

Emissions Reconsenting Report



Ravensdown Limited

Napier, New Zealand

Chemetics Project No. 217073-35836

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1. Introduction

Chemetics Inc., (“**Chemetics**”) is pleased to submit this Report to **Ravensdown Limited** (“**Ravensdown**” or “**Client**”) to provide support for Ravensdown’s air emissions consent application.

The purpose of this report is to independently assess if the Ravensdown site’s industrial processes, including air emission controls, meet international best practice. International best practice in this report is defined as practices that are commonly used on a global scale and can be considered an international benchmark. It will review Ravensdown’s current emissions control technology, compare these emissions to the performance of other acid plants globally, and identify possible process improvements.

2. Authors Technical Credentials

Chemetics Experience:

Chemetics’ standard of excellence in the sulphuric acid industry has been established on a world-wide basis for over 50 years. From its headquarters in Vancouver BC, Canada and its fabrication facility in Pickering ON, Canada, Chemetics® services clients in the fertilizer, non-ferrous metallurgical, and chemical industries around the globe, by providing engineering, equipment and complete turnkey plants for sulphuric acid manufacture and sulphuric and nitric acid concentration.

Supported by Research and Development at its Technology Centre in Burnaby BC, Chemetics has maintained a leadership role in process technology, equipment design, and the materials of construction that are incorporated into its high-quality plants. Chemetics’ continued success depends on its focus on understanding client requirements – all Chemetics plants and equipment items are specifically custom-designed to ensure client’s needs are fully satisfied. Chemetics capabilities range from the performance of engineering studies through to undertaking of turnkey projects.

Chemetics is a leading global provider of services related to design, construction, maintenance, modification and operation of both large and small industrial facilities. In addition, the group provides advanced technology products, either on their own or as part of integrated solutions.

Chemetics is part of the Worley group and provides expertise in engineering, procurement and construction and offers a wide range of consulting and advisory services. We cover the full lifecycle, from creating new assets to sustaining and enhancing operating assets, in the energy, chemicals and resources sectors.

We are proud to have created a diverse and inclusive workplace and our subject matter experts use their deep technical knowledge to deliver what we promise, and what matters, to customers. Our resources and energy are focused on responding to and meeting the needs of our customers over the long term and thereby creating value for our shareholders.

Chemetics has decades of experience in supplying Sulphuric Acid Plants, executing major retrofit projects, and supplying associated equipment designed to meet local regulatory emissions limits. Chemetics is a world-leader in understanding the sulphuric acid process and confidently offers

emissions guarantees to clients. Chemetics supplies sulphuric acid technology to every region of the world and therefore has a deep understanding of global emissions standards and best practices.

Subject Matter Experts:

Jesse Huebsch (Acid Technology Service Engineer) is a Senior Process Engineer who is specialized in Sulphuric Acid Technology and is recognised as a Subject Matter Expert within Worley. Jesse works primarily with retrofit projects, focusing on the early stages that establish the design basis. In the sulphuric acid industry, many such projects are driven by emissions requirements. As such Jesse has extensive experience in determining what is achievable in a practical manner for Sulphuric Acid Plants, as well as establishing the design basis that meets the local regulatory requirements for emissions.

Matthew King is a Principal Process Engineer with over 26 years' experience mainly in the field of sulphuric acid manufacture. He is a recognized Subject Matter Expert within Worley and completed his Ph.D. focused on sulphuric acid plant control and optimisation while working at a copper smelter in the United States. A key aspect of this work dealt with process optimization to minimize emissions. His experience includes acid plant and smelter operations, project engineering and fifteen years as a global sulphuric acid consultant. In that role he contributed to emissions benchmarking exercises that assisted clients in establishing both point source and ground level concentration permit values. He now provides technical services, sales and support for Chemetics' valued customers in the Australasia region.

Additional Report Authors:

Dana Mraz is a Junior Process Engineer who has experience with a variety of technologies within Chemetics including converter retrofit projects, new sulphate removal system (SRS) projects, and R&D testing of new converter technology.

Report Reviewers:

John Wright (Chief Process Engineer) leads the process team at Chemetics and has been specialized in Sulphuric Acid Technology since 1994. He joined Chemetics in 1986. Previously, he was the Acid Technology Manager at Chemetics and in this role was responsible for oversight on studies, proposals, and projects including emission requirements. Prior to that John led many projects and retrofit studies.

Rene Dijkstra (Acid Technology Manager) started his career as a process engineer supporting a Sulphuric Acid Regeneration Plant in the UK, before joining Chemetics in 1997 as a process engineer. Starting in the Spent Acid Recycling Group where he was responsible for process development, process design and startup assistance. His technical role has continued to expand, and he was promoted to Chemetics Acid Technology Manager in 2007. His role now covers the entire range of sulphuric acid and sulphur technologies offered by Chemetics including responsibility for technology development. The role also includes technical oversight on all acid related studies, proposals, and projects including emission requirements.

3. Methodology

The following approach was used to complete the study:

- Review of the existing acid plant configuration and emissions data
- Benchmarking of other acid plants and their permissible emissions limits and measured emissions
- Comparison of Ravensdown to international best practice (IBP) and other acid plants
- Option identification and evaluation of improvements to lower existing acid plant emissions

3.1 Information and Data Received

Ravensdown provided the following information for the study:

- P&ID drawings
- Control System Screenshots
- Current catalyst loading
- Equipment list
- Environmental testing records
- Description of typical start-up and shutdown procedures
- Historical plant operating data

Due to COVID travel restrictions, a local Worley New Zealand engineer completed an onsite inspection and met with the Napier team. Note that Chemetics has worked with the Napier site for multiple previous projects including replacing the Absorption Towers, and the lead author has visited the site previously. The acid plant's current configuration was established using HMI screenshots and the existing P&ID drawings. Environmental testing records and plant operating data were gathered and used to evaluate the existing facility's performance. The data collected was used to determine average emission rates during normal operation, plant start-up and shut down.

3.2 Benchmarking

Proposed emission limits for new and retrofit projects were determined from public information and Chemetics knowledge. Benchmarking of other acid plants with similar installed capacity and technology was completed.

Acid plant consent limits are easily accessible in the public domain and are presented in Section 5.3 to allow comparison. Measured acid plant emissions values are generally more difficult to obtain. Where possible, publicly available measured values are also provided for comparison.

Emissions guidelines published by the International Finance Corporation - World Bank Group (IFC)) are also included for reference. A summary table is shown in Section 5.3.

3.3 Option Identification and Evaluation to Lower Emissions

Options to decrease emissions were identified and evaluated. These options were determined based on in-house Chemetics experience. Two main options were evaluated:

- Catalyst change, loading and/or type
- Tail gas scrubbing

A specification was prepared and issued to catalyst vendors who provided budgetary quotes and catalyst loading information. The design basis assumes the catalyst would be installed in a new converter, as this project has already been initiated by Ravensdown.

With regards Tail Gas Scrubbing a significant number of technologies are commercially available to remove SO₂ from process gas. This study focused on a few key systems that have proven operating histories at other acid plants around the world. Systems considered and evaluated include:

- Caustic (NaOH)
- Seawater
- Ammonia (NH₃)
- Hydrogen peroxide (H₂O₂)
- Catalytic
- Amine (Regenerable SO₂)

Fugitive emissions were also addressed based on Chemetics' experience. The possible improvements for the various emissions control technology available are described in Sections 6/7/8.

4. Site Description and Emission Sources

4.1 Overall

The Ravensdown double absorption sulphuric acid plant at Napier Works was commissioned in 1976. For a description of the entire Napier Works site refer to Appendix C. Many plants today are built using the same double absorption process, but with improved equipment design and more active (efficient) catalyst. The 650 tpd Napier acid plant is one of the largest in New Zealand; however, globally, it is considered a small plant. For example, the First Quantum Minerals Ltd. Ravensthorpe acid plant in Australia has a capacity of 4400 tpd. The highest capacity single train sulphur burning acid plant produces approximately 5000 tpd. Note that there are only 4 sulphuric acid plants in New Zealand, two of this size class, and two smaller plants.

4.2 Emission Sources and Characterization

Potential harmful emissions from a sulphur burning acid plant operating under steady state conditions include: SO₂, SO₃, H₂SO₄ (as mist and vapour), H₂S and NO_x (as NO and NO₂). Most are discharged to the atmosphere through the tail gas stack. The remainder escape from the process as fugitive

emissions. The overall process and control points for a double absorption acid plant is shown in Figure 1.

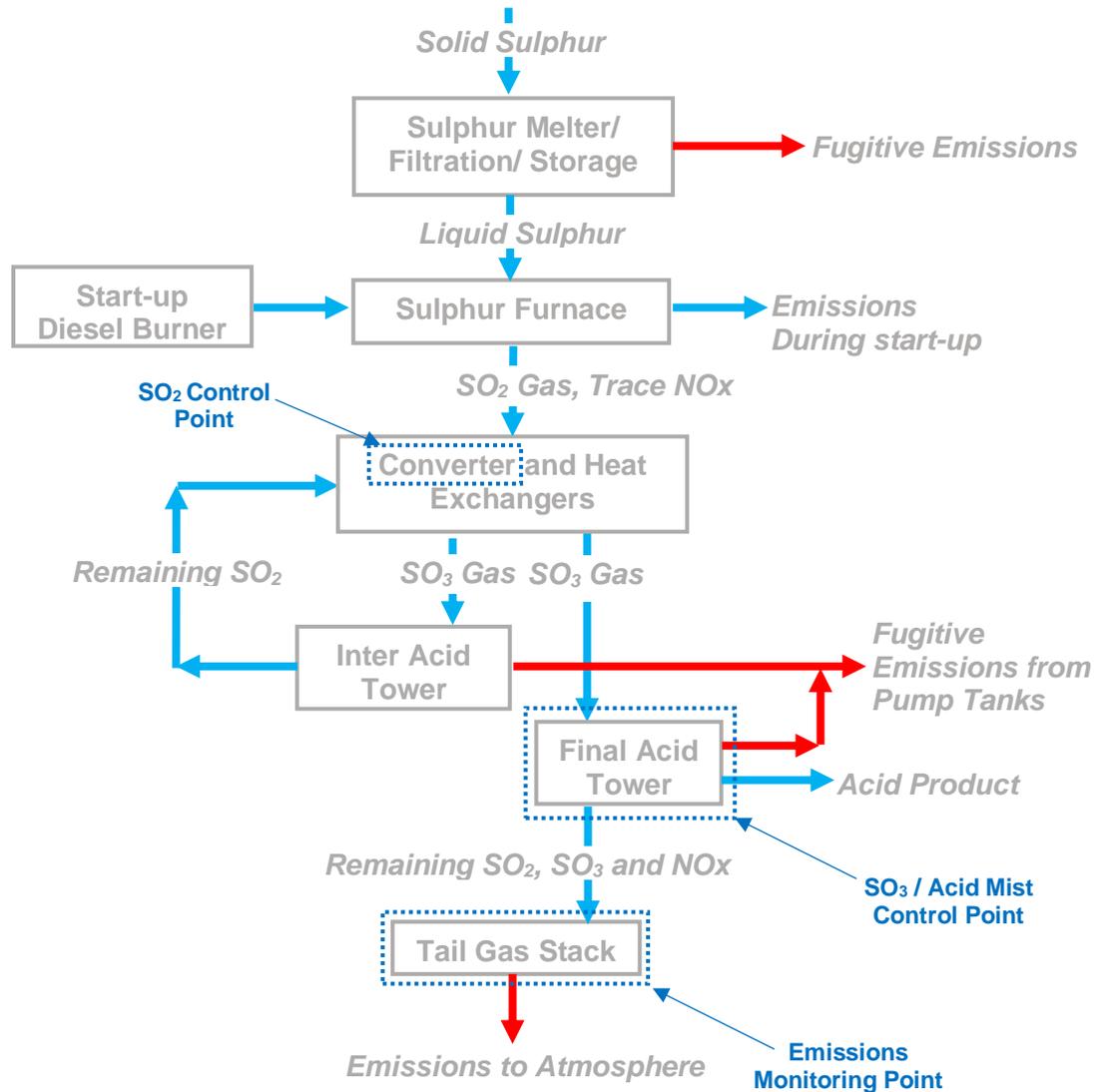


Figure 1: Ravensdown Napier Works Current Process Flow Schematic

4.3 Measurement

Three key measurements to monitor emissions from an acid plant are SO_2 , stack gas flowrate and $\text{SO}_3/\text{H}_2\text{SO}_4$.

For continuous SO_2 monitoring of the stack gas Ravensdown Napier works uses the 43i Pulsed Fluorescence SO_2 Analyzer, approved by the US EPA for use, and is normal practice.

Continuous gas flow rate from the stack is collected by the Durag D-FL 200 Ultrasonic flow meter, ultrasonic measurement for stack flow is unusual in the sulphuric acid industry, but still a valid method.

Laboratory analysis of SO₃ / H₂SO₄ mist and confirmation of SO₂ is done using US EPA Method 8. This method is normal practice, however Ravensdown Napier Works measures SO₂ and SO₃/H₂SO₄ twice per week whereas other plants, such as Nyrstar Hobart and Simplot Pocatello, are required to test once every six months or once per year. It is common to perform a qualitative stick test weekly on the Final Tower exit. A stick test is a qualitative indication of SO₃ and acid mist / drops in the gas.

IBP for SO₂ measurement is to monitor SO₂ with a continuous measurement and to do a manual stack test with EPA method 8 or equivalent on a bi-annual to semi-annual basis.

IBP for stack flow rate is to use a Continuous flow measurement with annual or semi-annual manual stack measurements for validation.

IBP for SO₃ / H₂SO₄ mist is for testing using EPA method 8 or an equivalent on an bi-annual to semi-annual basis (where required at all) with routine PM's and qualitative checks, such as stick tests, used to indicate any changes of condition. Under condition 46A of the current consent Ravensdown is required to report on the availability of a method of continuous monitoring of SO₃ / H₂SO₄ mist emissions. Chemetics is not aware of any sulphuric plants with continuous monitoring for SO₃ or acid mist, or aware of any available or in development technology that would be able to achieve this.

4.3.1 Stack Flow Measurement

An evaluation of the consistency of the stack flow measurement against the other operating parameters of the plant was done. This evaluation found that the measured stack flow was inconsistent with the measured Dry Tower exit flow rate and with a calculation of expected flow rates from acid production and the Bed 1 inlet SO₂ concentration. The SO₂ inlet concentration is not directly measured but can be indirectly calculated by the thermodynamic properties of sulphur combustion reaction and SO₂ to SO₃ conversion reaction. This is done by using the furnace temperature and the converter Bed temperature rises to estimate the SO₂ concentration.

Based on these findings Ravensdown commissioned a third-party testing company to manually measure the stack flow rate on June 2, 2021 and this test found similar results. At the time of the test the stack flow measured by the online meter was 43% less than by the manual measurement and was 40% less than the expected flow calculated from the production rate. Conversely this implies that the actual flow rate is approximately 70% higher than the online measured flow rate, which implies that the actual stack emissions discharge rate is approximately 70% higher than recorded.

The Stack and Dry Tower exit flow meters are recalibrated annually which means this error may be different from year to year. Re-analysing the long-term historical data from the plant is beyond the scope of this review and the data available only provides an indirect estimate of the actual stack flow.

For the rest of the report the emissions data is shown as the as recorded value multiplied by 1.7 to correct for the measurement error. This is noted as an approximation in the text. This error was corrected in July 2021 following the third-party stack measurements.

The other plant operating parameters were found to be generally consistent with the plant production rate and design during the periods analysed. The key parameters used were Furnace temperature, Dry Tower exit flow rate, Sulphur flow rate, Product Acid flow rate, and the converter bed temperatures.

5. Benchmarking

5.1 Basis

Ravensdown Napier Works provided the results of their SO₂ and SO₃ emissions measurements completed twice per week. In August 2020, the sampling results changed to correct for a temperature of 0°C (New Zealand standard) instead of 20°C when reporting concentrations in ppm. To compare the time ranges when at different production rates and to other facilities, all emission data has been converted to units of kg/t H₂SO₄ (100% basis) in order to determine the baseline SO₂ and SO₃ emission rates using the appropriate temperature conversion for the date range. Emissions data is available for the period of June 2009 – October 2020.

5.2 Current Consent Limit and Plant Performance

5.2.1 SO₂

The current consent limit for SO₂ emissions at Ravensdown Napier Works is 60 kg SO₂/hr or 2.22 kg SO₂/t H₂SO₄ (at the maximum production rate of 650 tpd). All emissions will be normalized to units of kg SO₂ /t H₂SO₄ so that the emissions can be directly compared to other plants with different production rates. The emissions are calculated by multiplying a measured stack concentration with the measured stack flow rate and converting to mass flow. The actual average emission rate at Ravensdown Napier Works is 1.7 kg SO₂/t H₂SO₄ at the corrected stack flow rate. Note this is an approximation due to the measurement error described in section 4.3.1. The converter is the original from 1976 and uses conventional vanadium catalyst (MECS XLP-110), the performance is better than most plants of this vintage but not as good as is typical for a newly built facility. The current converter catalyst loading of 155 L/MTPD is lower than a newer designed plant that achieves IBP emissions levels would be for the feed gas conditions. However, with the low average operating rate of 350MTPD versus a design rate of 650 MTPD, the effective average catalyst loading is higher than the design rate comparison suggests. Ravensdown Napier Works operates at a feed gas strength of 10.5% SO₂, which is at the low end of the typical range of a sulphur burning acid plant, and will tend to result in lower emissions for the equivalent catalyst loading than at higher concentrations. To increase the catalyst volume requires a new converter to be installed. In a separate study it was determined the converter should be replaced in the next 2-4 years based on its condition. This project has been initiated by Ravensdown.

5.2.2 SO₃ / H₂SO₄ Mist

Ravensdown Napier Works has an average actual emission rate of 0.007 kg SO₃/t H₂SO₄ during normal operation at the corrected stack flow rate. Note this is an approximation due to the measurement error described in section 4.3.1. This is among the lowest known to Chemetics in the Industry. This value is within the current consent limit of 0.3 kg SO₃/hr for start-up or 0.011 kg SO₃/t H₂SO₄ for normal operation and is to be expected given the final tower and its mist eliminators were replaced in 2012 with the highest efficiency type generally used in this service, and with the average production rate being below the design rate for the equipment.

5.3 Comparison to Guidelines and Other Facilities

5.3.1 SO₂

IFC/World Bank Group guidelines are set at 2 kg SO₂/t H₂SO₄ or 450 mg/Nm³, whichever is more restrictive. At the operating conditions of the Napier Works plant of 10.5% SO₂ at the Converter inlet the parameter of 450 mg/Nm³ is more restrictive and is equivalent to 0.826 kg SO₂/t H₂SO₄. Note that the IFC guidelines can imply tighter controls are required and some plants have ended out significantly lowering their target emissions to avoid any question of compliance. Acid plants with a new converter and/or catalyst technology, such as Ballance at Mount Maunganui, can be designed to operate well below this limit with an average SO₂ emission rate of approximately 0.6 kg SO₂/t H₂SO₄. Tail gas scrubbers, located downstream of the final tower, can be used to further decrease SO₂ emissions, or can be used in retrofit applications. An example is the Freeport McMoRan acid plant in Safford, USA which has an average emission rate of 0.09 kg SO₂/t H₂SO₄. Current international best practice for SO₂ emissions is to use catalytic only abatement in a double contact double absorption (DCDA) 4 or 5 bed configuration, with catalyst loading volumes and types optimised to achieve the specified levels. Note that Chemetics has been seeing requests for emissions rates at 0.5 kg/tonne acid produced for some new plant projects. While not universal at this point this is a value that IBP may be evolving to.

A tail gas scrubber goes beyond best practice to the lowest achievable emissions. Tail gas scrubbers are typically only required in specific situations where the plant is close to a major city or a region with many industrial sites which also emit SO₂ such that the ambient levels of SO₂ are problematic, or where retrofitting an existing facility would otherwise be too difficult to implement. Reduced capacity tail gas scrubbers are often used for start-up or upset conditions only, when the facility can achieve the required emissions at normal operating conditions but not during start-up or upset conditions.

5.3.2 SO₃/H₂SO₄ Mist

IFC/World Bank Group guidelines are currently 0.075 kg SO₃/t H₂SO₄ or 60 mg/Nm³, whichever is more restrictive. At the operating conditions of the Napier Works plant of 10.5% SO₂ at the Converter inlet the parameter of 0.075 kg SO₃/t H₂SO₄ is more restrictive and is equivalent to 40.8 mg/Nm³. In Chemetics' experience, the specified (0.011 kg SO₃/t H₂SO₄) and actual (0.007 kg SO₃/t H₂SO₄) SO₃/acid mist levels at Ravensdown Napier Works are among the lowest known in the industry and already better than international best practice level.

5.3.3 NO_x/H₂S

NO_x and H₂S have not been measured and are typically not measured in sulphur burning acid plants unless an issue is otherwise noted from stack opacity or product quality. A small amount of NO_x is generated in the sulphur burner due to the temperature in the furnace and the presence of oxygen and nitrogen from the air. The relatively low furnace temperature at Ravensdown Napier Works due to having a lower SO₂ concentration than typical (10.5% vs. 11.5%) will tend to result in a lower NO_x concentration being generated than for a typical sulphur burning sulphuric acid plants. A portion of the NO_x is absorbed in the candle filter drippings produced in the inter and final tower mist eliminators, where it drains into the main acid circuit and ultimately is exported in the product acid. The remainder reports to the product acid and tail gas stack. Sulphur burning Acid Plants generally have lower levels of NO_x than other types of Sulphuric Acid Plants and have limited ability to influence the amount of NO_x formed. The levels of NO_x from Sulphur Burning Acid plants are generally low enough to not require emission controls. NO_x reduction technology has been applied to Metallurgical Sulphuric Acid Plants where there are high levels of NO_x in the feed gas they are processing.

H₂S is typically present in the feed sulphur and can be found in the fugitive emissions in and around the sulphur melting and filtering areas or from the Melter stack. No H₂S is expected to be emitted from the acid plant stack as any remaining H₂S in the sulfur is oxidized to SO₂ in the furnace.

IFC/ World Bank Group guidelines are currently 200 mg/Nm³ for NO_x and 5 mg/Nm³ for H₂S emitted from sulphuric acid plants.

5.3.4 Summary

Table 1 provides a summary of emission rates at other selected facilities compared to Ravensdown Napier Works.

Table 1:

Emissions Comparison to other Operating Plants (Public information)

Owner	Ravensdown	Ballance	First Quantum Minerals Ltd.	Freeport McMoRan
Location	Napier New Zealand	Mount Maunganui, New Zealand	Ravensthorpe, Western Australia	Safford, Arizona USA
Capacity (tpd 100% H ₂ SO ₄ basis)	650	600	4,400	1,550
Technology	MECS	Chemetics Converter	Chemetics	MECS
Year commissioned	1976	1976, New Converter 2017	2007	2011
Single or Double Absorption?	Double, 3:1*	Double, 3:1*	Double, 3:1*	Double, 3:1*
Catalyst beds	4	4	4	4
Sulphur melter vent scrubber	No	No	No	No (molten S rec'd)
Tail gas scrubbing	No	No	No	Yes, Caustic
SO ₂ (kg/t H ₂ SO ₄) Consent Value****	2.22	3.60	1.85	0.70
SO ₂ (kg/t H ₂ SO ₄) Actual	1.7***	0.60	1.20**	0.10
SO ₃ + H ₂ SO ₄ , as SO ₃ (kg/t) Consent Value****	0.30 start up, 0.011 normal op	not available	0.049 normal op	0.061 normal op
SO ₃ + H ₂ SO ₄ , as SO ₃ (kg/t) Actual	0.007*** normal op	not available	not available	not available

*3:1 refers to the sulphuric acid plant arrangement, the process gas passing through 3 beds of catalyst before intermediate absorption, then 1 bed of catalyst before final absorption

**Emissions from entire site, not just acid plant

***Actual emissions shown and are estimated to be 70% higher than recorded value due to measurement error

****Many facilities have an allowance for higher emissions for a short duration at start-up

Note: some values converted from original units assuming SO₂ feed gas of 10.5%

Chemetics has been involved with new and retrofit acid plant projects in many countries around the world. Most emission requirements vary depending on the region and proximity to a city or other industrial sites. Some examples of these projects are listed in Table 2.

Table 2: Chemetics Experience for New Plant Emission Requirements

Location	Idaho, USA	Africa	India and Middle East (near a city)	China** (sulphur burners)	IFC International Guidelines
SO ₂ (kg/t H ₂ SO ₄)	0.6	2 (0.66****)	0.8	0.39	0.826*
SO ₃ + H ₂ SO ₄ , as SO ₃ (kg/t)	0.020	0.061	0.040	0.008	0.075

*Note: some values converted from original units assuming SO₂ feed gas of 10.5%

**Measurement method in china results in lower reported values than other jurisdictions

***Project in Morocco

6. SO₂ Emissions Control Technology

6.1 Configuration and Catalyst

SO₂ emissions are minimized by optimizing catalytic SO₂ oxidation (“conversion”) efficiency in the converter. This part of the process has the most significant impact on SO₂ emissions. Having more or enhanced catalyst results in higher overall SO₂ conversion and less remaining SO₂ which is sent to the atmosphere.

Advances in acid plant design have also led to decreased SO₂ emissions. Four relevant acid plant categories are defined as follows (in reverse order of SO₂ emissions performance):

1. Single Contact / Single Absorption (SCSA)
2. Double Contact / Double Absorption (DCDA) with 4 Bed Converter and conventional catalyst
3. DCDA with 5 Bed Converter and/or caesium promoted catalyst
4. Sulphuric acid plant with a Tail Gas Scrubber

First generation sulphuric acid plants with SCSA technology are limited by SO₂ to SO₃ reaction equilibrium. Typically, after the gas passes through 3-4 catalyst beds around 96% - 98% of the SO₂ is converted, but under the process conditions no further reaction can take place. Any remaining SO₂ is discharged to the atmosphere after the SO₃ is absorbed in an Absorption Tower. This style of acid plant is no longer built without additional emissions control technology and has been replaced by the DCDA process currently used at Ravensdown Napier Works.

In a double absorption process, SO₃ gas generated in beds 1 to 3 is absorbed in the intermediate absorption tower which shifts the SO₂/SO₃ equilibrium reaction and allows for further conversion of SO₂ gas. The remaining gas is converted in bed 4 (and bed 5 if present) with the subsequent SO₃ gas being absorbed in the final absorption tower. Overall SO₂ conversion rates up to 99.8% can be achieved with conventional catalyst.

Further DCDA enhancements include a 5th bed of catalyst and/or the installation of high vanadium / activity or caesium promoted catalysts. Both options increase SO₂ conversion thus further lowering atmospheric emissions. The use of caesium promoted catalyst in the final pass has the possibility for over 50% decrease in emissions. It also has a lower minimum temperature to be active than conventional catalyst resulting in faster and lower emission rate start-ups. Overall SO₂ conversion rates up to 99.9% can be achieved. Caesium promoted catalyst in the 4th pass is often used to achieve the current international best practice emissions levels.

The catalyst vendor Haldor Topsøe was contacted to provide estimates for different catalyst loading options for the Ravensdown conditions, these are outlined in Table 3. Haldor Topsøe is a global leader in catalyst supply, including in the sulphuric acid industry. Column 2 represents the options available if the current converter diameter is matched, column 3 shows the emissions if the converter diameter and therefore catalyst volume is increased. The current emissions consent limit at Ravensdown Napier Works is 2.22 kg/t H₂SO₄ at maximum production rates, as represented in the baseline case. Current normal operating emissions are 1.7 kg/t H₂SO₄. International best practice

would be considered as SO₂ emissions in the range 0.6 - 0.8 kg/t H₂SO₄ and actual emissions complying with any consent levels. This range is based on Chemetics experience of what new sulphur burner acid plants globally are expected to achieve in typical areas, with no special circumstances which would require lower emission levels. This could be achieved by using the same catalyst volume and upgrading all 4 beds of catalyst, however this option is expensive and would result in higher maintenance costs. Alternatively, when the converter is replaced it can be designed with larger catalyst beds. Upgrading only the 4th bed to caesium catalyst has a lower overall cost for catalyst and a larger impact on emissions. Replacing the converter also minimizes fugitive SO₂/SO₃ emissions. The converter can be designed with an internal superheater which significantly decreases the amount of hot gas ductwork and eliminates the superheater shell thereby decreasing the likelihood of cracks and leaks of SO₂/SO₃ to the atmosphere.

In Table 3, below, a summary is provided of the costs associated with increasing the catalyst loading in a new build converter over the current baseline loading. There are two aspects to this cost. The first is the extra installed cost for the Converter vessel. An indicative additional cost of \$330,000 USD is estimated for the larger volume vessel including allowing for a larger diameter to ensure no additional pressure drop. There is also an additional cost to add higher volumes of catalyst as well as upgraded performance types. Based on Chemetics recently observed pricing and the vendor specified volumes required the different design point incremental costs are summarised below. For the current volume cases the incremental cost represents the higher price point of the high-performance catalyst. For the increased volume case the incremental cost represents the extra volume required and the higher unit cost for the applicable cases. The reference 350 MTPD column shows the expected performance at the recent normal operating rate of 350 MTPD for the plant, as opposed to the higher 650 MTPD design capacity. The larger capacity converter represents a design catalyst loading of 174 L/MTPD with the potential for future loading of up to 195 L/MTPD as compared to current maximum loading of 155 L/MTPD.

Table 3: Catalyst Loading Options

Rate		650 MTPD				350 MTPD
Volume	m ³	94		113		94
Incremental Vessel Cost (compared to the 94m ³ vessel)	\$ USD	Base case for original estimate		330,000		N/A
Emissions/ Incremental Cost		kg/t	(\$ USD)*	kg/t	(\$ USD)*	kg/t
Conventional		2.14	Baseline	0.89	110,000	0.33
Cs 4th Pass		0.91	150,000	0.42	320,000	0.16
All Advanced Catalyst		0.55	500,000	0.28	740,000	0.12
International Best Practice	kg/t	0.6 – 0.8				

* The incremental costs presented allow for the increased catalyst volume or higher spec costs

The arrangement of acid circuits can also have an impact on SO₂ emissions. If the inter and final acid pump tanks are shared or have a cross over line this allows a small amount of SO₂ to be absorbed in the Inter Tower to be released in the Final Tower to effectively bypass the 4th catalyst bed. A crossover stripper can be installed for some plant configurations to reduce the amount of SO₂ carryover. Ravensdown Napier Works has a separate Final Pump Tank and combined Inter / Dry Pump Tank. the product acid is drawn from Dry/Inter pump tank which eliminates the risk of carryover entirely, by not having any SO₂ containing acid transfer to the Final Tower Pump Tank.

The final improvement to an existing DCDA acid plant is to remove the tail gas SO₂ by sending it through a scrubber. This option is beyond international best practice and reduces SO₂ emissions to the lowest possible level. A tail gas scrubber can decrease tail gas SO₂ concentrations to < 0.1 kg/t H₂SO₄. However, scrubbers typically require a reagent, generate wastes and/or by-products and produce a tail gas with a visible plume potentially resulting in a negative public perception of the facility. For further details on tail gas scrubbing refer to Appendix B. This option is commonly considered when it is not practical or cost effective to make changes to the plant configuration to meet international best practice such as if the converter would be required to be replaced solely for emissions improvements. Continuous scrubbers of the types described cost on the order of \$5-10M USD installed depending on the technology and can have a significant ongoing operation cost through chemical consumption and effluent treatment. A start-up scrubber is estimated to have a total installed cost of \$2-3M USD.

6.2 Procedure Changes

Implementing best practices for start-up and shutdown will minimize SO₂ emissions. During start-up, a spike in tail gas SO₂ concentration always occurs, but its magnitude and duration can be minimized by optimizing catalyst beds and sulphur burner temperatures prior to feeding sulphur.

Burning off residual sulphur in the burner prior to shutdown also decreases emissions from the start-up stack. Note that the start-up stack is used during this heating process only, and emissions are not measured with a continuous monitor.

A set of recent and historical start-ups were analysed with the results presented in Figure 2 showing a typical plot before (07-14) and after (08-20) Ravensdown implement these best practice procedures. Note that the plots show the relative initial emissions spike between start-ups. They are not corrected for the stack measurement error discussed in section 4.3.1 as the review of detailed operating data did not extend this far back to confirm that the correction would be the same for each plot.

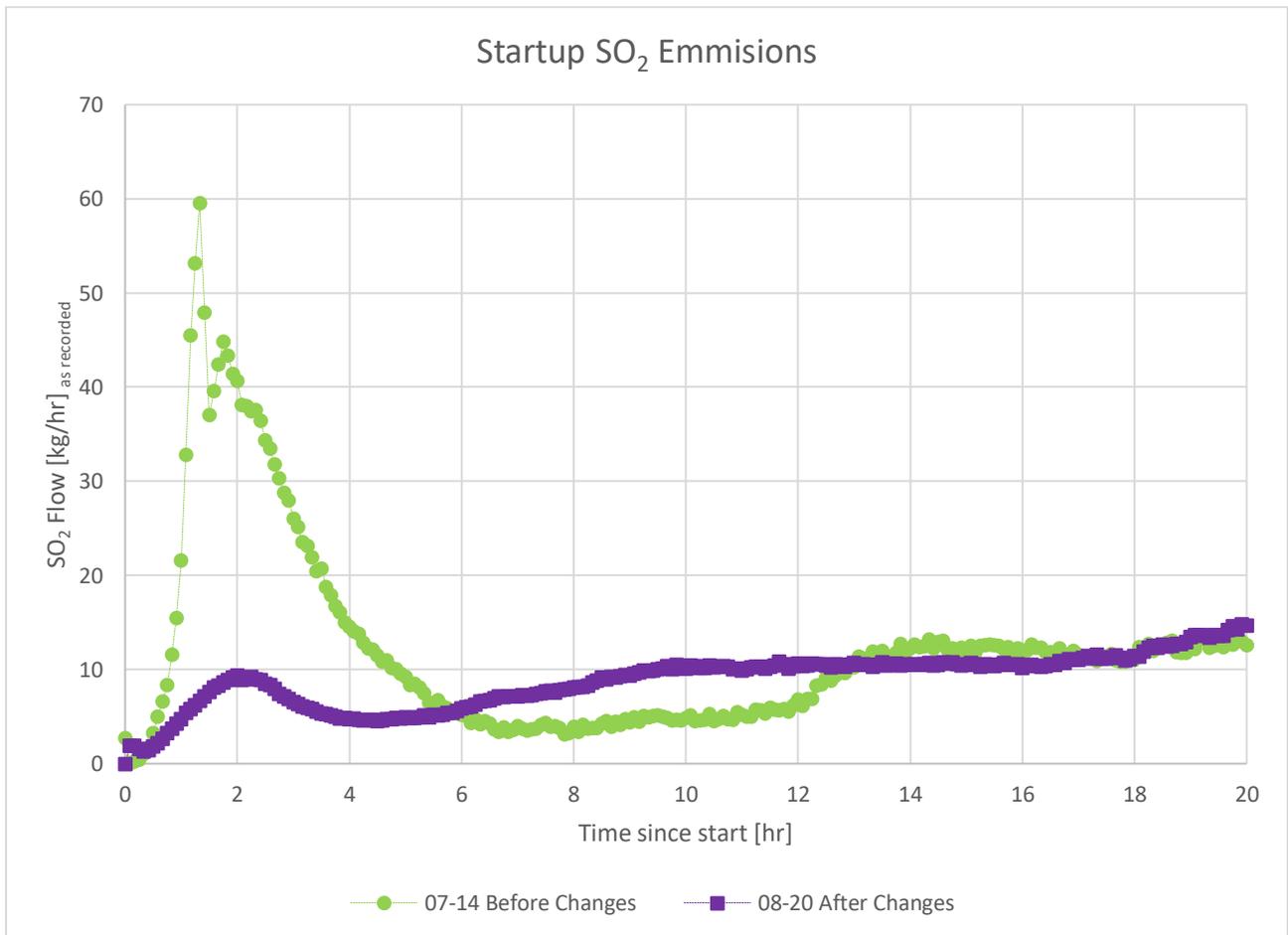


Figure 2: SO₂ emissions during start-ups

7. SO₃/ Acid Mist Emissions Control Technology

SO₃, produced by the oxidation of SO₂ in the catalyst beds, is absorbed and reacted with 98.5% H₂SO₄ flowing downward through packed beds – one each in the inter and final acid towers. The efficiency of the acid mist eliminators located above the distribution system and packed bed in each tower has the greatest impact on SO₃/acid mist emissions from the acid plant. The gas and acid distribution and packing condition in the packed section can have an influence on the SO₃ gas content if it is not performing effectively. Note that a small amount of acid vapour is also present in the stack. This typically is less than the acid mist and the unabsorbed SO₃. Absorption towers and mist eliminators do not remove this acid vapour.

In the absorption towers in a Sulphuric Acid Plant fine mist is formed when the hot SO₃ rich gas is quenched by the circulating acid. A significant portion of the mist can be under 1 micron in size. Three common styles of mist eliminators are used to capture acid mist and droplets leaving an acid tower: Mesh Pads, Impaction Candles, and Brownian Diffusion Candles. Mesh pads are effective for removing particles 5 microns or larger in size, which are typically found in the Drying Tower. They are typically made of woven metal wire, and sometimes include glass or PTFE fibres which improves the collection efficiency. Impaction Candles have improved collection efficiency over mesh pads, collecting smaller particles 1 to 3 microns in size. They are made of glass fibres packed between metal cages. Brownian Diffusions candles have the highest collection efficiency and can capture particles <1 micron in size. Ravensdown uses high efficiency Brownian Diffusion candles in the final tower and this is considered international best practice for this application.

Wet tail gas scrubbers will remove the residual acid vapour and unabsorbed SO₃ present, but they are not effective in removing fine acid mist.

8. Fugitive Emissions Control Technology

Fugitive H₂S, SO₂ and SO₃/acid mist sources include the sulphur melter area, acid pump tanks and any ducting or mechanical equipment failure points (e.g., cracks). Ducting and equipment leaks are often visible as the process gases are under pressure and SO₃ in the gas immediately reacts with H₂O in the air making it visible as white 'smoke' consisting of fine acid droplets. In addition, H₂S gas can be present in the sulphur melting area and is mainly dependent on the H₂S content of the solid sulphur processed on site.

The sulphur melter area emissions are typically SO₂ and H₂S. Many facilities simply vent the tanks to the atmosphere through a small stack as is presently done at site, which is current international best practice. At least one plant is known to have a dedicated package scrubber and fan to collect and treat the vent gas, going beyond international best practice. Additional reagents are required to control sulphur build up in the circulating solution to prevent fouling. Additional oxidising reagents are also required if H₂S is present. This should only be considered if measured emissions in the area pose a safety risk to personnel or are required as part of the consent to operate.

SO₂ emissions from the acid pump tanks can be controlled by installing a vent line from each tank connected to the inlet (suction side) of the blower. In sulphur burning plants these emissions are

typically low and dedicated emissions control is not required. This configuration is used at nearly all metallurgical sulphuric acid plants, and can be used at new sulphur burner plants which have the blower installed downstream of the Dry Tower. However, at Ravensdown Napier Works the main blower is located upstream of the Dry Tower which increases the risk of accelerated blower corrosion caused by the presence of acid mist in the vent lines from the acid pump tanks. As an alternate the pump tank vent can be connected to the stack or top of the final tower to avoid ground level emissions from the tank. For this reason, a small dedicated vent system package scrubber with a fan is preferred for Ravensdown Napier Works if required. Any emissions control on the acid pump tanks would be considered going beyond international best practice.

Package scrubber systems like the ones described above are on the order of \$100,000-500,000 USD installed cost (depending on the complexity and chemistry) and would have ongoing operating costs.

9. Diesel Burner Emissions

9.1 Diesel Burner Emissions

The Acid Plant makes use of three diesel burners which are used predominantly to provide the necessary start-up thermal energy to enable the acid plant to start-up with minimal SO₂ and other emissions. These are as follows:

9.2 Diesel Start-up Boiler

This boiler is used to generate steam to heat the Sulphur Melter and the various molten sulphur lines. It is a proprietary package diesel boiler that is located inside a dedicated boiler room with a dedicated 15.8m high discharge stack. This boiler typically runs for 3-6 days from when the plant is cold until the acid plant furnace heating is advanced enough to generate low pressure steam from the waste heat boiler. Once the plant is operating at steady state on sulphur the heat source for the Melter and steam jacketed lines comes from the Waste Heat Boiler, when this occurs, the diesel boiler is shutdown. The diesel boiler will also be put into operation at any time when sulphur is stopped to the furnace. This provides low pressure steam to maintain liquid sulphur, and also helps to cool the sulphur gun in the furnace face.

9.3 Furnace Pre-Heater Diesel Burner

This burner is inserted into the Furnace after a prolonged period of shutdown and used for approximately 2-4 days to preheat the furnace prior to start-up. The exhaust gases are diverted after the waste heat boiler to a fixed start-up stack during this period. Once up to temperature, the diesel burner is shut down, removed and the sulphur burners are installed. The furnace exhaust is then routed to the acid plant and the combustion of sulphur provides the process heat required for sustained operation.

9.4 Air Preheater Diesel Burner

The Converter needs to be preheated above the "strike temperature" to allow the catalyst to function properly, which is necessary for the conversion of SO₂ to SO₃. Without this preheat inadequate conversion occurs and would lead to excess SO₂ discharge through the main stack. The Converter is preheated using a proprietary package diesel burner located in the Air Preheater Tower. This typically runs for 2-4 days after a prolonged period of shutdown when there is insufficient temperature

in the Converter. Once sulphur is introduced to the plant the conversion of the SO_2 to SO_3 is exothermic and therefore maintains its own heat without using the diesel burner. Note that a separate Preheating system for the converter is unusual, typically the Furnace Pre-Heater is used to heat both the Furnace and the Converter.

These three burners only run during start-up after a planned maintenance shutdown or after a prolonged unexpected stoppage, all other times in the year they remain shut down. The auxiliary boiler remains in standby mode where it is maintained at temperature by using waste heat from the acid plant so that if called upon it can provide steam at short notice. It does not consume diesel when in stand-by mode. These events typically occur 1 - 3 times per annum, they consume low sulphur diesel and do not have any emissions controls on the exhaust gases. Globally, diesel, natural gas, or LPG burners are typically used to preheat acid plants depending on the local fuel availability. Exhaust emission controls are typically not used as this is considered to be beyond international best practice considering the short duration of use and high cost that additional exhaust emissions controls would add.

10. Summary

Current SO₂ emissions are well below IFC International guidelines but could be further improved to meet the standards of international best practice and other operating plants. International best practice in this report is defined as practices that are commonly used on a global scale and can be considered an international benchmark. The following improvements could be implemented at Ravensdown Napier Works to lower SO₂ emissions:

- Replacing bed 4 conventional catalyst with caesium promoted catalyst
- Increasing the size of the converter to increase catalyst volume
- Installing a ventilation system for the acid pump tanks if testing indicates a requirement (gas to blower, a new package scrubber, or a new vent gas blower to the Dry Tower)
- Adding a tail gas scrubber

Of these options, given the requirement to replace the end of life converter, replacing the converter designed with a catalyst system capable of achieving international best practice emissions levels is expected to be the most practical approach for improvement. Installing ventilation systems on the acid pump tanks or sulphur melter area go beyond what is required to meet international best practice, however, may be required if the fugitive emissions exceed working standard limits and pose a safety risk to personnel on site. Adding a tail gas scrubber would go beyond what is required to meet international best practice to the lowest achievable SO₂ emission levels, and a scrubber can negatively impact other operating and environmental parameters. See Appendix C for a review of various scrubber technologies.

After replacement of the Final Tower in 2012, SO₃/acid mist emissions are at industrial best practice and below guideline values for all comparison plants. Laboratory analysis testing frequency could be decreased. A periodic qualitative stick test could be performed instead.

Start up and shutdown procedures have already been adjusted to follow international best practice and has provided a measurable decrease in emissions.

During the data analysis the stack flow was found to be lower than expected. This deviation was confirmed by a third-party manual measurement of the stack flow rate. If the deviation is consistent over the historical time period, the actual SO₂ and SO₃/acid mist stack emissions are approximately 70% higher than recorded. This error was corrected in July 2021 and calibration procedures updated. Future recorded values are expected to be correct.

Current H₂S from the sulphur melting area are not measured. If H₂S emissions are found to be high, the following could be implemented to reduce emissions:

- Installing a ventilation system in the sulphur melting area (gas to a new package scrubber)

11. Appendix A – References

- IFC – World Bank Group General EHS Guidelines:
https://www.ifc.org/wps/wcm/connect/topics_ext_content/ifc_external_corporate_site/sustainability-at-ifc/policies-standards/ehs-guidelines/ehsguidelines
- Ballance Mount Maunganui: <https://ballance.co.nz/Our-Business-and-History/Manufacturing>
- First Quantum Minerals Ltd. Ravensthorpe:
<http://www.npi.gov.au/npidata/action/load/individual-facility-detail/criteria/state/WA/year/2019/jurisdiction-facility/WA0947>
- Freeport McMoRan Safford: https://static.azdeq.gov/pn/200226_freeport_dp.pdf
- Nyrstar Hobart: <https://nyrstarhobart.com/wp-content/uploads/2020/05/Nyrstar-Hobart-Public-Environment-Report-2015-2017.pdf>
- Simplot Pocatello: <https://www.epa.gov/sites/production/files/2015-12/documents/simplot-cd.pdf>

12. Appendix B – List of Acronyms

IBP	International best practice
P&ID	Piping and instrumentation diagrams
IFC	International Finance Corporation (World Bank)
US EPA	United States Environmental Protection Agency
MTPD	Metric tonne per day (production rate)

13. Appendix C – Tail Gas Scrubbing

Six scrubbing technologies were considered: caustic, peroxide, regenerative, catalytic, ammonia and sea water scrubbing. All have been used to treat tail gases generated by sulphuric acid plants. Caustic, seawater, ammonia, peroxide and amine scrubbing all use a packed bed tower or reactive bed (catalytic) to contact the SO₂ bearing tail gas with a scrubbing liquid which absorbs and removes SO₂ from the gas. The main difference is the characteristics of the waste or by-product stream that is produced from each process. Peroxide, catalytic and amine all produce H₂SO₄. Caustic, seawater and ammonia do not. Each are described in Appendix B. It should be noted that all scrubber systems have the following disadvantages:

- Wet stacks – a visible water vapour plume is formed under certain atmospheric conditions
 - The wet stack also can lead to corrosion if the original stack containing acid and sulphate accumulation is re-used. A new stack is almost always required
- Water consumption – all scrubbers evaluated in this study evaporate enough water to saturate the dry gas exiting the final tower
- Pressure drop – the additional equipment imposes additional pressure drop in the gas path, which can reduce acid plant production in retrofit applications where there is not enough additional capacity in the main blower
- Power consumption – the additional gas pressure drop increases the main blower power consumption and the pumps for circulating the scrubber liquor use additional power
- Space requirements – all options require a new tower and associated pumps and tanks. Some options require more than one tower
- CAPEX – All options require a significant capital investment and add at least one major unit operations to the site

15.1 Caustic

A caustic solution (~10% NaOH) is pumped over a packed bed and flows downward while the tail gas flows upward. As the tail gas passes through the packed bed, SO₂ is absorbed and reacted in the solution. The cleaned, saturated tail gas leaves the scrubber and is discharged to the atmosphere. A portion of the circulating solution is drawn off and sent to disposal. It contains soluble NaHSO₃, NaOH, Na₂SO₃, and Na₂SO₄. Fresh caustic solution is added as make-up. Caustic or soda ash can be used. Key reactions for a caustic based system are as follows:

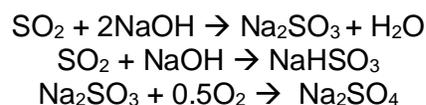


Figure 2 shows a photo of a Chemetics designed caustic tail gas scrubber used to continuously treat gas at a 650 t/d sulphur burning acid plant. Notable features include an all FRP construction, 3.2 m

ID packed bed with a design inlet of 7500 ppm SO₂ for start-up and 360 ppm SO₂ continuous. It generates a tail gas with <20 ppm SO₂.

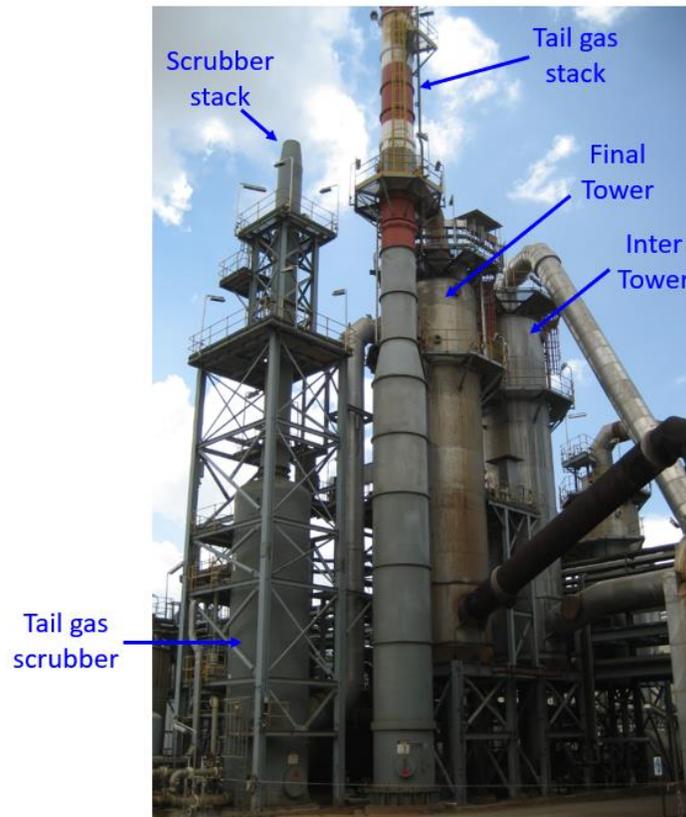


Figure 3: Example Chemetics Caustic Tail Gas Scrubber – 650 t/d Acid Plant (825 t/d Expanded)

The advantages of this process are:

- High SO₂ removal efficiency (99.7+%)
- Ability to maintain high SO₂ removal efficiency with variable feed gas conditions (e.g. start-up)
- Low scaling potential (compared to lime-based systems)
- Simple process, easy to operate
- Low capital cost compared to other options
- Comparatively small footprint compared to ammonia and regenerative scrubbers

Its disadvantages are as follows:

- Waste stream has little (and sometime negative) value

- Requires safe disposal of soluble sodium-bearing compounds (sometimes sent to wastewater treatment plants)

The total installed costs for a caustic based tail gas scrubber used continuously is estimated to be in the range of US\$5 to \$10 million dollars. A start-up scrubber also using caustic is estimated to have a total installed cost of US\$2 to \$3 million dollars. The key design values for the continuous scrubber is shown in Table 4.

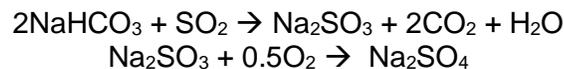
Table 4. Caustic Scrubber Design Parameters

Item	Units	Continuous
Inlet SO ₂	ppmv	360 steady state
Outlet SO ₂	ppmv	<20
Caustic required (10% NaOH)	m ³ /d	10
Waste produced	m ³ /d	12
Make-up water*	m ³ /d	62
Power consumption (feed + circ. Pumps only)	kW	24

*water typically supplied from scrubber 10% NaOH make-up solution

15.2 Seawater

Seawater is drawn from the ocean, treated and sent over a packed bed where it flows downward and is contacted with the SO₂ bearing tail gas flowing upward. A seawater scrubber generates a solution that is returned to the ocean after use and must be demonstrated to not affect marine life. Temperature control, oxidation state and pH of the return seawater are all critical control parameters. The seawater's natural alkalinity from bicarbonate can sometimes be augmented with lime to improve efficiency. The main reactions are shown below based on sodium bicarbonate in the seawater:



Its advantages are:

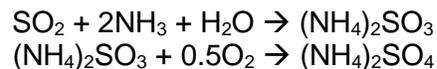
- Low-cost, readily available reagent

Its disadvantages are:

- Comparatively low SO₂ removal efficiency (~98%)
- Must always return seawater within control parameters and permitted limits (pH, temperature)
- High capital cost – seawater intake system, pumps, piping
- Permitting may be difficult – public opinion, perception, ocean contamination, etc.

15.3 Ammonia

Ammonia is used as an SO₂ scrubbing reagent. By-product solid ammonium sulphate can be produced that has a market in some locations. The SO₂ bearing tail gas passes through a packed tower and is contacted with an ammonia solution flowing downward. Ammonium sulphite, produced in the scrubber, is then oxidized to sulphate, filtered and dried to produce solid ammonium sulphate. The main reactions are as follows:



Its advantages are as follows:

- Proven technology in use at other fertilizer plants
- Produces valuable ammonium sulphate by-product instead of a waste

Its disadvantages are as follows:

- Comparatively low SO₂ removal efficiency (~98%)
- Requires high efficiency mist eliminators or a wet ESP to mitigate “blue plume” in stack gas
- Requires energy for drying and crystallization
- Requires ammonia – may be expensive depending on local conditions
- More complex flowsheet with higher capital costs compared to other options
- Ammonia is a highly regulated hazardous chemical. It must be received, stored and handled in a safe manner

15.4 Hydrogen Peroxide

Similar to caustic scrubbing, a peroxide solution flows downward through a packed bed where it is contacted with SO₂ bearing tail gas flowing upwards. In the packing, hydrogen peroxide (H₂O₂) reacts with SO₂ making dilute sulphuric acid (~50% H₂SO₄). This dilute acid is added to the DCDA plant acid circuit and displaces some required dilution water. The main reaction with SO₂ is as follows:



Make-up peroxide is received in 35% H₂O₂ or 50% H₂O₂ solutions. Its key advantages are:

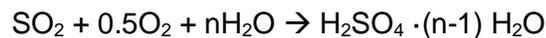
- Produces H₂SO₄
- High SO₂ removal efficiency (~99.9%)
- Does not produce waste so long as dilute acid can be consumed in acid plant
- Low scaling potential (compared to lime-based systems)
- Comparatively small footprint compared to ammonia and regenerative scrubbers
- Lower capital costs compared to options other than caustic scrubbers

Its disadvantages are as follows:

- High reagent costs (peroxide) compared to caustic or soda ash
- Hydrogen peroxide is a strong oxidiser and must be received, stored and handled in a safe manner

15.5 Catalytic

In catalytic scrubbing, humid SO₂ is catalytically oxidized to SO₃. The SO₃ reacts immediately with water in the gas to produce weak sulphuric acid (~10% H₂SO₄). This weak sulphuric acid can be added to the strong acid circuit to offset dilution water addition. Activated carbon has historically been used as the catalyst and Chemetics has a fixed media option available. The main reaction is as follows:



Its key advantages are:

- Produces H₂SO₄
- Activated carbon catalyst readily available
- High SO₂ removal efficiency (99+%)

Its disadvantages are as follows:

- Large footprint, multiple catalyst beds required to treat high SO₂ concentration feed gas
 - In this application the SO₂ concentrations is relatively low, so a single bed is expected to be able to be used.
- Minimum amount of O₂ in the gas (typically 7 vol.%) required to efficiently oxidize SO₂ to SO₃
- Higher CAPEX than chemical scrubbers

15.6 Amine (Regenerative SO₂)

SO₂ is absorbed in an amine solution in a regenerative scrubber. The absorbed SO₂ gas is then stripped from the amine as a saturated, pure SO₂ gas (90 - 95% SO₂) and recycled to the inlet of the DCDA plant. A small bleed stream from the amine purification circuit is necessary and requires disposal. Fresh amine must be added as make-up. A significant amount of process heat (supplied as low-pressure steam, 3 - 5 barg) is required for the SO₂ stripping step.

Its advantages are:

- Produces H₂SO₄
- High SO₂ removal efficiency (99+%)
- Low scaling potential (compared to a lime-based systems)
- Can handle variable feed gas SO₂ concentrations
- Excess low-pressure steam from the acid plant can be used to lower operating costs

Its disadvantages are:

- Steam consumption is high and must always be available to strip SO₂ from the amine
- Fuel fired package boiler required for low pressure steam supply if none is available from the acid plant
- Cooling water system required to indirectly removed excess energy from SO₂ stripping circuit
- Amine reagent is expensive with a limited number of suppliers
- Amine purification required to prevent formation of heat stable salts that decrease efficiency
- Much more complex flowsheet with higher capital costs compared to other options

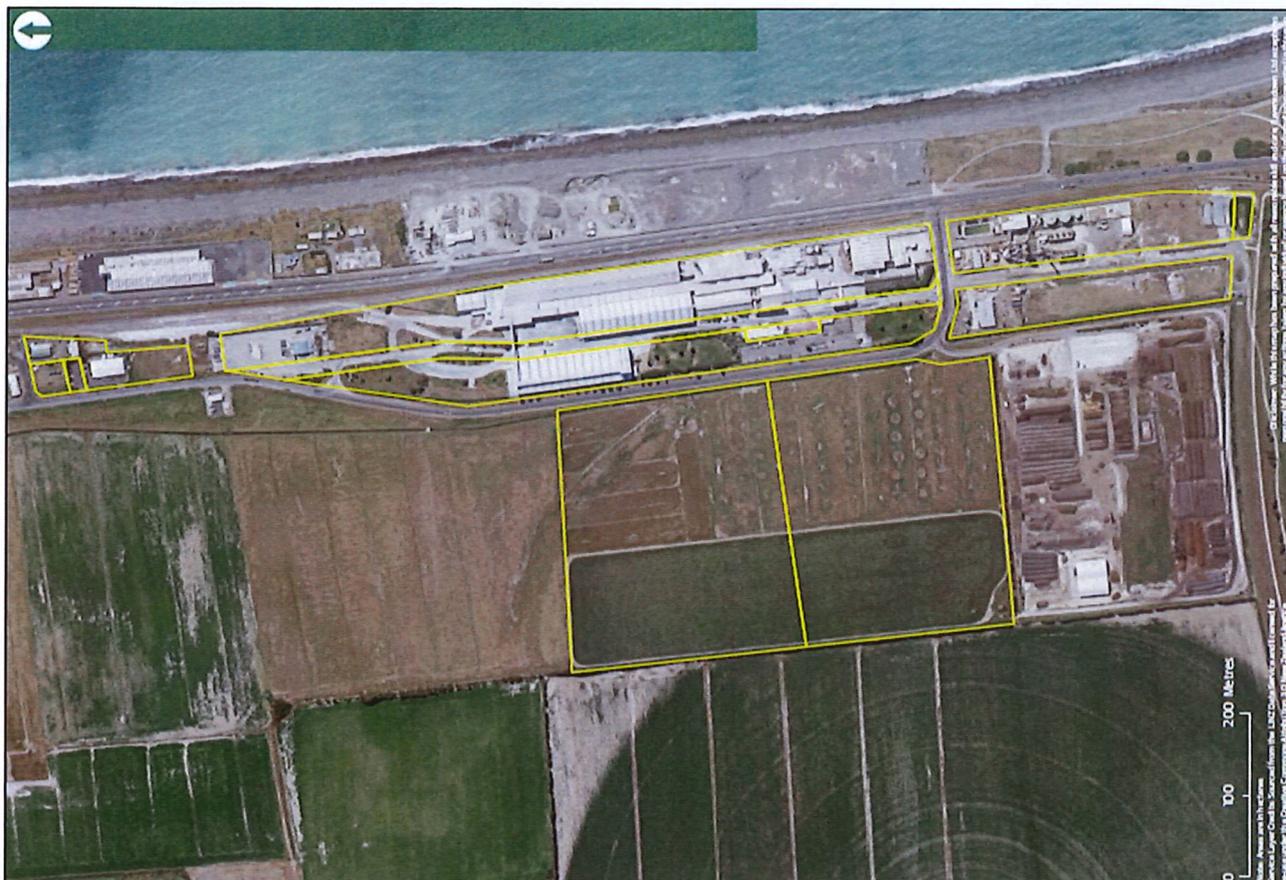
14. Appendix D – Napier Works Process Description

Napier Works Process Description

Revision History

Revision	By	Date	Description	Approved
A	RDM	05/09/2019	First Draft	AJT
O	RDM	16/09/2019	Issued for Use	AJT

Below is a map showing our legal property boundaries



2. Sulphur Melter

2.1. Melter Process

Elemental sulphur is imported primarily from Canada as a by-product of the petrochemical industry. The sulphur is received by ship at the Napier port and is transported by truck to the manufacturing site. The sulphur is in a prilled form intended to reduce dust emission during the handling and conveying process. Prior to shipping the elemental Sulphur will have SLS (Sodium Laurel Sulphate) applied to stop formation of hydrogen sulphide (H₂S).

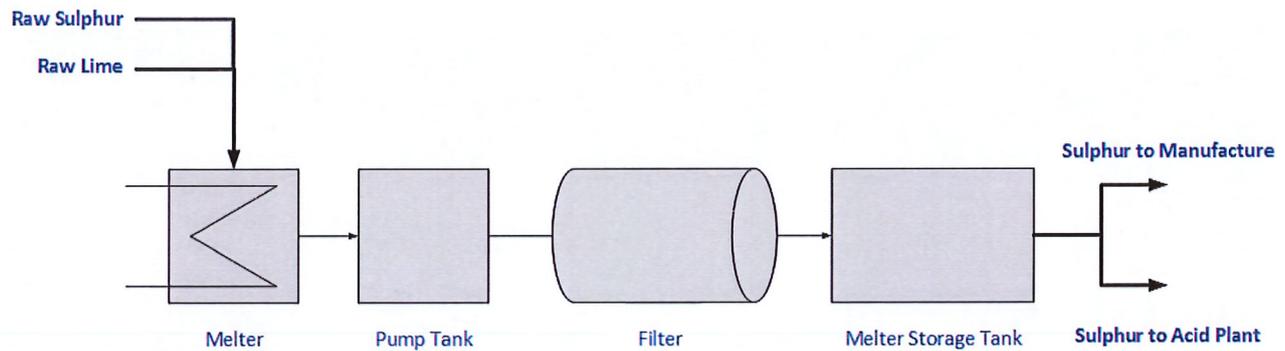
The prilled sulphur is received at the site into an intake hopper and then conveyed into one of two bulk sulphur storage sheds. Napier Works can hold up to 20,000T of prilled sulphur.

The sulphur prills are loaded into the melting plant where it is melted using indirect heat from steam, filtered to remove any impurities and pumped in molten form to the sulphuric acid plant or manufacturing plant.

The melter process vessels are approaching the end of their useful life, and a project has been initiated for their replacement. One option being considered is relocating the melting process within the Acid Plant complex on the southern side of Waitangi Road.



Sulphur Melter Flow Diagram



2.2. Melter Emissions

During the melting process any water contained in the raw sulphur feed is driven off as steam. This steam is vented to atmosphere through a vent above the melter vessels. The steam is likely to contain sulphur compounds not currently measured in process.

One of the discharges from the vent is H_2S . Current consent condition is for two one week monitoring periods per year, results of which are reported to council.

Solid sulphur is spilled from storage and loader operations to ground where fines may be picked up by wind and also discharged to the site stormwater system affecting pH.

2.3. Melter Emission Monitoring and Control

Automated and logged Sulphur dioxide (SO_2) meters are located in the Sulphur storage sheds and around the Sulphur melter. These monitor SO_2 concentrations which provide early warning of a sulphur fire and trigger an alarm to notify the site.

Sulphur fires originating in the melter vessel itself are 'quenched' with steam by the operator remotely from the melter control room.

3. Sulphuric Acid Plant

3.1. Acid Plant Process

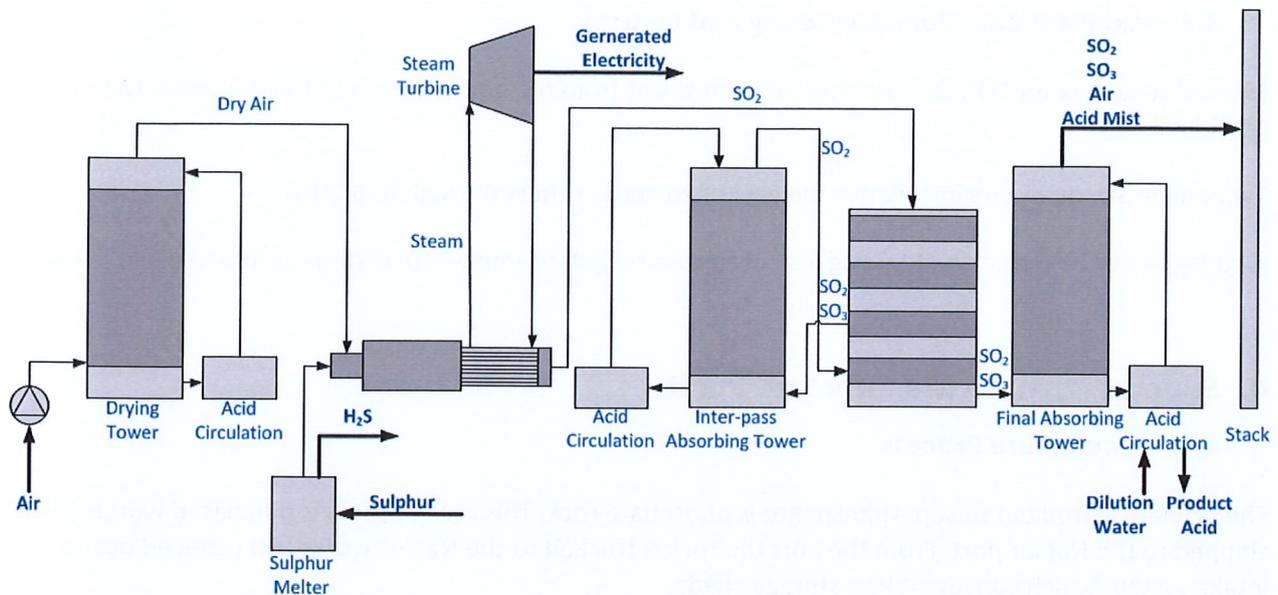
Sulphuric acid is produced in a Sim-Chem (Monsanto) designed plant using the contact process. This involves spraying molten sulphur into a burner vessel in the presence of excess air. The sulphur burns forming sulphur dioxide and releases a large amount of heat. The Sulphur dioxide is then passed over a catalyst which converts it into sulphur trioxide. SO_3 is scrubbed from the gas stream and reacted with water to create concentrated sulphuric acid. (H_2SO_4). The sulphuric acid is pumped to storage tanks for use in the fertiliser manufacturing plant or commercial sales.

The Napier works operates a double adsorption acid plant. This two-step conversion and adsorption process reduces the amount of SO_2 released to atmosphere for a given production rate when compared to single adsorption plants.

Many of the reaction steps in the acid plant generate excess heat. This waste heat is collected and used to make low pressure steam for use in the plant and high-pressure steam which is fed to a steam turbine to generate electricity.



Double Absorption Sulphuric Acid Plant Flow Diagram



3.2. Acid Plant Preheating Emissions

The diesel-powered auxiliary boiler is used to generate low pressure steam when the acid plant process is not operating. This boiler is used intermittently and discharges products of combustion.

Diesel combustion emissions and SO₂ are also discharged from heating the process vessels during restart of the acid plant.

Heating of the catalyst and other process equipment also occurs before starting the acid plant and this results in discharge of diesel combustion products.

3.3. Acid Plant Emissions

The acid plant performs its conversion reaction in the presence of excess air. After the acid reactions have taken place any unused air is vented to atmosphere through the acid plant stack. The nature of an equilibrium reaction such as the one used in this process means that a proportion of SO₂ and SO₃ will be left in the exhaust gas stream as it exits the acid plant stack.

The acid plant operates two cooling towers. The bulk of the heat generated in the acid manufacture process is reclaimed and used to generate steam, however manufacturing steps such as acid dilution release low grade heat which is not hot enough to be used to create steam. This heat must be removed from the plant and is dissipated through cooling towers. The cooling towers consume fresh water and remove heat from the plant through evaporation. The evaporated water can be seen as a plume above the cooling tower fans.

The key consent conditions for the acid plant are that SO₂ discharges shall not exceed 1.5 kilograms per minute for more than two minutes or shall not exceed 60kg per hour.



3.4. Acid Plant Emission Monitoring and Control

Manual stack test for SO₂, SO₃ and acid mist emissions from the acid plant occur twice a week. Uses USEPA Method 8.

Two online SO₂ analyzers installed in the acid plant stack, report through to SCADA.

Cooling tower biological load testing also occurs and regular samples are tested for total cfu and legionella.

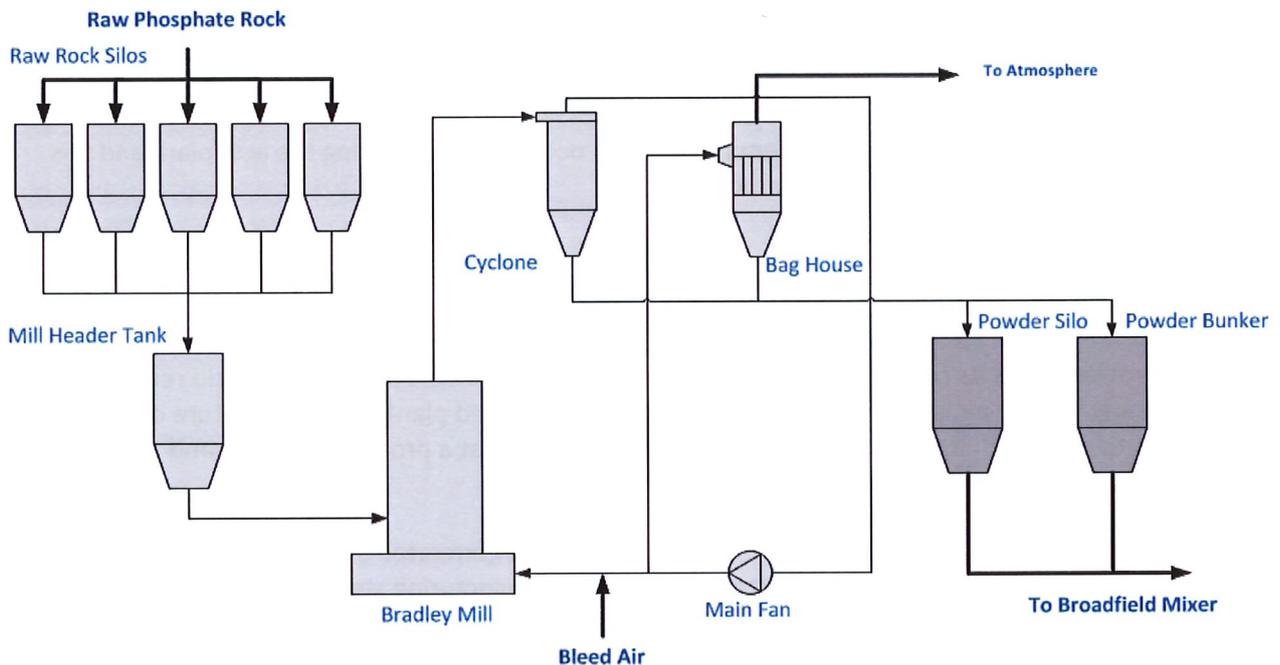
4. Superphosphate Manufacture Plant

4.1. Manufacture Process

The primary ingredient of superphosphate is phosphate rock. This raw material is purchased worldwide and shipped to the Napier port. From the port the rock is trucked to the Napier works and received over an intake system which conveys it into storage sheds.

The phosphate rock in its raw form can vary in consistency from a dry sand like material, a coarse chip or a topsoil. In this state the rock is too coarse to react with acid and make superphosphate. Prior to processing the rocks are blended through a weighed silo system to create a mix which satisfies the chemical characteristics required by the plant. It is then fed to the milling plant where it is ground to the consistency of talcum powder (more than 80% passing a 75µm sieve) and conveyed to a storage tank.

Rock Grinding Plant Flow Diagram



From the storage tank the finely ground powder is fed into the mixer. In the mixer sulphuric acid and phosphate rock is reacted alongside Hydrofluoric Silicic Acid (FSA) and fresh water to form a product with the consistency of wet concrete.

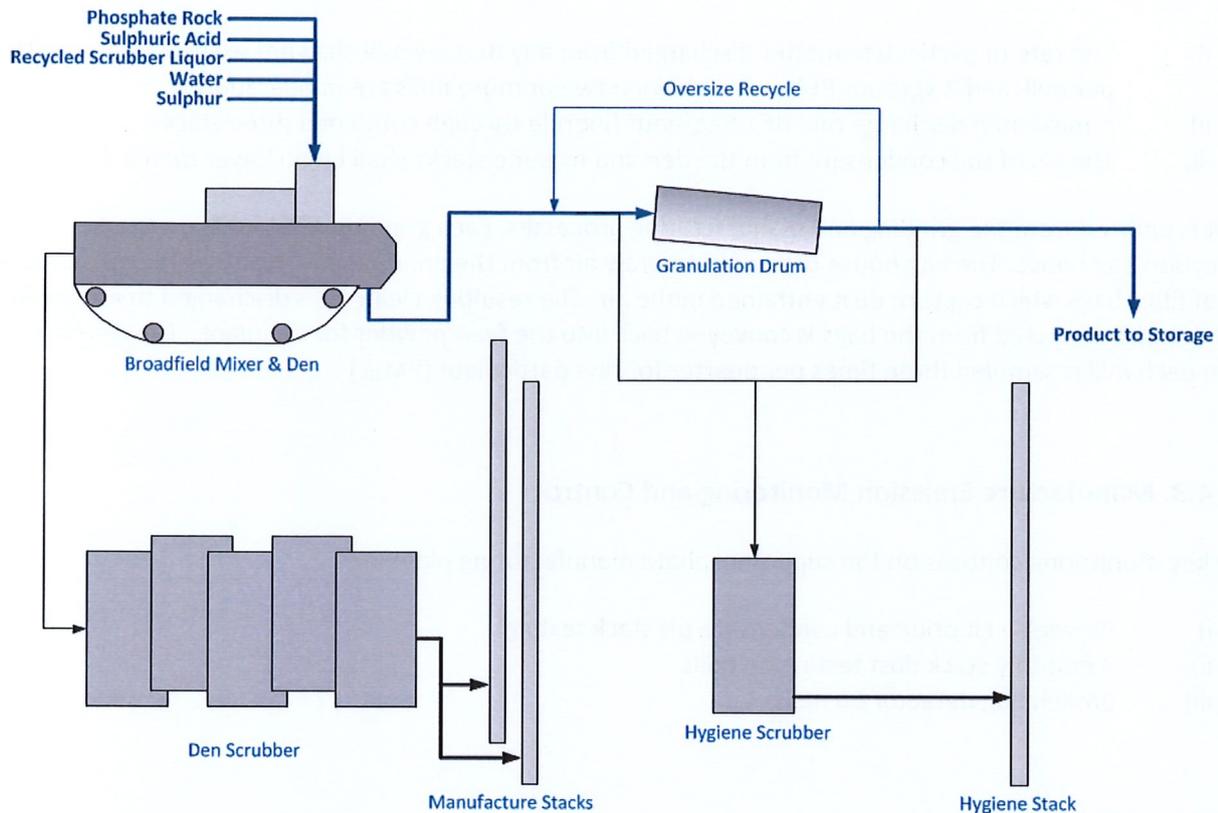
Two reactions occur. The first one creates phosphoric acid and happens quickly. The second one makes monocalcium phosphate, progresses over a couple of weeks.

The product continues to react over approximately 20 minutes inside a reaction chamber called the Den. Once cured the material is crushed into fine particles and passed through the granulation system to form



the final granulated product. This product is conveyed into the storage sheds and allowed to mature until the granules fully harden and the reaction completes.

Superphosphate Plant Flow Diagram



4.2. Manufacture Emissions

All phosphate rocks contain a varying proportion of fluoride which is bound in the same complex mineral (fluorapatite) which carries the phosphate needed for the fertiliser. When sulphuric acid is added to the rock to convert the phosphate to a soluble form, heat, steam, and fluoride are also released. The fluoride containing steam is the primary emission from the manufacturing process.

A wet scrubbing system is used to absorb fluoride gases from the process. The scrubbing system comprises of a series of large towers each containing sprays which wash the steam capturing the fluoride before the gases are discharged to air via the manufacture stacks. Fluoride is very soluble in water and as such the actual discharge of fluoride through the stack is quite low.

The fluoride containing water generated by the scrubbing system is used to control the product consistency within the mixer, and fresh water is taken from the storm water collection pond to replace the water consumed by the plant. None of the scrubbing liquor is discharged through the stormwater system.

The plant also operates a second scrubbing system which collects gasses released around the granulation and conveying systems in order to control fluoride levels within the building. This waste water from this scrubbing process is also re-used in the mixing process.

A project is underway to replace the existing scrubbing system as it is considered "end of life". An upgraded scrubbing system will be placed on the north eastern aspect of the manufacture building. The project objective is to meet world best practice for fluoride emissions. As part of the project the three existing



stacks will be replaced by one stack. The two scrubber air flows will be mixed together resulting in a cooler gas, and therefore a less visible plume.

The key consent conditions for fertiliser manufacture are:

- i) The rate of particulate matter discharged from any Bradley mill shall not exceed 1kg/hour PM₁₀ per mill, and 2 kg/hour PM₁₀ in total when two or more mills are in operation.
- ii) A maximum discharge rate of 1.5kg/hour fluoride through combined three stacks.
- iii) The pH of the condensate from the den and hygiene stacks shall be no lower than 2.7.

Dust is emitted from the grinding and manufacturing processes. Each grinding mill has its own dust collection bag house. The bag house uses a fan to draw air from the grinding mill. It passes the air across a set of filter bags which capture dust entrained in the air. The resulting clean air is discharged to atmosphere and the dust collected from the bags is conveyed back into the feed powder for the plant. The discharge from each mill is sampled three times per quarter for fine particulate (PM₁₀.)

4.3. Manufacture Emission Monitoring and Control

The key monitoring controls on the superphosphate manufacturing plant are:

- i) Bi-weekly Fluoride and condensate pH stack testing
- ii) 3 monthly stack dust testing on mills
- iii) Broken bag detector on mills

5. Despatch

5.1. Despatch Process

In the despatch plant the cured superphosphate is collected from storage sheds with a loader and fed into a dressing plant. This plant breaks up any lumps in the product before it is fed on to trucks to be despatched from the site. A portion of the superphosphate is also fed into a blending plant which allows other products which are not manufactured on the site to be blended with it to achieve the required nutrient characteristics required by a customer. This product is also conveyed in its bulk form into trucks to be despatched from site.

5.2. Despatch Emissions

Dust is the primary emission from the despatch plant. Conveying, dressing, and loading of fertiliser components causes a some of the dust trapped in the products to become airborne. The bulk of this dust settles back to ground either inside the despatch buildings or on the buildings and roadways within the site. This deposited dust is managed through manual cleaning by staff or captured in storm water runoff by the site storm water system.

The manufacture of Flexi-N (a MgO coated urea product) releases ammonia gas. The quantity released can vary on the batch process, and the urea used.

5.3. Despatch Emission Monitoring and Control

The primary method of dust control in the despatch area is extraction of dust to baghouses and venting heated air inside the despatch buildings.



6. Site General

6.1. Site Processes

Many of the processing steps employed in the manufacture of superphosphate generate dust as a result of handling the bulk materials. To limit the release of dust all manufacturing processes are carried out inside buildings designed to contain the particulate. However the buildings are not sealed (doors open, etc) and therefore an amount of dust inevitably escapes these buildings often carried on the mobile equipment and bulk vehicles which pass in and out of the buildings. This dust settles on the surrounding road ways and buildings. Despite regular cleaning a portion of this phosphate containing dust gets washed into the site storm water system.

To reduce the sites impact on the surrounding environment the storm water system employs a catchment pond which collects all rain water washed from the site. This pond is used as a water supply to feed the manufacturing plant. During low rain periods it is possible for the site to consume the bulk of the water which enters the site drains.

When rain fall is greater than the catchment system can accommodate the excess water is monitored for contaminants and pH corrected if required before releasing it to the offsite storm water outlet.

Not all site processes are able to consume the grey water collected from the storm water catchment pond. As such the site also operates a number of fresh water bores which supply water for uses such as drinking water, fire service supply, steam generation, cooling tower make up and acid make up. The site uses five septic tanks to treat wastewater from amenities (cafeteria, showers, toilets, laboratory).

The Ravensdown water take consent allows groundwater to be abstracted up to:

- 21,000m³ in any 7 day period
- 1,092,000m³ within the 12 month period 1st July to 30th June

6.2. Site Emissions

Storm water discharged from the site is required to achieve the following:

- a) pH to be within 6.5 – 8.5
- b) Fluoride not to exceed 30 mg/litre.
- c) Suspended Solids not to exceed 100 mg/litre.
- d) Rate of discharge not to exceed 265 litres/second
- e) Total Phosphorus not to exceed 17 mg/litre (95% of time); and 22 mg/litre (99% of time)
- f) Soluble Reactive Phosphorus not to exceed 15 mg/litre (95% of time); and 20mg/litre (99% of time).

6.3. Site Emission Monitoring and Control

Ambient Fluoride is monitored as gaseous and particulate each week from five sites with two close to the Works and three further afield.

Online PM₁₀ dust monitoring occurs with online monitors located at Archimedes and Winstone Aggregates sites.



Stormwater pH, phosphate, heavy metals, fluoride, suspended solids are monitored using automatic samplers and a composite sample is analysed each week. An upgraded sample collection unit is being installed.

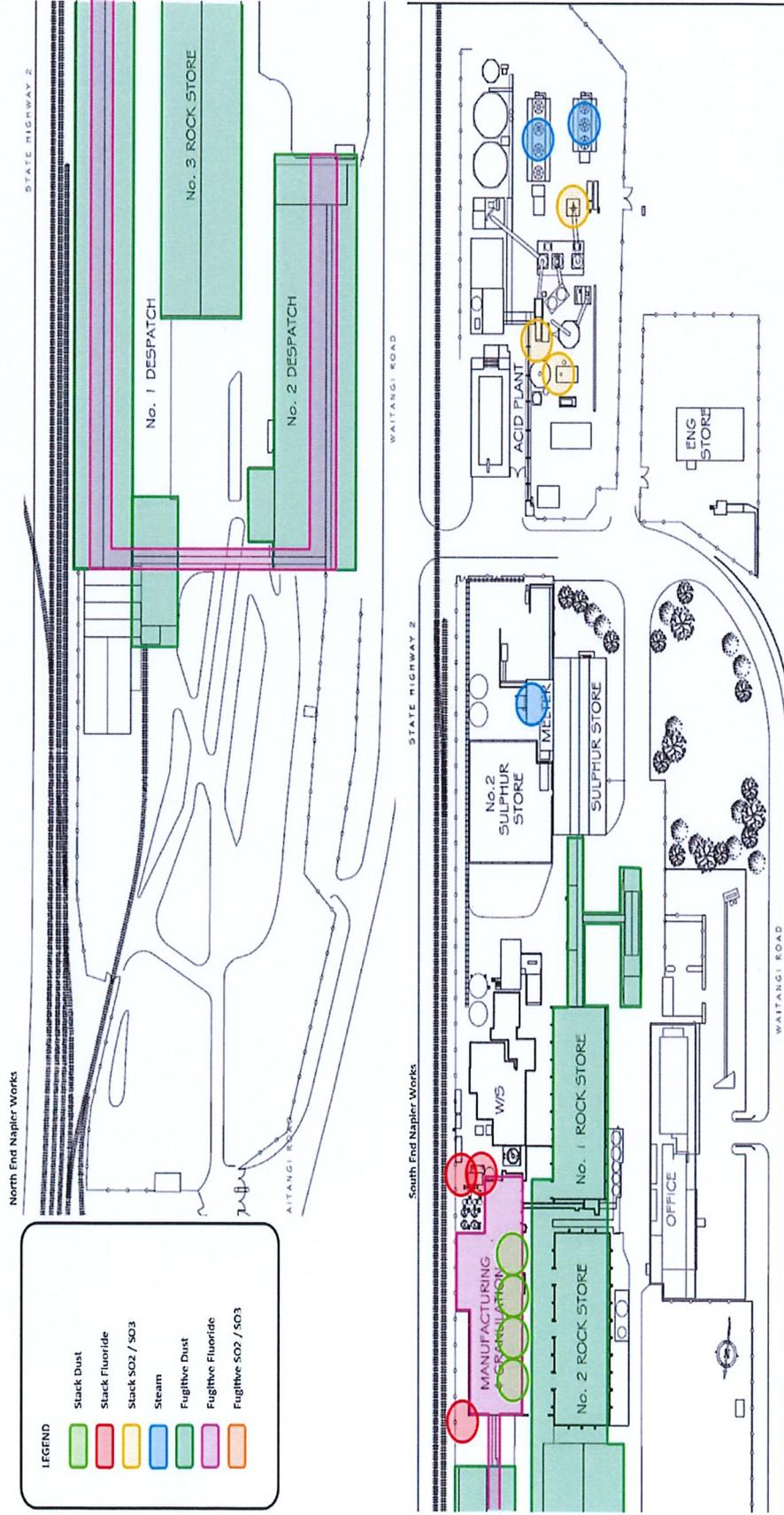
Dilution water is added to control phosphate concentration in stormwater while caustic is added to control storm water discharge pH. The settling pond allows suspended solids to drop out of suspension before stormwater is discharged to the environment.

Online pH monitoring of stormwater occurs to ensure that stormwater discharges are within specification.



Appendix A

Site map with Emission sources identified



Corporate Context

About Ravensdown

Ravensdown exists to enable smarter farming for a better New Zealand. As a farmer-owned co-operative, Ravensdown's products, expertise and technology help farmers reduce environmental impacts and optimise value from the land.

Ravensdown is an integral part of the food creation process, whether the food is grown for livestock or for humans. Ravensdown tests for, advises about, buys, manufactures, ships, stores, spreads, measures and maps food-creating nutrients and fertiliser for its farmers in an integrated way.

Ravensdown is a science-focused organisation delivering quality agri-products, technologies and services. Ravensdown provides:

- Practical insights, trusted guidance and lab-based diagnostic data on soil and plant samples.
- Environmental consultancy to assist farmers to mitigate impacts and move beyond compliance.
- Quality agri-products including agrichemicals, seeds and animal health products.
- Manufacturing superphosphate and superphosphate-based products at dedicated plants in Christchurch, Dunedin and Napier.
- Lime quarries producing mainly agricultural lime products.
- Logistics and storage of bulk fertiliser and other products to ensure they are available when needed.
- Global sourcing from top tier suppliers.
- Capability for precision fertiliser application by ground and by air.
- Map-and-measure technology for better on-farm decision making.
- Innovation and research to ensure advice and solutions are based on sound science.

Ravensdown operates three superphosphate and superphosphate-based product manufacturing plants and a network of fertiliser bulk stores and quarries throughout New Zealand.

Ravensdown provides the nutrients that nourish New Zealand's soil which, in turn, feed the plants and animals that deliver the products that can command a premium on the world stage. Smarter farming is all about smarter choices for the environment. Sales are important but as a farmer-owned co-operative, it is not Ravensdown's policy to sell farmers more than they need. Precision agriculture is about the right amount of the right inputs in the right place, applied at the right time. Smarter farming is also about always having the right reason – the focus on the environment, community and kaitiaki (stewardship).

Site History and Production

Fertiliser manufacture commenced at Napier Works in 1954. When Ravensdown Fertiliser Co-operative bought the site in 1987 from East Coast Fertiliser Co-operative, the plant had a production capacity of 100,000 tonnes of superphosphate per year. Following various plant upgrades and subsequent additions, Napier Works currently produces about 300,000 tonnes of superphosphate per year, and has capacity to produce up to 440,000 tonnes per year. In addition, the plant produces approximately 90,000 tonnes of sulphuric acid which is used in the manufacturing process or sold directly to consumers (approximately 1%). Bulk sulphuric acid is used in a range of industrial processes (e.g., pulp and paper industry, primary processing industry).

A key raw material in the manufacture of superphosphate is phosphate rock. Phosphate rock is imported from a number of sources including Africa, Vietnam and Christmas Island. Some phosphate rock is imported from Western

Sahara which is subject to a complex, ongoing dispute. Ravensdown monitors the activities of its supplier to ensure they continue to comply with the United Nations framework. For further information see:

<https://www.ravensdown.co.nz/services/product-availability/phosphate-rock-supply>

Importance of Napier Works

Napier Works is a key manufacturing site for Ravensdown. It is also the largest superphosphate manufacturing plant in New Zealand. The annual production of all Ravensdown's major superphosphate manufacturing plants is summarised below.

	Napier	Christchurch	Dunedin
Superphosphate Plant Production Capacity (tonnes/year)	440,000	200,000	214,000
Actual Annual Production of Superphosphate (tonnes/year)			
2018-2019	283,313	117,579	104,622
2017-2018	261,395	110,512	101,046
2016-2017	273,446	106,547	100,253
2015-2016	292,223	116,592	104,050
2014-2015	286,507	97,869	92,086
2013-2014	248,054	140,474	117,722
2012-2013	278,920	127,464	118,902
2011-2012	337,907	183,196	116,109
2010-2011	340,850	126,375	185,112
2009-2010	234,779	132,621	144,045
2008-2009	199,320	158,907	149,321
2007-2008	366,426	162,357	142,468
2006-2007	333,584	118,419	123,826
2005-2006	352,230	126,388	118,629
2004-2005	538,860	138,695	150,886
2003-2004	457,529	166,641	144,181
2002-2003	538,934	192,648	148,543
2001-2002	512,833	174,733	148,791
2000-2001	476,695	177,000	147,040
1999-2000	429,995	141,348	152,105

Note: From 2005, production at Napier Works was lowered following a site upgrade that reduced costs and resulted in improved quality.

Locally, Napier Works is an important industry in Hawke's Bay. The site provides 70 jobs, of which about 54 are associated with the manufacturing plant. In addition, approximately 170 contractors work on-site to assist with maintenance and development projects. In the last financial year, Ravensdown spent \$5.4 million directly on salaries and wages, and a further \$5 million with local contractors

The Napier Works supports essential infrastructure in the region. It is also the largest importer of product through the Port of Napier, with 27 vessels docking in the past 12 months and 200,000 tonnes of raw material imported for the manufacture of superphosphate. The Port of Napier also received 160,000 tonnes of compound farm nutrients imported for direct application to farm. In addition, Ravensdown shipped 25,000 tonnes of superphosphate to other New Zealand ports.

Direct economic activity, and indirect employment and economic activity associated with the Napier Works is significant. The Napier Works is a major user of local road transport carriers, spending \$9 million in the distribution of products to stores around the North Island.

The Napier Works is a key contributor to both the local and national economy. It also plays an essential part in providing the key nutrients required for the ongoing development of New Zealand agriculture.

Further Information and Terminology

For further information on Ravensdown please refer to:

<https://integratedreporting.ravensdown.co.nz/>

To ensure consistency in terminology please refer to:

Ravensdown Limited (Ravensdown)

Napier Works

(note – while the location of the Works is at Awatoto, the site is no longer referred to as Awatoto Works)

Plant – refers to manufacturing infrastructure

Site – refers to the location or site as a whole

Sulphur/sulphuric NOT sulfur/sulfuric