 2 (aliphatic) and Figure 3 (aromatic).

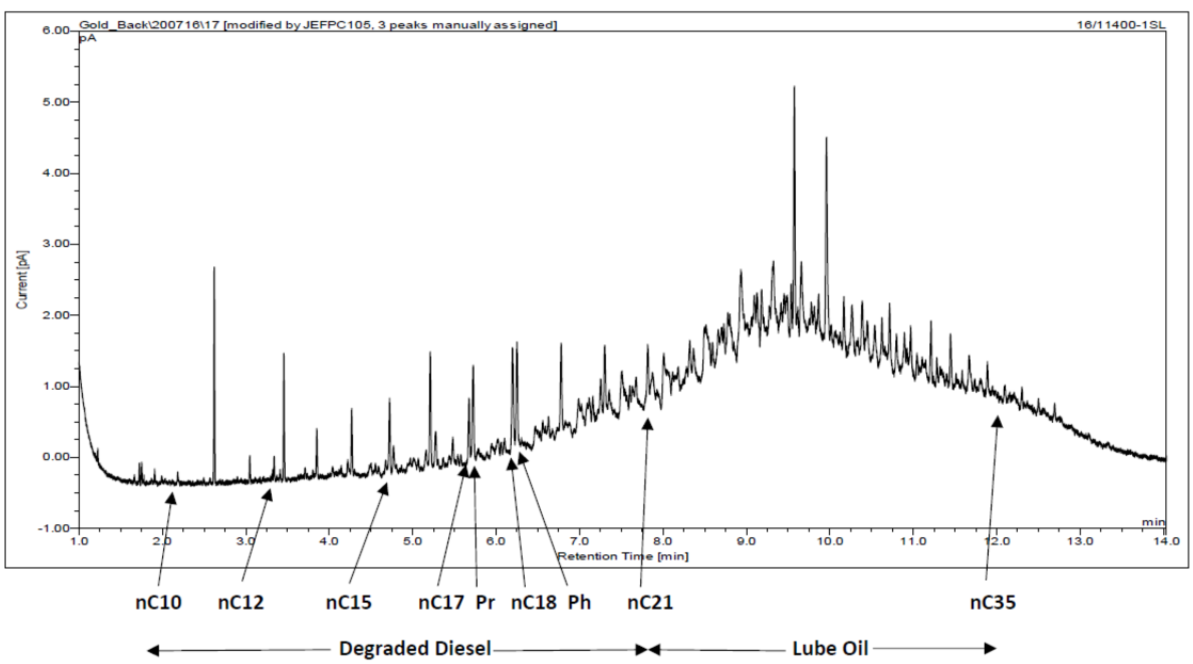

Figure 2. TPH-CWG Aliphatics chromatogram. Pristane (Pr) and Phytane (Ph) are markers used to help identify diesel.

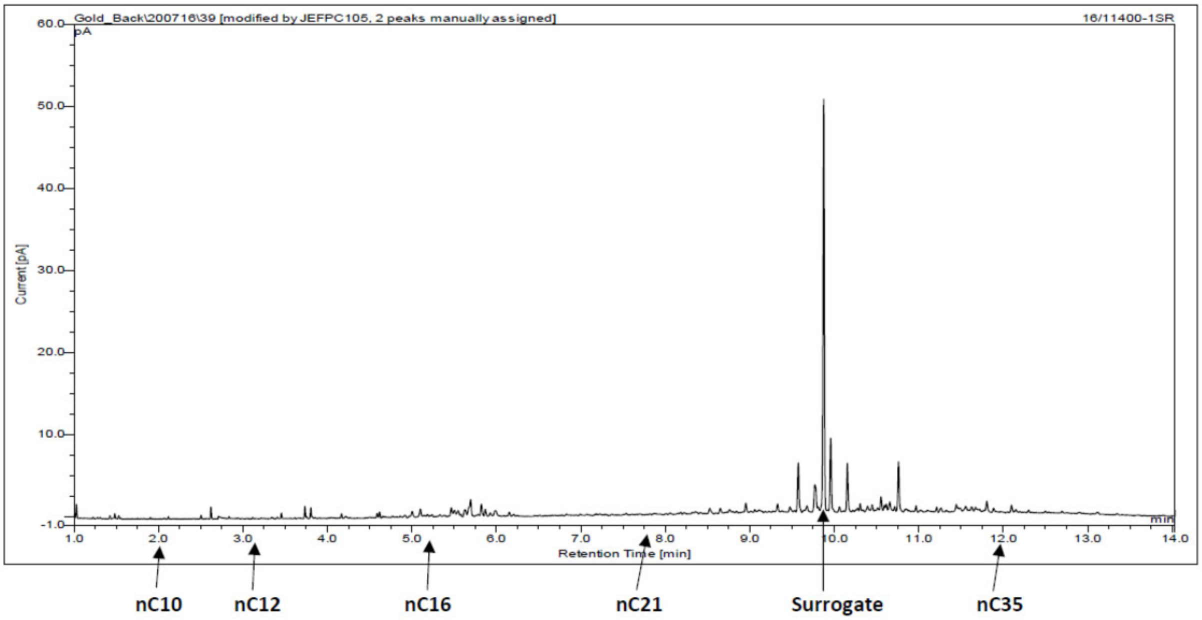

Figure 3. TPH-CWG aromatics chromatogram

It is worth noting that the analysis found low amounts of both PAHs and phenols which could also indicate contamination of the material by oils. The marker, benzo[a]pyrene, could not be used to mitigate the carcinogenic/mutagenic classification of the TPH due to the presence of the diesel.

Further samples were taken and the TPH-CWG results are summarised in Table 3.

TPH-CWG	Mean	95th percentile	Max	Standard Deviation	Standard Error	No. samples
dry weight (mg/kg)	1447	1961	2136	382.5	95.6	16
wet weight (mg/kg)	1299	1900	2070	389.5	97.4	16

Table 3. Statistical summary of the analytical results for TPH-CWG.

The conclusion was that the filter cake was contaminated with small but significant amounts of diesel and lubricating oil. As Angus's process doesn't use diesel and is not known to be releasing any lubricating oil, the suspicion for the source of the oil fell on the hoof & horn meal manufactured in India. This hypothesis was confirmed when the hoof and horn meal was subseqiently analysed and also found to contain degraded diesel and lubricating oil. Further, the amounts of chromium(III) in the hoof & horn meal were of the same order as in the filter cake, while concentrations of iron were an order of magnitude lower than in the filter cake.

Following these results Angus explored three other sources of hoof and horn meal: a European meal, an alternative Indian meal plus a mammalian/avian meal; neither these feedstock nor the resulting filter cakes had any chromium, diesel or lubricating oil in them.

Angus also talked to the supplier about the source of the hydrocarbons and have been assured that the contamination was related to a flood event which inundated the holding area in Mumbai. Initial tests of the filter cake in 2018 supports this statement in that TPH-CWG results are an order of magnitude lower and interpreted as fatty acids and naturally occuring compounds.

6. CONCLUSIONS

This work showed that the filter cake, produced from the hydrolysis of hoof and horn meal, is unexpectedly contaminated by small but significant amounts of diesel and lubricating oil, amounts which exceed the 0.1% hazardous threshold defined in UK guidance for unknown oils. The source of the contamination was tracked back to the hoof and horn meal feedstock sourced from a supplier in India rather than something introduced by the hydrolysis process. Analysis of other sources of hoof and horn meal and their resultant filter cakes didn't find any oil contamination, so filter cakes from these feedstocks would all be classified as non-hazardous.

The filter cake also had raised levels of iron and unexpectedly, chromium. Iron, in the form of iron(II) sulphate is added to the hydrolysis process to mitigate hydrogen sulphide emmissions and raised levels were found in all the filter cakes. In the case of the chromium, it was discovered that the meal included waste from the Indian leather industry which uses chromium(III) sulphate in the tanning process. Testing of other sources of hoof and horn meal (and their filter cakes) showed much lower or negligible levels of chromium. Neither of these metals makes the filter cake waste hazardous. No other metal concentrations or other substances were found to be significant.

The conclusion reached is that the hoof and horn meal was contaminated by TPH at source in India, reportedly by a monsoon flood event which inundated the holding area prior to shipment. If this contamination hadn't happened, the filter cake would not be hazardous.

Angus are undertaking a number of steps to ensure that they can produce a non-hazardous filter cake in the future, including

- Working with the Indian supplier to ensure that future batches of their hoof and horn meal are not contaminated with oil. Initial tests of a new batch of hoof and horn in February 2018 have confirmed that this feedstock is not contaminated by oils.
- Sourcing and testing other sources of hoof and horn meal and obtaining a licence to import these feedstocks into the UK.

Assuming one or both of the above come to fruition, then Angus will be able to show that the filter cake produced during the manufacture of their firefighting foam should be classified as a non-hazardous waste (under List of Waste code: 07 07 10*). Once this evidence has been gathered, Angus will appeal to the UK Secretary of State for a declaration that they agree that the waste is a non hazardous waste and can be handled under the duty of care regulations. Of course, regular sampling and testing will have to continue in case the feedstock suffers from another contamination event.

7. REFERENCES

EA (2015). Waste Classification: Guidance on the classification and assessment of waste (1st Edition 2015): WM3 Technical Guidance. Environment Agency, NIEA, SEPA, Natural Resources Wales. www.gov.uk/government/publications/waste-classification-technical-guidance