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2007: Biological Scrubber for Hydrogen Sulphide Removal. A New Zealand first treating air stream with up to 300ppm of hydrogen sulphide. Hydrogen sulphide removal is in excess of 99.4% at a flow rate of 0.8 cu.m./sec

Biological Scrubber for Hydrogen Sulphide Removal

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ABSTRACT:
A biological scrubber is being used to remove up to 300ppm of hydrogen sulphide from a vent stream on a sulphur melter at a fertiliser plant. This is a first for this technology in New Zealand and the paper reports on 3 years of successful operation. Odour complaints from neighbours due to emissions from this source ceased once the unit was operational. The biological scrubber was chosen as it has a footprint of only 10% of a traditional soil bed filter, and there are no continuous dosing of chemicals required as for a standard hypochlorite based chemical scrubber. Thus this new technology is cleaner and more environmentally friendly. The biological scrubber is achieving reductions in hydrogen sulphide of over 99% on an ongoing basis. This technology is also applicable to a wide range of applications including emissions from trade waste plants, municipal wastewater treatment plants, biogas generation plants, pump station vents and food processing plants emitting odorous gases.

1. INTRODUCTION
Sulphuric acid is manufactured worldwide in large quantities for a variety of uses such as in the production of single super phosphate. The first step in the manufacture of sulphuric acid is to melt sulphur. In the case being considered, the sulphur is melted in underground brick lined pits utilising steam coils for heat. This brings the sulphur to a temperature of 135° C and allows it to be pumped directly to a burner via steam jacketed pipes. An unwanted by-product of the sulphur melter operation is the evolution of an odorous gas stream containing hydrogen sulphide and traces of sulphur dioxide. The gas stream also contains some particulate sulphur. The temperature of this gas stream ranges from 60°C to 80°C, with variable humidity. The hydrogen sulphide concentration in this gas ranges typically from less than 1 ppm to 200 ppm, but has on occasion peaked at 400ppm. The sulphur dioxide concentration ranges typically from 5 ppm to 35 ppm. The discharge of this gas stream has resulted in odour complaints from neighbours located approximately 100 m from the site. As part of Ravensdown Fertiliser's Air Discharge Consent, this hydrogen sulphide odour had to be controlled.

Originally, a soil bed biofilter was installed by others and operated for 6 years. It failed a number of times, most probably because of accumulation of sulphate and acidification of the biofilter packing. It proved unreliable, difficult to control, and at times required manual intervention. Primarily this was because it was slow to adapt to changes in hydrogen sulphide gas concentrations and temperatures from the cyclic process, and it was too small. The biofilter was rebuilt each time, but the complaints from neighbours continued. A decision was then taken to look at alternative technologies.

A wet chemical scrubber using sodium hydroxide and an oxidant such as sodium hypochlorite or hydrogen peroxide was considered. However the anticipated chemical costs were excessive based on a similar unit that had been operated at another fertiliser plant.

A biological scrubber was then considered as it promised the following benefits as well as meeting the scrubbing requirements:

- Smaller footprint than the soil bed filter (typically about 10%)
- Completely enclosed operation eliminating influence of weather and outside temperature
- Very low chemical consumption costs – occasional nutrients and caustic only
- Exhaust able to be discharged via a higher stack providing some dispersion
- Relatively simple operation
- Able to withstand fluctuating loads and stand-by periods

Biological scrubbers have been proven to be very effective in scrubbing hydrogen sulphide in Orange County, California (Gabriel and Deshusses, 2003; Gabriel et al., 2003). Recent accomplishments in California have included the successful conversion of chemical scrubbers to biological scrubbers while keeping a very low gas contact time. The biological scrubbers minimised on-going chemical consumption costs while achieving treatment objectives.

2. BIOLOGICAL SCRUBBER DESIGN AND OPERATION

The principle of a biological scrubber is that the waste air stream is contacted with a scrubbing solution in a vessel packed with an inert support material. On the surface of the packing, a biofilm of pollutant degrading micro-organisms forms which aerobically degrades the absorbed pollutants (Cox and Deshusses, 1998).

At the Ravensdown plant, the warm exhaust gas contains small quantities of particulate matter, which is removed in a small venturi scrubber located just before the inlet of the biological scrubber. In addition to removing the sulphur particles, the venturi scrubber cools and humidifies the gas stream and dampens any sudden fluctuations in temperature. These operations are important to avoid clogging of the biological scrubber packing, and to ensure favourable conditions for the micro-organisms.

The biological scrubber was designed for a gas flow rate of 0.8 cubic metres per second at an operating temperature of 40ºC. The biological scrubber was designed for the maximum hydrogen sulphide and sulphur dioxide inlet concentrations, and to provide a buffering capacity for the fluctuating loads. The gas residence time selected was a function of these parameters and to achieve a removal of hydrogen sulphide of over 96%. The support for the micro-organisms is made from an inert porous foam material, which gives a high surface area but still allows sufficient drainage and high porosity for gas flow. The biological scrubber is constructed entirely of corrosion resistant fibreglass in order to handle the corrosive hydrogen sulphide gas, the humid conditions and the corrosive circulating liquors.

The biological scrubber vessel has an integral sump in its base, and from this a circulating pump irrigates the top of the packing. Nutrients (N, P, K and traces) are dosed once per day to the circulating stream from a 200 litre container of a diluted liquid fertiliser based solution. Caustic is dosed from a 200 litre container. The caustic dosing is on demand only when the pH drops below pH 3. The purpose of the caustic is to raise the pH so that the scrubber blowdown is not too acidic for the drains. Fig 1 is a simplified flowchart of the biological scrubbing system.

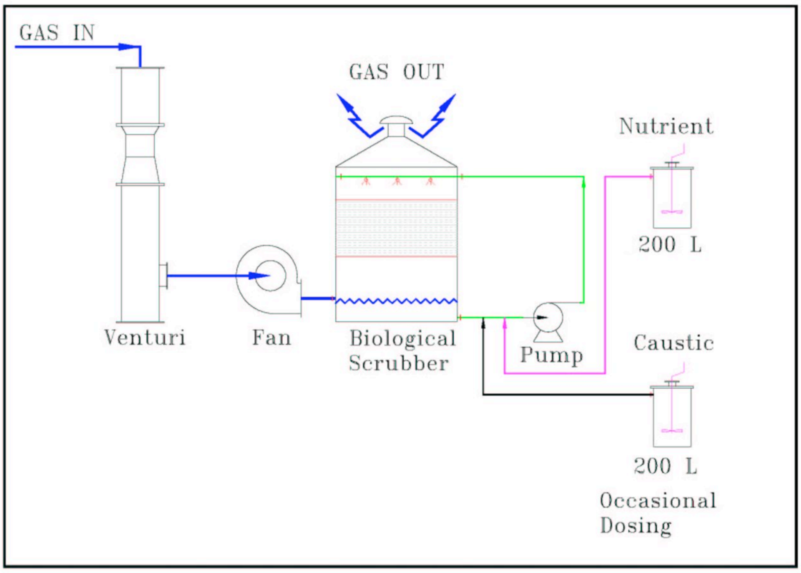

Fig 1: Flowchart of Biological Scrubber

The biological scrubber was commissioned on the 4th February 2004. Sludge from the Christchurch City Council's wastewater treatment plant was dosed into the circulating liquor in order to seed the system and establish the micro-organism population. As mentioned, a metered stream of essential nutrients (N, P, K, + traces) is fed to the system daily, over a period of half an hour, to maintain healthy sulphide degrading culture. At the same time, a small stream is purged from the system to remove the biologically-formed sulphate.

Photo 1: Biological Scrubber At Start-up

3. HYDROGEN SULPHIDE MONITORING SYSTEM

Hydrogen sulphide concentrations were initially measured using App-Tek Odalog meters, which allowed continuous monitoring of the biological scrubber operation. A solenoid switched the unit between the inlet and outlet of the biological scrubber every 3 minutes allowing the same instrument to measure both the inlet and outlet concentrations. The solenoid routinely got sulphur dust in it and would jam and require weekly cleaning. The gas pump had similar problems. The accuracy of these measurements is approximately ± 2 ppm for the higher inlet concentrations, and ± 1 ppm for the lower outlet concentrations. When uploading the data typically weekly, it was found that the data was good immediately after cleaning, but as the week went on the unit would drift and cease working. This resulted in extended periods of nil readings. The data presented in this paper has been identified as being representative data from times when the Odalog was functioning correctly.

Beginning in early 2006, Draeger tubes were used to verify the Odalog results. The measurements suggested that there was carryover from the inlet cycle when measuring the outlet with the Odalog. This combined with the mechanical failures of the solenoid and gas pump led to discontinuing the use of the Odalog. The problems stressed the needs for using two separate gas meters when monitoring a reactor exhibiting a high pollutant removal. From March 2006, the hydrogen gas concentrations were measured with a handheld gas analyser manufactured by Biosystems Ltd in the USA (Model: Toxipro 13-264) three times a week. This hand held unit is calibrated every 180 days with calibration gas and air. The data post March 2006 is thus more consistent and reliable. The data presented in this paper has been identified as being representative in that time period. The limitation from the hand held unit is whole number resolution, typically giving a result of 0 ppm when the actual concentration is between 0.00 ppm and 0.49 ppm. An analyser capable of measuring ppb on the outlet gas has been investigated but the expense could not be justified.

4. HYDROGEN SULPHIDE REMOVAL RESULTS

Figs 2 and 3 are the hydrogen sulphide gas concentrations into and out of the biological scrubber, and the hydrogen sulphide removal over the first 8 days of operation respectively. The inlet hydrogen sulphide concentrations fluctuate widely as they are directly dependent on the operation of the sulphur melter, which is very variable. Initially, the outlet hydrogen sulphide concentrations varied in line with the varying inlet concentrations, but after just 2 days the micro-organism population in the biological scrubber was sufficiently established to cope with the varying inlet concentrations.

As shown in Fig 3, the hydrogen sulphide removal performance of the biological scrubber was in excess of 96% within the first 8 days operation.

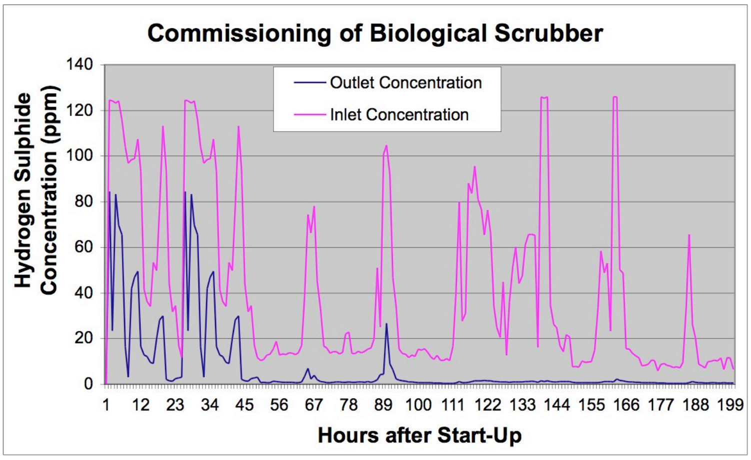

Fig 2: Hydrogen sulphide concentrations (ppm) in and out for first 8 days

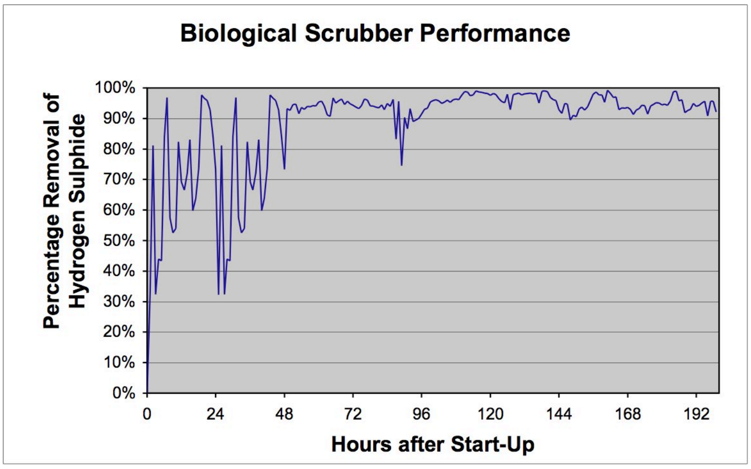

Fig 3: Hydrogen sulphide removal performance for first 8 days

Figs 4,5 and 6 report the hydrogen sulphide gas concentrations into and out of the biological scrubber, and the hydrogen sulphide removal over 40 months of operation. When using the Odalog, the hydrogen sulphide concentrations were logged at 3 minute intervals. This produced a very large set of data, which needed to be reduced to a smaller set in order to remove short time variations such as the ones reported in Fig 2. Thus each day was analysed separately to determine that the process was stable and the data representative. As mentioned previously there were several technical failures with the Odalog analyser and there are limitations with the accuracy and reliability of this data. These limitations do not apply to Fig 6. Annual maintenance shutdowns has left some gaps in the data. In addition most of the outlet data is 0 ppm due to whole number resolution on portable analysers. These limitations need to be considered when viewing Figs 4 and 5.

Overall, for the vast majority of time, a removal performance of over 96% was achieved. There were a number of times when there were technical difficulties and the biological scrubber was not operated as intended. However even in these instances a removal performance of over 88% was achieved (Fig 5).

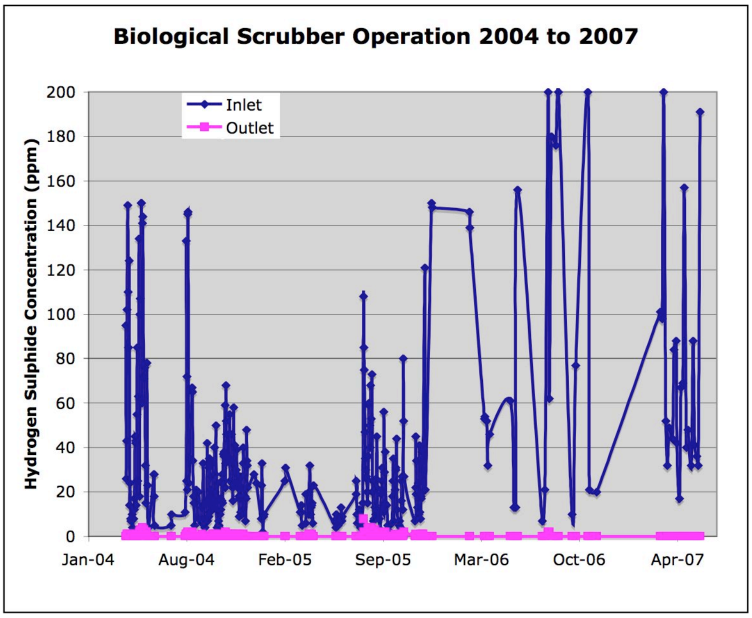

Fig 4: Biological Scrubber Operation from March 2004 to June 2007

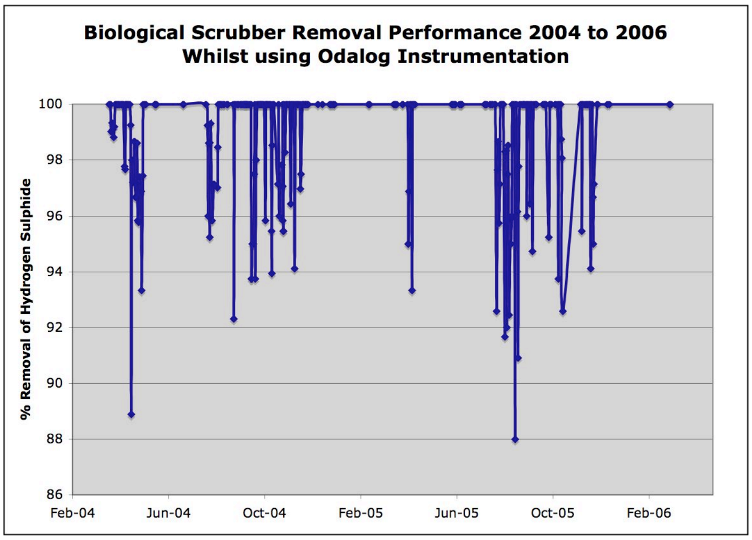

Fig 5: Hydrogen Sulphide Removal Performance from March 2004 to Feb 2006

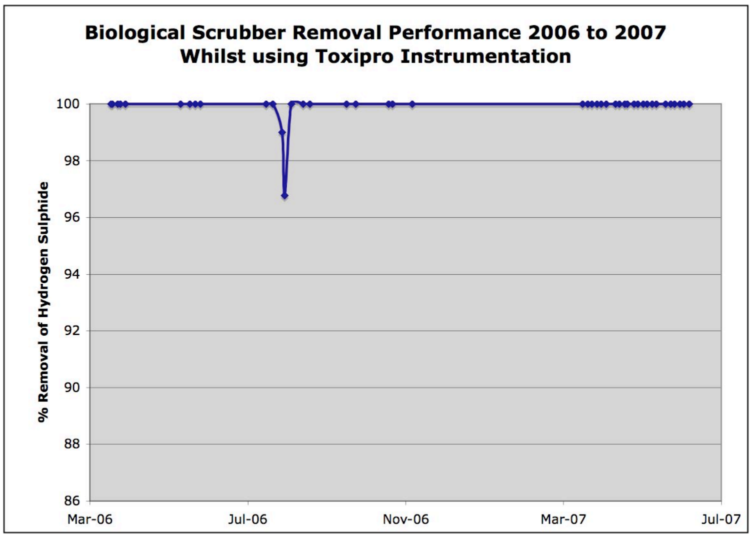

Fig 6: Hydrogen Sulphide Removal Performance from March 2006 to June 2007

5. PLANT RELIABILITY

The Biological Scrubber operation has proven to be extremely reliable. The only unplanned stoppages have been due to power cuts. When the biological scrubber was restarted after being switched off for a number of days, it almost immediately reached normal operation and performance.

In the second half of 2006 staff noticed the gas extraction was not as strong as it had been and the pressure drop across the biological scrubber bed was slowly increasing. An inspection during annual shutdown at the end of 2006 showed a biomass accumulation and residue from seeding material. This was removed from the packing with a washing step using a 5% sodium hydroxide solution recycled through the bed for 24 hours, and then flushing the reactor with fresh water. The pressure drop returned to normal and the biological scrubber has been performing well since.

The gas extraction system requires cleaning every 48 hours by site staff due to sulphur ingress and build up. This is an issue specific to the Ravensdown Hornby not associated with the biological scrubber performance.

6. DISCUSSION

The biological scrubber performance has been successful as there have been no complaints from neighbours about odours from this source since the commissioning of the scrubber.

The instrumentation used reported whole numbers only for the hydrogen sulphide concentrations. When the hydrogen sulphide concentration in the scrubber outlet is less than 0.49 ppm, it is reported as 0 ppm. Taking a typical result on say the 24^{th} April 2007, the hydrogen sulphide concentrations on the inlet and outlet were 88 ppm and 0 respectively, and the calculated removal performance is 100% (Fig 6). Allowing for the errors associated with the whole number integration, the actual scrubber performance will be somewhere between 99.4% (outlet 0.49 ppm) and 100% (outlet 0 ppm).

Due to the technical problems with particulate matter in the Odalog system possibly causing carryover of the inlet gas into the outlet gas, it is possible that the outlet concentrations pre March 2006 as given in Fig 4 are over stated and the brief periods of low performance in Fig 5 are not real.

The performance drop in August 2006 (Fig 6), where the scrubber performance dropped to 96.8%, occurred following a plant shutdown during June and July. On start up, the hydrogen sulphide inlet concentration increased from 7 ppm on the 26^{th} July to 200 ppm on the 7^{th} August. At the same time the outlet concentration increased to 2 ppm, and hence the spike while the micro-organism population became re-established. Subsequent to this, other spikes in the inlet concentration did not cause a spike in the outlet concentration.

The sulphur dioxide concentrations and removal have not been measured. Sulphur dioxide is not noticeable to the human nose in the exhaust stream, and is not causing an odour nuisance. As sulphur dioxide is relatively soluble it is assumed it is being removed in the biological scrubber.

Chemical operating costs have been confined to just a few nutrients and small quantities of caustic. Over the operating year of the biological scrubber operation, the average inlet hydrogen sulphide concentration has been 76 ppm. Assuming a gas flow rate of 0.8 m3/s for 2000 hours per year, and if a wet chemical scrubber had been used with sodium hydroxide and sodium hypochlorite as the oxidant, then the required stoichiometric quantities of these chemicals would have been 2000 litres of 50% sodium hydroxide and 30,000 litres of sodium hypochlorite. By comparison the quantities of chemicals actually used were 1200 litres of nutrients (diluted liquid fertiliser) and 100 litres of 50% sodium hydroxide. This exercise, whilst theoretical, demonstrates the significant savings in chemicals that can be achieved with a biological scrubber.

7. CONCLUSION

The biological scrubber performance has been successful as indicated by the continuous monitoring of hydrogen sulphide inlet and outlet concentrations. Also, there have been no complaints from neighbours about odours from this source since the commissioning of the biological scrubber.

The biological scrubber had a rapid start-up with high treatment performance obtained within days of commissioning. The process is relatively robust and operating costs have been confined to just a few nutrients and small quantities of caustic.

This technology is also applicable to a wide range of applications including emissions from trade waste plants, municipal wastewater treatment plants, biogas generation plants, pump station vents and food processing plants emitting odorous gases.

8. ACKNOWLEDGEMENTS

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