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Gore District Council
PO Box 8
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3 July 2015

Attention: Howard Alchin

Dear Howard,

Review of Ouvea Premix Water Inundation Bench Test.

Taha Industries Ltd (Taha) has applied for a resource consent seeking to store Ouvea Premix in a warehouse in Mataura. Part of the information submitted by Taha includes a practical "bench test" undertaken by Jacobs New Zealand Ltd (Jacobs) on behalf of Taha (Ouvea Premix Bench Test). Beca Ltd has been commissioned by Gore District Council to undertake an independent review on the testing undertaken by Jacobs.

Introduction

Beca has been requested to undertake a review of "*the method used for the bag test and the bench top test undertaken by Jacobs*". The review has been requested by the independent hearing commissioners following evidence provided at a hearing suggesting the testing method was not comprehensive enough. In particular the commissioners have asked that the review confirms that the approach used correctly replicates the effects likely to result from flooding and subsequent drying out of Ouvea Premix as stored at Matarua in 1-tonne bags placed on pallets.

Ouvea Premix is derived from aluminium dross from the Tiwai smelter after it has been milled to a consistent particle size and passed through eddy current separators to remove aluminium metal. It is described as being a by-product of Tiwai Point's aluminium smelting operations. The final product contains 20 to 40% by weight aluminium nitride (AlN). The AlN has potential residual value to Taha for use in fertiliser as it reacts with water to release nitrogen.

Pending beginning production of a fertiliser product, Taha has stored Ouvea Premix in a warehouse in Mataura. The warehouse is located adjacent to the Mataura river in an area recognised as being at risk of flooding. Taha is applying for a resource consent to store Ouvea Premix at the Mataura site subsequent to a quantity of the material already being stored at the site. The storage of Ouvea Premix is a discretionary activity as it is recognised as being a potentially hazardous material due to its ability to react spontaneously with water and potentially evolve ammonia and hydrogen.

Background

Typically residues from an aluminium smelter containing more than 45% metallic aluminium are called 'skimmings' and residues with less than 45% metallic aluminium are called 'dross'. Dross from a primary smelter is typically called 'white dross' and comprises 20% to 45% metallic aluminium and occurs as a fine white powder. (Tsakiridis, 2012). Primary production slags are classified as toxic and hazardous wastes in the European Catalogue for Hazardous Wastes (Environmental Protection Agency, 2002). This categorisation is primarily due to its leachability and its high reactivity with water, potentially leading to the formation of noxious gases such as ammonia (Tsakiridis, 2012).

Of primary concern to the storage of the Ouvea Premix at Mataura is the level of ammonia that may be produced by the material upon contact with water. Ammonia is produced from the hydrolysis of aluminium nitrides present in the Ouvea Premix. At room temperature the overall net chemical reaction for ammonia (NH_3) generation being:

$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$$

Laboratory Bench Test Summary

Jacobs undertook a laboratory bench test on the Ouvea Premix whereby they placed 500g of the loose material into a jar with 1.2L of water. They measured the pH of the water and the ammonia levels in the headspace of the jar at a number of time intervals up to a total period of 50hrs. At the conclusion of the experiment the total ammonia in the water from the jar was also analysed.

The results of the test are graphed in **Figure 1** below. The final concentration of ammonia in the water from the jar at the end of 50hrs was given as 220mg/L (N-NH_3). We assume the experiment was conducted at 'room temperature'.

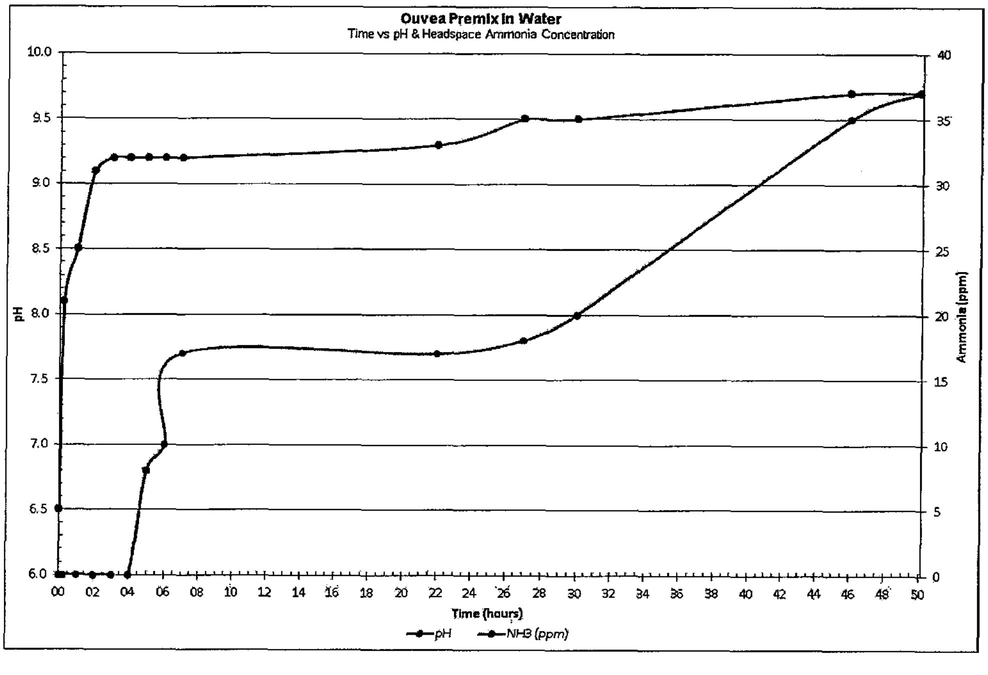

Figure 1: Graph of Jacobs Ouvea Premix Bench Test test results showing pH of water and ammonia headspace concentration

Based on **Figure 1** it can be seen that the reaction of aluminium nitride with water to form ammonia begins almost immediately, as indicated by the rise in pH. Ammonia produced by the reaction readily dissolves in water and it is alkaline; the dissolution of ammonia in water raises the pH. At pH <9, virtually all the ammonia present in the water dissociates to raise the pH. Once the pH of the water rises above approximately 9.0 to 9.1, 'free' ammonia starts to occur in the water.

Consequently the vapour pressure of ammonia begins to rise and subsequently ammonia starts to evaporate into the gaseous phase.

Applying Henry's Law and Ideal Gas Law it can be theoretically shown (see **Calculation 1**) what the ammonia concentration in the headspace of the test jar would be given the concentration of ammonia measured in the water.

$$Concentration\ of\ ammonical\ nitrogen\ in\ solution\ [N_{aq}] = 220g.m^{-3}$$

$$Henry's\ Law: P_i = \frac{C_i}{K_i}$$

$$P_{NH_3} = \frac{[N_{aq}](g.m^{-3})}{Molar\ Mass\ of\ nitrogen\ (g.mol^{-1}) \times Henry's\ Law\ Constant\ (mol.m^{-3}Pa^{-1})}$$

$$= \frac{220}{14.007 \times 0.750}(Pa)$$

$$P_{NH_3} = 20.9\ Pa$$

$$Ideal\ Gas\ Law: C_i = \frac{P_i}{RT}$$

$$At\ 20°C, the\ concentration\ of\ ammonia\ in\ the\ air\ [Ammonia_g]$$

$$[Ammonia_g] = \frac{P_{NH_3}(Pa)}{Gas\ Constant\ (m^3.Pa.mol^{-1}K^{-1}) \times Temperature\ (K)}$$

$$= \frac{20.9}{8.314 \times 293.15}(mol.m^{-3})$$

$$[Ammonia_g] = 0.00859mol.m^{-3}$$

$$At\ 20°C, the\ concentration\ of\ ammonia\ in\ the\ air\ (ppm) is$$

$$ppm = [Ammonia_g](mol.m^{-3}) \times 24055.0(mL.mol\ air^{-1})$$

$$= 0.00859 \times 24055.0$$

$$= 207\ parts\ per\ million\ of\ ammonia\ without\ dissociation$$

$$At\ pH\ 9.7\ and\ 20°C, the\ fraction\ of\ the\ ammonia\ existing\ as\ NH_3\ (undissociated)$$
$$in\ the\ solution\ is\ approx. 66.6\%\ of\ the\ ammonia\ concentration.$$
$$ppm\ ammonia = 0.666 \times 207ppm$$
$$= 138ppm$$

Calculation 1: Application of Henry's law and Ideal Gas Law to Jacobs Ouvea Premix Bench Test results. Henry's Law Constant for ammonia taken from (Sander, 2015) and percentage ammonia speciation was taken from (Thurston, Russo, & Emerson, 1979).

While the theoretical ammonia concentration of 138ppm in **Calculation 1** is higher than 37ppm as measured by the bench test, very small variations in temperature and pH affect the result as can the pressure in the bottle used for the bench test, if it was sealed. Therefore the results coincide for all practicable purposes and in this regard the test results are reasonable.

Finally, the question arises as to whether the level of ammonia produced by the 50 hour bench test represents the levels of ammonia that would be produced as the result of a flood. A literature search on the hydrolysis of aluminium nitride indicates one of the more frequently quoted chemical reaction models is that proposed by Bowen et.al. (Bowen, Highfield, & Ring, 1990). Bowen et.al. performed their experiment on aluminium nitride, as used for industrial purposes. Their results indicate that upon contact with water 80% of the aluminium nitride material had reacted after 24hrs.

The Bowen et.al. model is clearly at odds with the bench test results as it indicates that the level of ammoniacal nitrogen in the water at the conclusion of the bench test after 50 hours should be orders of magnitude more than what was found. Assuming 500g Ouvea Premix at 30% aluminium nitride content and 80% conversion to ammonia after 24 hours the reaction should yield closer to 34,000mg/L N-NH_3 when compared with 220mg/L. The bench test indicates that the aluminium nitride in the Ouvea Premix is *significantly* less reactive than that for a more pure form of aluminium nitride.

Further research indicates the hydrolysis reaction of aluminium nitride powders is affected by thermal oxidation (Li, Qiu, & Xu, 1997). Li et.al. "*describe[s] the influence of oxidation treatments at high temperature in air on the hydrolysis of [aluminium nitride] powder*". Assuming the dross Taha takes delivery of is sourced from the top of casting crucibles in the furnace, this material forms a layer on top of molten aluminium where it is directly subjected to gas burners at elevated temperatures (>700°C) in the presence of air. On this basis we can easily assume that the aluminium nitride present in the dross has been subjected to thermal oxidation. Li et.al. go on to explain that the rate of hydrolysis is significantly reduced for aluminium nitride powders treated at temperatures greater than 800°C as an aluminium oxide coating forms on the aluminium nitride particles. Li et.al. present a graph showing the hydrolysis of aluminium nitride after thermal treatment at a number of different temperatures which is reproduced in **Figure 2**.

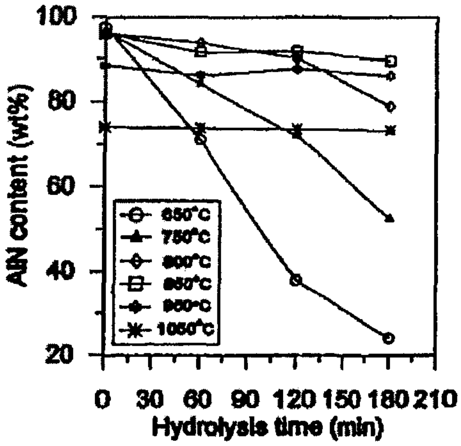

Figure 2: Rate of hydrolysis for aluminium nitride powders after thermal oxidation treatment.
Source (Li, Qiu, & Xu, 1997)

In the absence of any other explanation, the work by Li et.al. presents a reasonable explanation for the low ammoniacal nitrogen yield that was obtained from the Ouvea Premix as used in the bench test. The overall ammoniacal nitrogen yield from the 50 hour bench test is described by **Calculation 2**.

$$\mathit{Bench\ top\ test: Solution\ nitrogen\ concentration\ after}\ 50\ \mathit{hours}\ [N_{aq}] = 220 g.m^{-3}$$

$$\mathit{Assuming\ a}\ 30\%\ AlN\ \mathit{compound:}$$

$$\mathit{Aqueous}\ NH_3 - N\ \mathit{yield\ after}\ 50\ \mathit{hours} = \frac{\mathit{Moles\ nitrogen\ in\ solution}}{\mathit{Moles\ of\ nitrogen\ total}}$$

$$\mathit{Yield} = \frac{\left(\frac{[N_{aq}](g.m^{-3}) \times \mathit{Volume}(m^3)}{\mathit{Molar\ mass}\ N(g.mol^{-1})}\right)}{\left(\frac{\mathit{Mass}\ (g) \times \mathit{Mass\ fraction}}{\mathit{Molar\ mass}\ AlN(g.mol^{-1})}\right)}$$

$$= \frac{\frac{220 \times 0.0012}{14}}{\frac{500 \times 0.3}{40.99}}$$

$$\mathit{Yield} = 0.5153\%$$

Calculation 2: Ammonical nitrogen yield based on Jacobs Ouvea Premix Bench Test results.

Bag Test Summary

Following the bench test, a second trial was undertaken whereby four 1 tonne bags of Ouvea premix were placed in a skip and partially inundated with water (Jacobs New Zealand Ltd, 28 April 2015). The four bags average weight was 1,009kg. One bag had water ingress to a depth of 160mm and gained 128kg in weight.

Using this information in conjunction with the results gained from the bench test and assuming the Ouvea Premix contains 30% aluminium nitride we can calculate a theoretical concentration of ammonia likely to be found in a half inundated, 1m^3, 1 tonne bag. This is shown in **Calculation 3**. The calculation is based on the *yield* of ammonia found for the jar test, assuming the bag absorbs an equivalent mass of water per mm of height as per the bag test.

Based on the bench test results, which found a vapour concentration of 37ppm for a concentration of 220mg/L ammoniacal nitrogen, **Calculation 3** indicates that a half inundated 1 tonne bag would be expected to have an ammonia vapour concentration of approximately 112ppm after 50 hours. Based on the vapour concentration as per **Calculation 1** the theoretical gaseous ammonia concentration for the same half inundated bag scenario would be 418ppm.

Again these theoretical calculated results are consistent with the second trial results that were supplied (Jacobs New Zealand Ltd, 28 April 2015) where it is stated that four days after the trial one of the bags had inflated and was found to have a concentration of 100ppm ammonia. It has been presumed that this was Bag 1 where water had penetrated to a depth of 160mm as the remaining three bags 2 to 4 were described as being dry at the conclusion of the bag trial.

$$For\ a\ 1m^3\ bag\ (mass\ 1009kg) immersed\ to\ 0.5m\ absorbing\ 400L\ of\ water:$$

$$Assuming\ the\ yield\ is\ consistent\ with\ the\ bench\ top\ test$$

$$Moles\ of\ NH_3 - N\ in\ solution = Yield \times Moles\ of\ AlN\ nitrogen\ submerged$$

$$= Yield \times \frac{AlN\ Mass\ fraction \times Fraction\ of\ bag\ submerged \times Mass\ of\ bag(kg)}{Molar\ mass\ AlN\ (kg.mol^{-1})}$$

$$= 0.005153 \times \frac{0.3 \times 0.5 \times 1009}{0.04099} (mol)$$

$$Moles\ of\ NH_3 - N\ in\ solution = 19.027mol$$

$$[N_{aq}] = \frac{Moles\ of\ nitrogen\ in\ solution(mol)}{Volume\ of\ solution(m^3)} \times Molar\ mass\ N(g.mol^{-1})$$

$$= \frac{19.026}{0.4} \times 14(g.m^{-3})$$

$$[N_{aq}] = 665.9g.m^{-3}$$

$$Applying\ the\ experimental\ aqueous\ NH_3N\ concentration\ (220g.m^{-3})\ and\ the\ headspace\ ammonia\ concentration\ (37ppm) from\ the\ bench\ test\ proportionally\ to\ the\ theorised\ concentration\ in\ the\ 1m^3\ bag\ as\ described\ above:$$

$$ammonia_{bag}(ppm) = ammonia_{bench}(ppm) \times \frac{[N_{aq}]_{bag}(g.m^{-3})}{[N_{aq}]_{bench}(g.m^{-3})}$$

$$ammonia_{bag} = 37 \times \frac{665.9}{220} (ppm)$$

$$= 112ppm$$

$$OR;\ by\ applying\ \textbf{Calculation}\ 1\ to\ the\ theorised\ concentration\ of\ 665.9g.m^{-3} in\ the\ 1m^3\ bag:$$

$$ammonia_{bag} = 418ppm$$

Calculation 3: Ammonia concentration calculated to occur in a 1 tonne bag based on Jacobs Ouvea Premix Bench Test results.

Extrapolation of Results

Extrapolating the results consistent with the bench and bag test, indications are that after approximately 50 hours a minimum vapour concentration of approximately 100ppm can be generated in a bag of Ouvea Premix which has been partly inundated in water. This scenario represents just one bag and at a 'snapshot' of time. Assuming the following:

- 10,000 bags piled 3 high in the warehouse(s) and the bottom layer only is flooded (i.e. 3,330 bags affected);
- based on the bag trial, one in four bags leaks (i.e. ¼ of 3,330 is 833 bags); and
- after 50 hours the ammonia concentration within those bags is a minimum of 100ppm.

The concentration of ammonia in "a" bag is driven by the vapour pressure, not the air volume of the bag. Similarly, due to diffusion, a warehouse with 830 bags at 100ppm (and based on the bag trial, the bags will be warm at 25°C due to the exothermic reaction, hence increasing diffusion) will also have a concentration of 100ppm after approximately 50 hours. If 830 bags can diffuse even a small amount it is conceivable that such an overall mass of material will reach equilibrium within the confines of the warehouse.

A second issue that arises is that the bench test experiment was concluded after 50 hours, whereas in a flood it might be expected that this material would be wet for at least a week, (i.e. >168 hours). While Li et.al. describe the influence of high temperature oxidation effects on the hydrolysis of aluminium nitride powder, they only examine the impact over the first 3 hours and under artificial laboratory conditions at 60°C (Li, Qiu, & Xu, 1997).

Our literature search found a paper which examined longer aluminium nitride moisture exposure times (Li, Nakamura, Shirai, Matsumaru, Ishizaki, & Ishizaki, 2006). Unlike Bowen, this paper reports a three stage mechanism for hydrolysis of aluminium nitride powders. *"The first is an induction period, during which the surface aluminum oxide/oxyhydroxide layer is slowly hydrolysed. The length of this period is affected by the surface layer composition, which is in turn affected by the manufacturing methods".* Then, *"The second stage is one of fast hydrolysis controlled by a chemical reaction on the unreacted AlN surface".* Nakamura Li et.al. (not to be confused with the paper by Li, Qiu, & Xu) present a graph showing the rate of hydrolysis for aluminium nitrides manufactured by a number of different ways which is reproduced in **Figure 3**.

Nakamura Li et.al. performed their experiment on pure aluminium nitrides as used for industrial purposes. The most heavily oxidised form of aluminium nitride used in their experiment appears to be that described as "B1" as shown in **Figure 3**. It can be seen in **Figure 3** that there is in fact very little hydrolysis apparent for the first approximately 150 hours. This is consistent with the overall trial findings and the earlier mentioned paper by Li et.al. After this initial time however, the reaction rate significantly increases. Critical to the mechanisms proposed by both Bowen and Nakamura Li is that the hydrolysis of the aluminium nitride continues through to an 80% yield as long as free water is present. Put another way, in a saturated bag, ammonia will continue to be evolved until all the water has reacted. If this 3-stage mechanism applies to the aluminium nitride as present in the Ouvea Premix, than the bench testing undertaken by Jacobs was too short to adequately assess the potential after effects of a flood situation and the potential difficulties that may exist during the clean-up phase.

It should be noted that Nakamura Li et.al. presented their findings for hydrolysis of aluminium nitride in a high humidity atmosphere but it is *not* our hypothesis that this is analogous to the Ouvea Premix material as stored in a warehouse. In a warehouse the reaction rate is not just limited by diffusion of atmospheric humidity through the storage bag but additionally by diffusion through the outside surface of the bagged material and this being the case, the evolution of ammonia due to atmospheric humidity would be expected to continue to diminish overtime.

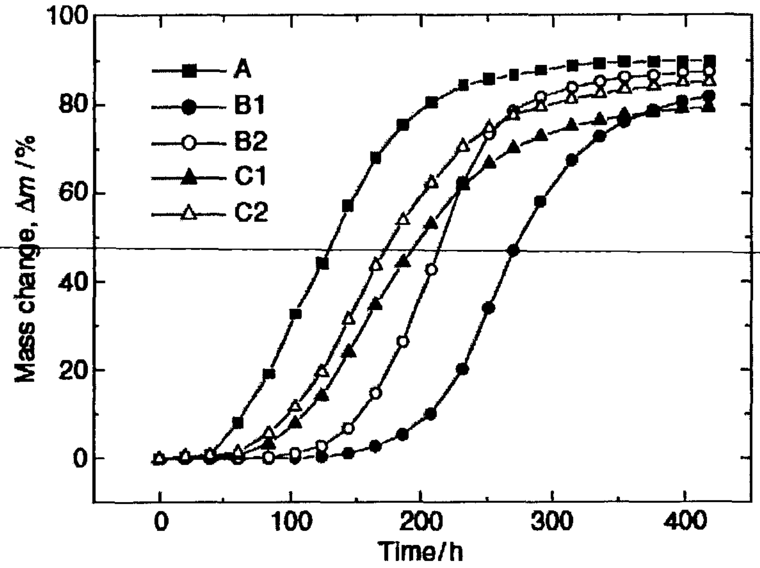

Figure 3: Mass change in the degradation of aluminium nitride powders in moist air at 20°C
Source, (Li, Nakamura, Shirai, Matsumaru, Ishizaki, & Ishizaki, 2006)

Summary

The experiments undertaken in the Ouvea Premix trials presented by Jacobs appear to present reasonable results which at first glance appear to be explained by published research. The literature review indicates that the duration of the bench trial for 50 hours is potentially too short to adequately assess the effects of flood. Our literature review indicates ammonia may continue to evolve from the Ouvea Premix, for a period beyond the duration of exposure of the material to elevated water levels and may potentially increase in rate over time. Once a bag has absorbed water, indications are that ammonia will continue to be evolved until all the water has reacted, even after the flood waters have dropped.

Our interpretation of the results is that in the event of a flood, a contingency plan would be required to manage the material stored in the warehouse in order to prevent adverse effects arising from the generation of ammonia. We believe that this contingency plan would need to clearly explain how any actions required would be conducted in an environment that is likely to involve elevated levels of ammonia in the air.

Should you have any questions please don't hesitate to contact the undersigned.

Yours sincerely
Brian Mills
Senior Environmental Scientist

on behalf of
Beca Ltd
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Bibliography

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ANDERSONLLOYD

23 July 2015

For: Howard Alchin

Gore District Council
PO Box 8
GORE 9740

By email - HAlchin@goredc.govt.nz

Dear Howard

Bond

1. We refer to your email instruction dated 20 July 2015 where you sought advice on the ability of Council to impose a bond.

Advice

2. We have reviewed the evidence of Mr Cubitt.

3. We advise that the Commissioners are lawfully able to impose a bond as a condition of resource consent under section 108A RMA in these circumstances. The Commissioners need to decide if consent is to be granted, and if so whether a bond is justified, and if so its amount.

4. Any bond should focus on securing compliance with a condition of consent. Assuming consent is granted we would expect a condition requiring removal of all consented material in excess of the quantities permitted by the District Plan at the conclusion of the consent term. We note condition (vi) proposed in draft by Mr Cubitt achieves this. To secure compliance with that condition a bond could be required.

5. We do agree with Mr Cubitt that a condition of consent should not require disposal of material at a landfill as the only option. A condition should focus on removal of the material from site, and its lawful disposal or storage elsewhere. However, we do consider that a bond could factor in the cost of disposal or storage of material in the event that the consent holder does not comply with the conditions of consent. Ultimately if Council does need to rely on the bond and remove material from the site it would need to have the bond cover the cost of transporting it and either storing it or disposing of it in a lawful manner somewhere. We consider that the cost of that disposal is directly related to the purpose of the condition and would be an essential aspect of a bond requiring the removal of material from the site.

Reasoning

6. Section 108A RMA enables the Commissioners to require imposition of a bond to secure compliance with a condition of consent.

7. We agree with Mr Cubitt that a condition of consent should be careful to specify what needs to happen with the product when it is removed from site. We consider it is not necessarily for a resource management purpose to dictate that material should be disposed of or stored at a particular location. We consider any such condition should require removal from the site and either storage or disposal at some lawful location. How the applicant does so is for them to

determine. Similarly if Council needs to rely on the bond Council would need to determine how and where the product is stored or disposed of lawfully at the conclusion of the consent. We therefore recommend a condition along the lines of:

All ouvea premix and sulphate of ammonia stored on site in excess of the quantities permitted by the District Plan is to be removed from the site and either stored or disposed of at a lawful location prior to the expiry of this consent.

The applicant is to provide a bond of $ (including GST). The bond is to be provided in cash, or if not in cash in writing guaranteed by a guarantor. The form of the bond document and the guarantor are to be approved by the Chief Executive Officer of the Gore District Council as being acceptable to secure compliance with this condition.

8. In setting the bond amount Council should take into account the likely costs of removal and disposal or storage of the material in the event that the consent holder does not do so. Normally a contingency is added to take into account any unforeseen costs or potential cost escalation over time. 25% is usual. We note removal of this material may well be a specialised task with the potential for variable cost which may justify a higher level of contingency.

Yours faithfully
Anderson Lloyd

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Resource Management Act 1991

108A Bonds

(1) A bond required under section 108(2)(b) may be given for the performance of any 1 or more conditions the consent authority considers appropriate and may continue after the expiry of the resource consent to secure the ongoing performance of conditions relating to long-term effects, including—

(a) a condition relating to the alteration or removal of structures:

(b) a condition relating to remedial, restoration, or maintenance work:

(c) a condition providing for ongoing monitoring of long-term effects.

(2) A condition describing the terms of the bond to be entered into under section 108(2)(b) may—

(a) require that the bond be given before the resource consent is exercised or at any other time:

(b) require that section 109(1) apply to the bond:

(c) provide that the liability of the holder of the resource consent be not limited to the amount of the bond:

(d) require the bond to be given to secure performance of conditions of the consent including conditions relating to any adverse effects on the environment that become apparent during or after the expiry of the consent:

(e) require the holder of the resource consent to provide such security as the consent authority thinks fit for the performance of any condition of the bond:

(f) require the holder of the resource consent to provide a guarantor (acceptable to the consent authority) to bind itself to pay for the carrying out of a condition in the event of a default by the holder or the occurrence of an adverse environmental effect requiring remedy:

(g) provide that the bond may be varied or cancelled or renewed at any time by agreement between the holder and the consent authority.

(3) If a consent authority considers that an adverse effect may continue or arise at any time after the expiration of a resource consent granted by it, the consent authority may require that a bond continue for a specified period that the consent authority thinks fit.