

Outcomes and Implications of the Upstream Treatment Investigation

Boundary Creek and Big Swamp Contingency Planning

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Introduction

Background

In June 2017, Barwon Water acknowledged that the historic management of groundwater pumping activities at the Barwon Downs borefield had resulted in water level decline and depressurisation of the Lower Tertiary Aquifer (LTA). These activities also led to some unintended consequences, such as the reduction in baseflow to Boundary Creek that relied on baseflow to sustain streamflows during dry periods. When combined with drought conditions and the ineffective regulation of passing flow conditions at a private on-stream dam located along Boundary Creek, this reduction in streamflows led to an increased occurrence of wet-dry cycling in Boundary Creek and Big Swamp. This in turn led to the oxidation of naturally occurring acid sulfate soils which resulted in the acidification of the surface water and shallow groundwater system, the mobilisation of metals and the discharge of acidity and metals to the lower reaches of Boundary Creek and more broadly the Barwon River.

In response to this, in May 2018, Barwon Water established a community and stakeholder working group to participate in the design and development of a remediation plan for Boundary Creek and Big Swamp. The working group was made up of representatives from the Corangamite Catchment Management Authority (CCMA), Colac Otway Shire Council, Land and Water Resources Otway Catchment (LAWROC), Environment Victoria, Upper Barwon Landcare Group, Boundary Creek landowners, Traditional Owners and other interested community members. The remediation working group also benefited from three acid sulfate soil and remediation experts who they nominated to seek independent technical advice.

In September 2018, Barwon Water's commitment to undertake remediation was legally strengthened through the issuing of a Ministerial Notice under section 78 of the Water Act, 1989. This notice mandated the development and implementation of the Boundary Creek, Big Swamp and Surrounding Environment – Remediation and Environmental Protection Plan (REPP), which was subsequently approved by Southern Rural Water in February 2020. The objectives of the REPP are twofold:

- The Boundary Creek & Big Swamp Remediation Plan To address remediation of confirmed impact in the Boundary Creek catchment resulting from historical management of groundwater extraction at the Barwon Downs borefield; and
- 2. **The Surrounding Environment Investigation** To investigate whether other areas within the regional groundwater system have been impacted by historical management of groundwater extraction at the Barwon Downs borefield.



Boundary Creek and Big Swamp Remediation Plan

Although many factors (as shown in Figure 1) have contributed to changes in the Boundary Creek Catchment, the two variables that have had the greatest influence are the historic management of groundwater pumping activities at the Barwon Downs borefield and climate, due to their impact on streamflows and water quality.

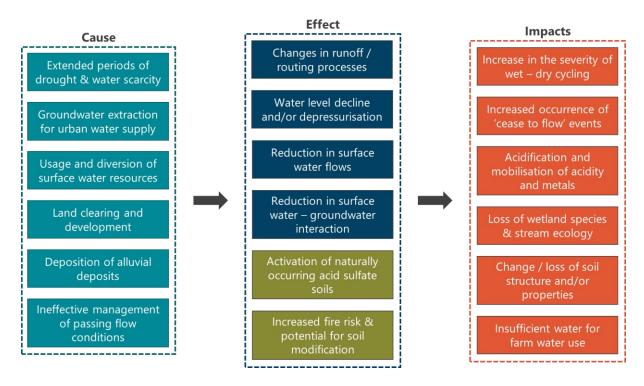


Figure 1: Cause and effect relationship in the Boundary Creek catchment

The primary remedial strategy for Boundary Creek and Big Swamp is to facilitate groundwater level recovery, maintain saturation of the naturally occurring Acid Sulfate Soils and minimise wet-dry cycling. However, the REPP also outlines Barwon Water's commitment to undertake additional data collection and testing to inform the feasibility of different contingency measures should high-risk events be identified which may adversely impact environmental receptors.

The focus of these contingency measures, to date, has been the development instream treatment options (i.e. either a downstream or upstream treatment system), with the detailed design of a downstream treatment system previously provided to Southern Rural Water and the ITRP as part of the Hydro-Geochemical Modelling – Design of Contingency Measure report (Barwon Water, 2021).



Objectives of this report

The objectives of this report are to:

- 1. Provide an overview of the feedback received on the Upstream Treatment Trial Plan (Barwon Water, 2022)
- 2. Provide an overview of the outcomes from Phase 1 and Phase 2 works associated with the upstream treatment investigation
- 3. Provide an overview of the current 'state of knowledge' based on the data collected since the implementation of the REPP
- 4. Outline the implications of these findings on remedial planning and the proposed approach to inform the development of contingency measures; and

Overview of the Upstream Treatment Investigation

The upstream treatment investigation was initially instigated in 2021 in response to feedback from Southern Rural Water's Independent Technical Review Panel (ITRP), who suggested a potential passive treatment system as an alternate approach to conventional active treatment methods, such as the downstream dosing plant. The focus of this system was to treat the acidity at the source, thus, improving the conditions both within and downstream of the swamp and removing the need for conventional active treatment systems, such as the pH Adjustment – Flow (PAF) plant as proposed by Jacobs in 2021.

Due to the novelty and limited commercial application of the proposed system, Barwon Water developed a staged approach with which to investigate the applicability of the proposed system, as outlined in Figure 2 to:

- 1. To investigate the potential application of caustic magnesia (MgO) in neutralising acidity-affected portions of the swamp and assess any potential ecological risks associated with this approach
- 2. Quantify the benefits and clarify the capital and operating costs of the proposed semi-passive treatment system
- 3. Assess the chemical interaction between the source water and the caustic magnesia under a range of scenarios using a small-scale system, and
- 4. Inform assessment of the feasibility of implementing the proposed upstream treatment method and development of a potential full-scale system.



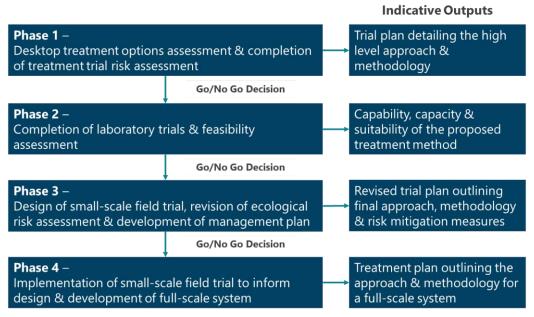


Figure 2 Treatment Trial Roadmap

In January 2022, the outcomes of the Phase 1 works were captured in an Upstream Treatment Trial Plan that outlined:

- 1. The potential treatment options
- 2. The proposed concept design for a semi-passive caustic magnesia treatment system; and
- 3. The potential risks associated with implementing such a treatment system within Big Swamp

This Trial Plan was submitted to Southern Rural Water and their ITRP, and the Remediation Reference Group (RRG) and their nominated experts for feedback in mid-January 2022. The feedback received on the trial plan was discussed at the Remediation Reference Group Meeting held on 21 March 2022.

Following submission of the Trial Plan, Barwon Water engaged Earth Systems to commence the laboratory trials on the proposed caustic magnesia (MgO) reagent to determine the potential soluble alkalinity that can be generated from this treatment methodology to assess the viability of implementing such a novel treatment system.

What has informed this process?

The Big Swamp Upstream Treatment Trial Plan was informed by:

- The Boundary Creek, Big Swamp and Surrounding Environment Remediation & Environmental Protection Plan (REPP)
- The environmental monitoring data collected since acceptance of the REPP in February 2020



- GHD's Big Swamp Integrated Groundwater-Surface Water Modelling for Detailed Design completed in April 2021
- Barwon Water's Hydro-Geochemical Modelling Report Design of Contingency Measure completed in July 2021
- Feedback received from our Remediation Reference Group (RRG) and their nominated experts regarding the detailed design of hydraulic barriers, review of remediation success targets, hydro-geochemical modelling, Barwon Water's high level program outline for upstream treatment and the proposed upstream treatment trial approach
- Feedback received from the Independent Technical Review Panel (ITRP) and SRW regarding the detailed design of hydraulic barriers, review of remediation success targets, hydro-geochemical modelling and Barwon Waters outline program for upstream treatment trial
- Barwon Water's Upstream Treatment Trial Plan completed in January 2022
- Feedback received from our Remediation Reference Group (RRG) and their nominated experts regarding the proposed semi-passive upstream treatment system
- Feedback received from Southern Rural Water and their Independent Technical Review Panel (ITRP) regarding the proposed semi-passive upstream treatment system; and
- The test work program undertaken by Earth Systems to assess the viability of the proposed semi-passive upstream treatment system.



Feedback on the Upstream Treatment Trial Plan

Following submission of the Upstream Treatment Trial Plan, the following feedback was received from the various community and stakeholder groups.

- Concerns were raised regarding the water source and risks associated with emergency management e.g. flood and fire. The preference of the community group was for a gravity fed system.
- There was concerns regarding the novelty of the proposed treatment system and the potential for this to cause harm to the ecological values of the swamp given the lack of existing case studies in similar environments with the RRG nominated experts questioning if this work constitutes research and development rather than remediation.
- There was concerns regarding the lack of regulatory oversight from EPA in the potential remedial options. Noting that Barwon Water received advice from EPA Victoria that no permission is required from EPA to undertake the small-scale field trial as part of Phase 4 works Implementation of small-scale trial.
- General feedback was that the trial plan is appropriate, but additional data and input is required to determine the suitability of the proposed treatment option and expand on the monitoring requirements.
- Community and stakeholder groups questioned if active intervention is required given the observed natural recovery of the swamp and surrounds. The preference was to allow natural recovery processes to continue and minimise further impacts that may occur as a result of implementing remedial actions.
- Expert groups highlighted that the system appears to be recovering faster than anticipated, but questioned how much of this can be attributed to the wetter than average conditions.
- While the plan was generally clear and logical, deficiencies were identified in the potential risks and controls associated with the potential small-scale field trial.
- Concerns were also raised regarding the appropriateness of establishing such a system in a natural environment.
- Experts indicated that the current ecological values of Boundary Creek and Big Swamp are not well defined in terms of the species present and their sensitivities and indicated that further work would be required to better assess the risks.
- Some concern was raised regarding the differences in feedback from different expert groups. Community and stakeholder groups expressed an interest in seeing the experts meet to discuss the next steps to ensure alignment before progressing to the next phase.



In line with roadmap outlined in Figure 2, many of these concerns were to be addressed during Phase 3 works – i.e. design of small-scale field trial, as part of the required approvals process. This was due to the uncertainties around whether the dissolution of the caustic magnesia reagent would be sufficient to address the acidity loads within Big Swamp, which was to be the focus of the laboratory trials. Rather, much of this feedback related to the potential small-scale field trial or the potential full-scale system and therefore would need to be addressed if the investigation progressed beyond the laboratory trials.



Laboratory testwork program

The objectives, methodology and findings of the laboratory trials undertaken by Earth Systems are provided in Appendix A. These are focused around assessing the key variables that affect the solubility of MgO in water, and include:

- The manufacturing process used to produce the MgO i.e. the calcination temperature and duration
- The composition (i.e. purity) of the reagent
- The grainsize of the reagent, and
- The length of time spent in contact with the water (i.e., dissolution kinetics).

A summary of the key findings are outlined in the sections below. The full report by Earth Systems is provided in Appendix A.

Range and composition of reagents tested

The laboratory trials assessed four locally sourced potential caustic magnesia (MgO) based reagents, as outlined in Table 1 below. Preference was given to local suppliers due to the current supply chain issues and to ensure availability of reagent for subsequent phases of the investigation. In addition to these, one alternate reagent – hydrated lime, was also tested following completion of the initial laboratory testwork.

Sample No.	Category	Grain Size (μm)	Composition	Supplier	Residence Times (mins)
1	Coarse	3000 – 5000	MgO with minor CaO		17, 30, 63 &
2	Grained	-3000	enrichment	Causmag	119
3	Fine Grained	-100	MgO with minor CaO enrichment	International	14, 19, 25 & 69
4		-100	MgO with negligible CaO enrichment	Calix	22 & 25
5	Fine Grained	N/A	Ca(OH) ₂	N/A	16, 45, 48 & 59

Table 1 Summary of the potential caustic magnesia (MgO) based reagents

While there are a range of other potential suppliers globally, the mix of different reagents and compositions was considered to give a good representation of the potential viability of caustic magnesia in treating the acidity loads within Big Swamp.

Testwork Apparatus

The potential reagents were separated into two main categories based on their grainsize (fine vs coarse), and two testwork apparatuses as shown in Figure 3, which were designed based on the concept design outlined in the Upstream Treatment Trial Plan.



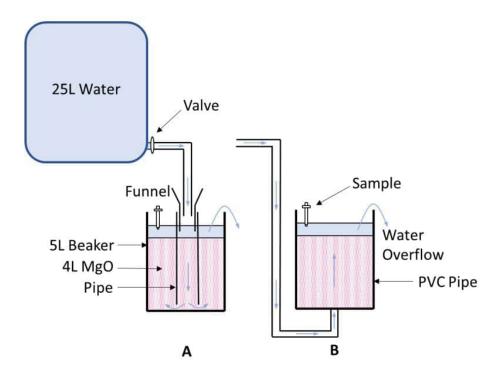


Figure 3 Schematic of the (A) course-grained and (B) fine-grained laboratory testwork apparatus (Earth Systems, 2022)

Water Source

Given the proposed water source for the treatment system was to be from the upper reaches of Boundary Creek, which is generally characterised by circumneutral pH and low acidity loads, the laboratory testwork also involved the use of non-acidic water sources.

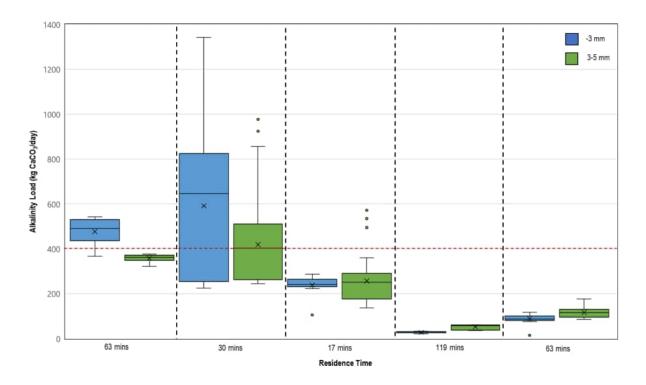
During initial trials, distilled water (with a pH of 5-5.4) was used due to concerns about the precipitation of minerals upon exposure to the reagent. However, after initial trials established that this was not an issue, subsequent trials were completed using mains water (with a pH of ~6.9).

Ability to neutralise acidity loads

As outlined in the Upstream Treatment Trial Plan (Barwon Water, 2022), the proposed semipassive caustic magnesia based treatment system would need to be capable of treating average daily acidity loads of between 300 - 400 kg CaCO₃/day, with peak values of at least twice this value.

As outlined in Figure 4 and Figure 5 below, the laboratory trials indicate that only the coarse grained caustic magnesia based reagents were able to achieve the alkalinity loads required to neutralize the acidity loads within Big Swamp. However, this could not be achieved at the consistency required to be a feasible treatment option.





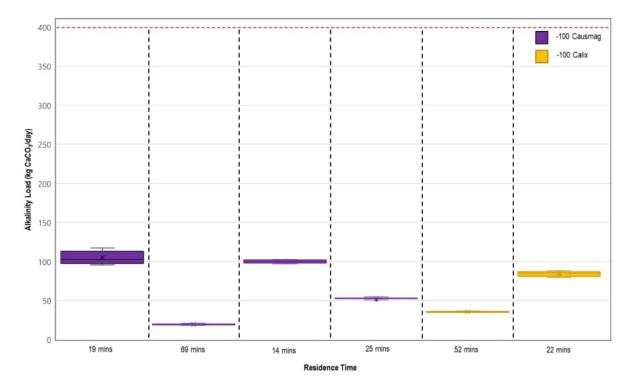


Figure 4 Alkalinity loads generated for coarse grained materials (Earth Systems, 2022)



Figure 4 also indicates a rapid decrease in alkalinity during subsequent test runs, which may be indicative of reagent depletion. However, Earth Systems report that this likely reflects the depletion of the more soluble calcium based minerals rather than the caustic magnesia. In either case, this indicates that these materials are not suitable for long-term treatment



applications. This is supported by the pH data which reports values greater than the saturation pH of caustic magnesia.

On the contrary, additional testing conducted on an alternate reagent – hydrated lime, revealed that this was capable of producing average alkalinity loads from 580 – 1,828 kg CaCO₃/day. This suggests that hydrated lime would be more applicable for this type of application. However, this was not considered as a potential reagent as part of the Upstream Treatment Trial Plan due to the elevated saturation pH (12.4), potential to increase the precipitation of metals, and need for specialist storage and handling equipment (Barwon Water, 2022).

Implications of the laboratory trials on the potential risk profile

The pH values reported during the laboratory trials on the caustic magnesia based reagents were in excess of the theoretical saturation pH (i.e. 9.5 - 10.8) (Barwon Water, 2022). While this relates to the composition of the reagent, this also has ramifications for the proposed concept design which set an upper pH threshold of 9 pH units to minimise the potential ecological risks. In accordance with this concept design, the system would be shut-off when pH values within the mixing zone exceeded this threshold.

In the context of the concept design, this in-turn increases the potential for shut-off events (i.e. when the system is shut down due to pH values within the mixing zone exceeding the shut-off trigger), which were based on pH measurements within the mixing zone, and may lead to the discharge of un-treated water. Which in turn may preclude the intent of the treatment option.

This issue would also be the case for hydrated lime, which has a saturation pH of 12.4.

Further to this, the fine grained caustic magnesia and hydrated lime based reagents were also found to increase the turbidity of the solution which may also result in a range of aesthetic and/or unintended ecological impacts.

Summary of findings from the laboratory testwork program

The laboratory trials indicate that caustic magnesia (MgO) should not be regarded as a suitable reagent to meet the acidity loads within Big Swamp.

While hydrated lime or a more reactive reagent may be more suitable for this kind of application, they may also:

- Increase the potential for shut-off events (i.e. when the system is shut down due to pH values within the mixing zone exceeding the shut-off trigger)
- Decrease the effectiveness and ability of such a system to meet the remedial objectives
- Increase the risks associated with the implementation of such a system, and



• Present additional storage and handling constraints

On this basis, the proposed upstream treatment system is not considered to be a viable treatment option for managing the acidity loads within Big Swamp and therefore won't be explored further.



Outcomes of the upstream treatment trial investigation

As per the Upstream Treatment Trial Plan (Barwon Water, 2022) and the findings and recommendations from the laboratory testwork program (Earth Systems, 2022) outlined above, Barwon Water have ruled out the use of the proposed semi-passive caustic magnesia treatment system.

This decision accounts for the following technical, social, environmental and economic factors:

- The solubility of caustic magnesia being too high for a truly passive system (i.e. for direct contact with acidic water) as initially postulated by the ITRP
- The inability of the proposed semi-passive caustic magnesia based system to treat the average daily acidity loads of between 300 400 kg CaCO₃/day i.e. this would not meet the intended objectives
- The novelty and untested nature of such a system in a similar environment which:
 - Require additional research and development beyond more conventional treatment system
 - Make the potential risks and effectiveness of risk mitigation measures difficult to ascertain, and
 - Are cause of concern for the community and stakeholder working groups
- Lack of alignment between the different expert groups
- The additional time and cost that would be required to further investigate this potential treatment system prior to approval, which precludes this from being a short-term solution
- The improvements in conditions (e.g. water levels and quality) due to the cessation of groundwater pumping activities, the use of supplementary flows and the recent climatic conditions involving high rainfall,
- The preference of the community and stakeholder groups to minimise engineering interventions and let the swamp recover naturally, and
- The potential for further harm to the environmental and ecological values within Big Swamp



Current 'state of knowledge'

In addition to the information provided above, and in previous annual and quarterly reports submitted to Southern Rural Water and made available on the Your Say webpage: https://www.yoursay.barwonwater.vic.gov.au/boundary-creek), the following information is provided to outline the current 'state of knowledge' with regard to Boundary Creek and Big Swamp.

Climate related factors

As outlined in previous work undertaken to determine the confirmed areas of impact (Jacobs 2018), modelling conducted to assess the differences between 'pumping' and 'no pumping' scenarios indicated that groundwater levels and baseflow would still have been impacted by climate related factors during the millennium drought, albeit to a lesser extent, even in the absence of groundwater extraction.

Regional modelling indicates that under 'no pumping' conditions, regional groundwater levels would have declined by up to 4m and led to approximately 1 ML/day reduction in groundwater contribution to Boundary Creek – which is equal to the total modelled baseflow contribution under 'no pumping' conditions.

Despite the uncertainty associated with the model, this highlights the need to consider a range of other factors, beyond Barwon Water's control, in the development of the remediation success targets to ensure these are practicable given the potential for future climate related impacts to occur.

Ecological condition

As outlined in the Big Swamp Vegetation Monitoring Report (Eco Logical, 2020), the data suggests that there has been no further encroachment of either woodland or lowland forest species into the swamp between 2019 and 2020.

In addition to this, there was no loss of structural or floristic diversity within the swamp between 2019 and 2020.

While the next vegetation monitoring event is due later this year, photos comparing the condition of the swamp since 2010 indicate substantial recovery, as shown below.





When combined, these findings indicate that natural recovery processes are occurring and that helping to facilitate the natural recovery processes is meeting the objective of improving the ecological values without active management (such as removal of vegetation and replanting).

Outcomes from Drilling works

In April 2021 an additional bore (BSBH13LTA) was installed in the western portion of Big Swamp, adjacent to BSBH15. This bore was installed to 30 m below ground level and screens the Lower Tertiary Aquifer system between 26.5 and 29.5 m below ground.

Depth	Description	Geological Formation
0 – 5 m	Silty CLAY with trace sand: black-brown, moist, soft, low plasticity	Quaternary alluvium
5 – 16 m	Sandy CLAY and CLAY: brown and grey, soft- firm, high plasticity	Demons Bluff / Narrawaturk Marl
16 – 30 m	SAND: red and cream, loose to medium dense, coarse sand. Becoming fine at depth	Dilwyn Formation

The lithology based on the logs from this bore are as follows:

Based on this, the Demons Bluff/Narrawaturk Marl that confines the Dilwyn Formation (i.e. of the Lower Tertiary Aquifer) extends further west than was initially mapped and conceptualised. This is reflected in the simplified long section taken along Boundary Creek as shown below.



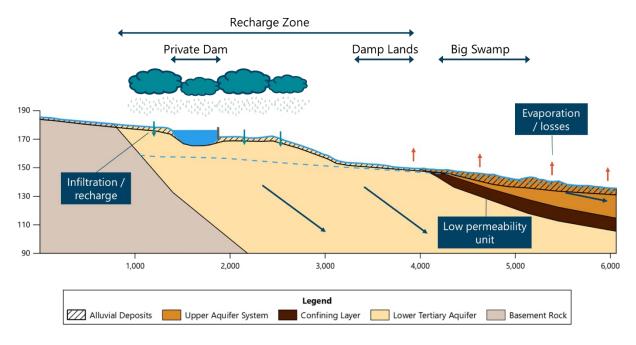


Figure 6 Simplified conceptual site model along Boundary Creek

Groundwater levels

Water level data indicates the recovery and re-pressurisation of the Lower Tertiary Aquifer system at both the eastern and western portions of Big Swamp (refer Figure 7 and Figure 8). It is noted that the spikes/dips observed at BSTB1C are likely due to the leaking headworks that has since been repaired.

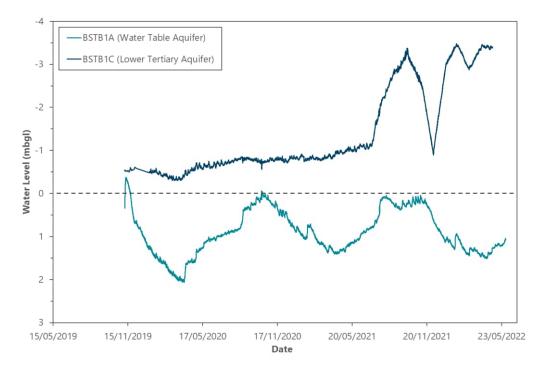


Figure 7 Groundwater levels in the eastern portion of the swamp



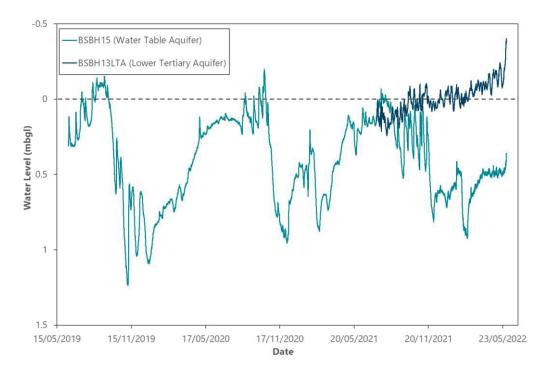


Figure 8 Groundwater levels in the western portion of the swamp

In addition to this, water level data from these nested monitoring sites indicate there is little hydraulic connection between the Lower Tertiary Aquifer and the Water Table Aquifer systems. This is consistent with the presence of a confining layer (i.e. the Narrawarturk Marl) that separates the two aquifer systems, as confirmed by the drilling works for bore BSBH13LTA. This indicates that any groundwater-surface water interaction that occurs within Big Swamp is related to the Water Table Aquifer system and the rejected recharge/baseflow that fed Boundary Creek and Big Swamp would have entered Boundary Creek above the swamp closer to where the Lower Tertiary Aquifer outcrops at surface.

Spot sampling data

In addition to the water level recovery, spot water quality sampling data from routine monitoring undertaken since 2019 indicate an overall improvement in groundwater and surface water quality over time (refer Figure 9). This is due to the works undertaken to both maintain saturation of the naturally occurring acid sulfate soils and minimise wet-dry cycling to prevent further oxidation and generation of acidity.

As reported in the Hydro-geochemical Modelling Report (Barwon Water, 2021), the spot sampling data reflects the three mobilization pathways:

- Acidity runoff from surface soils
- Groundwater discharge to surface water, and
- Flushing of acidity from the unsaturated zone

In addition to this, the data obtained since December 2021 indicates a shift in the geochemical conditions which may be reflective of an increase in groundwater – surface



water interaction between Boundary Creek and the Water Table Aquifer system, and secondary acidification resulting from iron reduction processes. This is demonstrated by the relationship between Electrical Conductivity (EC), sulfate, iron and acidity concentrations shown in Figure 9.

This will be explored in greater detail as part of the annual reporting process which will look at water quality data for each monitoring location.

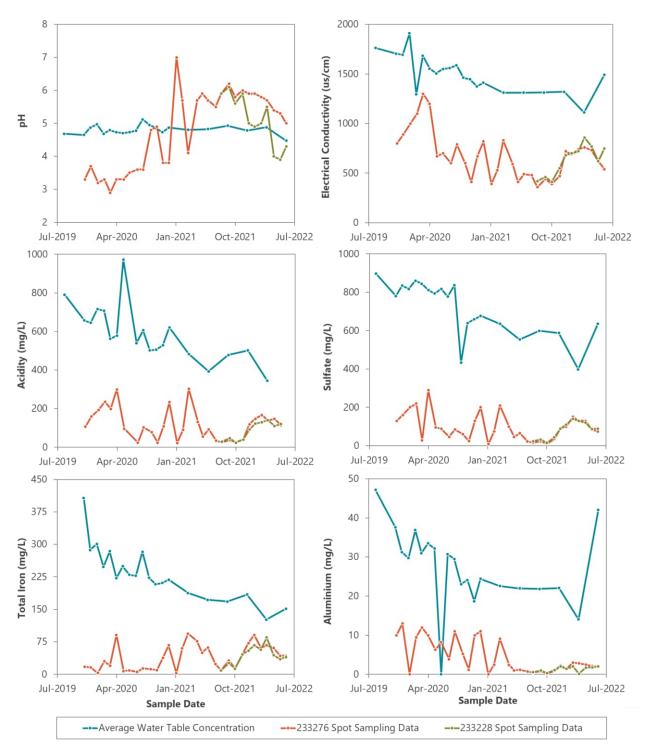


Figure 9 Concentrations of key analytes over time



Real time monitoring data

Real-time monitoring data from stream gauges installed along Boundary Creek indicate a decreased occurrence of no-flow events and a long-term increase in pH levels within Boundary Creek downstream of Big Swamp, despite some ongoing periodic flushing leading to low pH events (refer Figure 10 and Figure 11). Noting that the conditions that led to the previous fish kill events are increasingly unlikely.

The observed increase in Electrical Conductivity (EC) and corresponding decrease in pH levels since around October 2021 is consistent with groundwater – surface water interaction between Boundary Creek and the Water Table Aquifer system, as identified from the spot sampling data. From a conceptual perspective, this may also be indicative of bank storage – where soil pore water that is stored during wet conditions when water levels rise is partially or fully returned to the water body as water levels fall. This process may account for additional flushing of acidity from the unsaturated zone beyond the inundation area within Big Swamp.

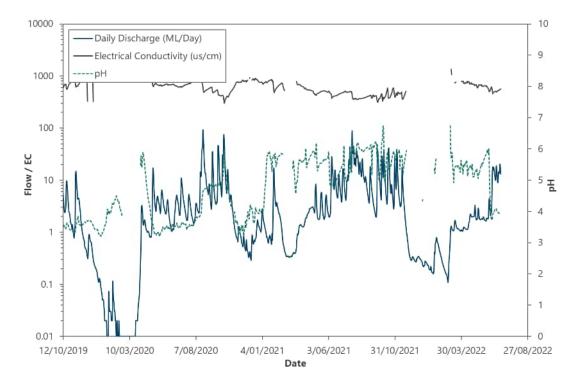


Figure 10 Streamflow, Electrical Conductivity and pH readings in Boundary Creek – Downstream of Big Swamp as recorded at stream gauge 233276



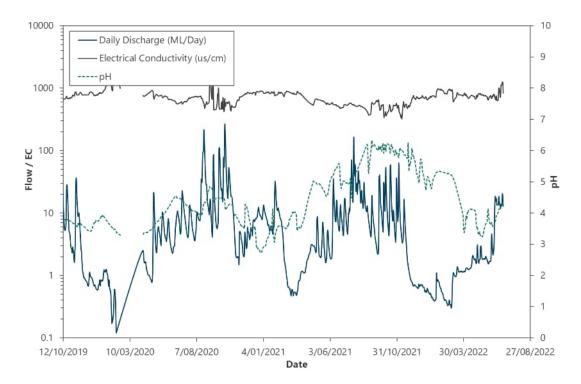


Figure 11 Streamflow, Electrical Conductivity and pH readings in Boundary Creek at Yeodene as recorded at stream gauge 233228

Applicability of Remedial Actions

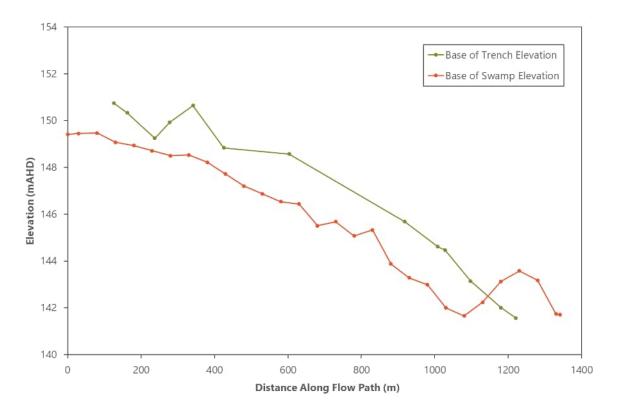
Based on the information above, a high-level review of the proposed remedial actions that were put on hold during the upstream treatment trial investigation has been undertaken. Specific comments in relation to each of these remedial actions are provided below.

Infilling of the fire trenches

Following further review of the fire trench survey data obtained by Jacobs in 2019 and the LiDAR data obtained by Barwon Water, which indicates the base of the trench is in the most part above the base of swamp and localised water table, infilling of the fire trench is unlikely to assist with maintaining moisture within the swamp (refer Figure 12).

Given this, and the fact that infilling of the trench would also lead to ecological impacts related to further soil disturbance and removal of vegetation, in line with community and stakeholder feedback regarding the "do no harm" concept, Barwon Water no longer proposes to implement this action. Instead, portions of the trench (i.e. in the eastern end where the trench is below the base of the swamp) may be modified as part of a proposed tiered risk-based contingency approach, should these portions of the trench prove to be a barrier to maintaining saturation of the reactive sediments within Big Swamp.







Installation of Hydraulic Barriers

The hydraulic barriers initially proposed were designed to help facilitate short-term water level recovery and keep the reactive swamp sediments (i.e., acid sulfate soils) saturated while groundwater levels recovered. Given the current and continued recovery of groundwater levels, installation of the hydraulic barriers in their current form are no longer required. The ecological impacts associated with the installation of the hydraulic barriers, which would require substantial heavy machinery and land clearing, would also not be in line with the "do no harm" concept which was reiterated by the community and stakeholder groups during the recent RRG meeting held on 8 June 2022.

Further to this, given secondary acidification processes (that occur as a result of iron reduction processes, particularly in the absence of sulfate reduction), have been identified as forecast by Cook and Wong in 2020, the installation of hydraulic barriers now would likely increase the acidity loads discharging from the swamp in the short-term and in turn increase the risks to the Barwon River. This is of particular concern given the water quality monitoring data outlined above in Figure 9.

As such, Barwon Water no longer considers hydraulic barriers, at least in their current form, as a potential remedial action. Instead, more targeted mechanisms such as the use of straw bales or other similar, less intrusive water diversion barriers to enhance the distribution of surface water flows through the swamp, could be considered as part of the tiered risk-based contingency approach.



Next Steps

Based on the findings from this investigation, Barwon Water propose to undertake the following actions to refine the remedial actions and integrate these into a revised REPP that reflects the additional work completed since implementation of the REPP began in March 2020.

ltem	Action	Deliverable	Timeframe
1	Update the REPP to reflect Barwon Water's commitment and actions to ensure no further groundwater extraction from the Barwon Downs Borefield and incorporate the previously accepted responses to earlier feedback from SRW and the ITRP on the REPP	Revised REPP	Estimated completion October 2022
2	Use the outcomes from the recent RRG meeting held on 8 June 2022 to reflect the community and stakeholder feedback regarding what remediation looks like, to provide a basis with which to assess the applicability of different remedial actions as required as part of the adaptive management approach. Barwon Water will also take these proposed amendments back to the RRG prior to submitting these to Southern Rural Water.	Revised REPP	Estimated completion October 2022
3	 Conduct a Level 3 Ecological Risk Assessment in line with Schedule B5a of the National Environment Protection (Assessment of Site Contamination) Measure (NEPM) to: a. Review the likely condition of the Boundary Creek & Big Swamp (a peat swamp) under natural conditions and confirm how the changes (e.g. drainage works, damming, groundwater pumping and climate etc.) have impacted the ecological condition/function b. Determine the current ecological values within Boundary Creek, Big Swamp and the Barwon River and the thresholds that account for the naturally occurring deposits/minerals within the region c. Quantify the risks associated with the metal and acidity loads to Big Swamp, Boundary Creek and the Barwon River The outcomes of this, will in turn, be used to: Inform the triggers for the implementation of contingency measures; and Further refine the success targets, if required. 	Ecological Risk Assessment Report	Estimated completion March 2022
4	• Further refine the success targets, if required. Continue to monitor and facilitate natural recovery processes	Quarterly Updates and/or Annual Reports	Quarterly
5	Review potential remedial actions such as the below items and how these can be integrated into a tiered risk- based approach, whereby actions may be implemented	Response to ITRP feedback on the detailed	Estimated completion

Table 2 Summary of proposed next steps



	based o	on a range of trigger conditions. This will include a	design for the	October
1	review	of:	downstream	2022
	a.	The existing design for the downstream	treatment	
		treatment option (i.e. a pH Adjustment – Flow	option	
		plant) to address the community and		
		stakeholder feedback received on the proposed	Revised REPP	
		design, with the aim to get an approved design		
		in place ready for implementation pending the	Review of the	
		outcomes of the risk assessment	potential	
	b.	The potential for the use of permeable reactive	application of	
		barriers, or similar, that were initially included in	permeable	
		the Remedial Options Assessment (ROA) (CDM	reactive barriers	
		Smith, 2019), to neutralise the acidity within the		
		swamp. Noting that unintended impacts would		
		also need to be minimised to achieve		
		community and stakeholder support.		
	С.	Other potential contingency measures that could		
		be implemented to prevent dewatering of the		
		swamp and improve flow distribution if the		
		current remedial actions cannot achieve the		
		remedial objectives. Such as:		
		i. Straw bales or other similar, less		
		intrusive water diversion barriers		
		ii. Adjustment of existing drainage lines		
		iii. Flow enhancement options; or		
		iv. Revegetation		



References

Barwon Water (2022), Upstream Treatment Trial Plan, Boundary Creek, Big Swamp and Surrounding Environment – Remediation and Environmental Protection Plan

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Cook and Wong (2020), Big Swamp acid sulfate soil study: Spatial extent of acid sulfate soils and potential for neutralization of acidity upon re-flooding

Earth Systems (2022), Semi-Passive Water Treatment Using Caustic Magnesia – Testwork Program Assessing Treatment Viability

Eco Logical (2020), Big Swamp Vegetation Monitoring Report – November 2020

Jacobs (2018), Barwon Downs Hydrogeological Studies 2016-17 - Numerical model calibration and historical impacts



Appendix A – Semi-Passive Water Treatment Using Caustic Magnesia – Testwork Program Assessment Treatment Viability (Earth Systems, 2022)





Semi-Passive Water Treatment Using Caustic Magnesia

Testwork Program Assessing Treatment Viability

prepared for

Barwon Water



by

Earth Systems



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EARTH SYSTEMS



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1. INTRODUCTION

Big Swamp is a groundwater dependent ecosystem that is located along the lower reaches of Boundary Creek near Yeodene, south-western Victoria. Since the 1990's, water levels within Big Swamp and Boundary Creek have declined, primarily in response to historic groundwater pumping activities at the Barwon Downs borefield. This groundwater level drawdown is likely responsible for the exposure of naturally occurring iron sulfide-rich sediment and soils, better known as acid sulfate soils (ASS) within Big Swamp (Sullivan et al., 2018). ASS generate acidity through exposure of the iron-sulfide rich sediments and soils to atmospheric oxygen, and acidity generation typically begins with pyrite oxidation according to Reaction 1.

$$FeS_2(s) + 3.75 O_2 + 3.5 H_2O \leftrightarrow Fe(OH)_3(s) + 2 SO_4^{2-} + 4 H^+$$
 (Reaction 1)

The acid (H⁺) produced through this reaction can react with other minerals, resulting in the production of dissolved metals and the consumption of acid. However, some dissolved metals, for example, Fe³⁺, have the potential to regenerate acidity through hydrolysis and precipitation of their respective metal hydroxides (e.g., Reaction 2 for Fe³⁺), a process referred to a *latent (or mineral) acidity*.

$$Fe^{3+} + 3 H_2O \leftrightarrow Fe(OH)_3(s) + 3 H^+$$
 (Reaction 2)

Thus, the precipitation of metals can lead to the generation of further acidity.

Acidity is typically reported as total (or net) acidity, or as acidity load. *Total acidity* combines the concentrations of acid measured by pH and latent acidity and is reported as milligrams calcium carbonate or sulfuric acid equivalent per litre (CaCO₃/L or H₂SO₄/L, respectively). Reporting as CaCO₃/L provides an indication of how much base / alkalinity is required to neutralise the acidity whereas reporting as H₂SO₄/L provides an indication of the amount of acid to be neutralised. *Acidity load* refers to the product of total acidity and flow rate and is reported in kg of H₂SO₄ (acid) or CaCO₃ (base) per unit time (e.g., day). Thus, acidity and acidity load provide an indication of the treatment requirements (i.e., alkalinity and alkalinity load) needed to neutralise the available and latent acid.

The oxidation of ASS in Big Swamp has resulted in acidification and discharge of water with elevated acidity loads over several decades, with a study completed by Jacobs in Barwon Water (2021) suggesting that acidity concentrations in discharging water may range from 90 to 300 mg/L CaCO₃. From this, it has been estimated that a minimum average alkalinity load of 300-400 kg (CaCO₃) is required to treat the discharging water and reduce risks to the receiving environment. Barwon Water engaged Earth Systems to assess the viability of a novel approach involving upstream water treatment at Big Swamp to assist in safely and cost effectively managing discharging water quality until natural groundwater recovery at the site occurs (or full remediation is implemented). As part of this upstream treatment trial, Earth Systems first completed a desktop review of available active and passive water treatment systems, and pH control treatment technologies. Earth Systems (2022) identified that:

- As acidity loads are >150 kg CaCO₃/day, no existing passive treatment systems are likely to be appropriate for treating the acidity loads being discharged at Big Swamp.
- Active treatment systems are likely to be appropriate for treating the acidity loads being discharged at Big Swamp, and the active treatment approach suggested by Jacobs in Barwon Water (2021) is likely to be a chemically successful method for addressing the acidity loads being discharged at Big Swamp.
- A novel semi-passive treatment system using caustic magnesia (MgO) could substantially lower the capital and operating cost of a treatment system in Big Swamp, as well as significantly lowering the environmental and OH&S risks related to its operation.

Many treatment systems involve reacting acidic water directly with a neutralising reagent to treat the acidity. The semi-passive treatment system using caustic MgO is novel in that clean catchment water is fed into a reagent reactor (under gravity) to generate alkaline water. The alkaline water is then fed into the acidic water to neutralise



the acidity, thus avoiding potential reagent passivation (i.e., coating) resulting from direct contact of acidic, metalbearing water with a solid neutralising reagent.

Earth Systems (2022) proposed laboratory trials as the second step of the upstream treatment trial to assess the viability of implementing a novel semi-passive water treatment strategy using MgO at Big Swamp. This report outlines the results and conclusions from the laboratory trials.

📚 Barwon Water

2. SCOPE OF WORKS

The scope of works included two main components:

- 1. **Laboratory Reagent Trials:** Laboratory trials on various commercial MgO reagents were conducted to assess geochemical behaviour and optimum operational parameters during treatment. This involved:
 - a. **Preliminary MgO Testing:** preliminary testing was done on one MgO reagent to examine variables that influence MgO solubility.
 - b. **Development of Testwork Program:** based on findings of the preliminary MgO testing, a testwork program for the laboratory trials was designed to examine the alkalinity loads generated during dissolution of MgO reagents with varying compositions and grainsizes over several residence times (i.e., amount of time the reagent and water are in direct contact).
 - c. **Laboratory Trial Completion:** The laboratory trials were conducted over several weeks. Reagent and water properties were assessed through in-house and laboratory chemical analysis.
- 2. **Report compilation**. A report was prepared summarising the results of the testwork and providing conclusions and recommendations.

3. METHOD

3.1 Rationale

To determine whether a semi-passive system using MgO could be used to treat the water discharging from Big Swamp, it was necessary to establish whether the dissolution of MgO could produce sufficient alkalinity to treat the acidity loads being generated (i.e., establish the kinetics of MgO dissolution). The solubility of MgO in water is highly variable and depends on how it has been manufactured (e.g., calcined, crushed) and how it interacts with water. Thus, key variables that affect MgO solubility are:

- 1. Calcination temperature of heating duration;
- 2. The composition (i.e., purity) of the MgO;
- 3. Grainsize; and
- 4. The length of time spent in contact with the water (i.e., dissolution kinetics).

It was therefore important to establish how these variables affect MgO solubility (dissolution kinetics), and accordingly, the alkalinity loads that can be generated through dissolution of MgO. From this, the viability of using MgO for water treatment could be determined, as well as the optimal operating parameters for treatment.

3.2 Preliminary Testing

To develop the testwork program, it was important to develop a basic understanding on how the composition, grainsize, and residence time could influence MgO solubility. To achieve this, a preliminary test was completed on one MgO reagent. The MgO reagent selected was sourced from Causmag International and comprised of MgO with minor CaO enrichment at a particle size of minus (-) 5 mm. Coarse-grained MgO was selected for the preliminary testing as larger MgO particle sizes would be more ideal for facilitating water flow in an MgO treatment reactor.

Preliminary testing involved filling a 250 mL beaker with ~ 200 mL of -5 mm MgO and creating rapid "flush" events using tap water over ~1.5 weeks. Flushing of the reagent was conducted as it allowed quick establishment of the effects of composition, grainsize, and residence time on MgO solubility. pH and electrical conductivity (EC) were measured periodically. pH provides an indication of the presence of CaO (i.e., MgO has a saturation pH of 10.8 – pH values >10.8 indicate dissolution of CaO in the MgO). EC is a measure of the concentrations of ions present in a sample. Thus, it is affected by changes in ions such as carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) and therefore has a direct relationship with alkalinity.

The main finding from the testing was that the pH ranged from 12.4 to 11.2. This could be explained by the initial dissolution of MgO with elevated CaO content, resulting in the of water becoming saturated with respect to Ca(OH)₂, and elevated Ca concentrations remaining throughout the duration of the testing. Under such conditions, MgO cannot dissolve.

From these results it was evident that the testwork program needed to include:

- Both coarse and fine grained MgO.
- MgO with and without CaO
- Significant flush rates to remove all initial CaO material, thus permitting MgO dissolution.
- Sufficient contact time between the reagent and water (hereafter referred to as residence time) to ensure all CaO is flushed out early in the testwork.

Thus, the testwork program was designed to include these variables.

3.3 Testwork Program

3.3.1 Parameters

To assess the effect of composition, grainsize and time on MgO solubility, four MgO materials that can be split into two types, "coarse grained" or "fine grained", were selected for the testwork program, and their details are provided in Table 3-1.

Sample Number	MgO Type	Composition	Grainsize (µm)	Supplier
1	Coarse	MgO with minor CaO enrichment	3000-5000	Causmag International
2			-3000	
3	Fine	MgO with minor CaO enrichment	-100	Causmag International
4		MgO with negligible CaO enrichment	-100	Calix Ltd

Table 3-1: Summary of MgO materials used in the testwork program.

To assess the effect of water residence time on MgO dissolution, several residence times were selected for the testwork program. The residence times were selected such that they are equivalent to clean catchment water flow rates that could be produced in a 40ft reactor (i.e., residence times that could be expected during implementation of a full-scale treatment at Big Swamp). For simplicity, the testwork residence times in this report will be presented as equivalent residence times in a 40ft MgO reactor.

3.3.2 Apparatus

The trial treatment plan suggested by Earth Systems (2022) included a caustic magnesia reactor with plumbing to allow Boundary Creek Water (from a storage tank) to percolate through a bed of MgO and discharge alkaline water to an acid-affected waterway. To simulate this outcome during the testwork, two testwork apparatuses were designed and they are illustrated in Figure 3-1.



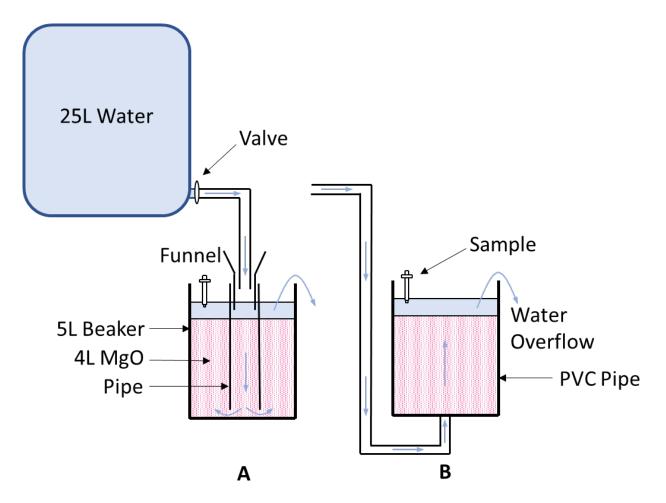


Figure 3-1: Schematic of the (A) coarse-grained and (B) fine-grained laboratory testwork apparatus.

The first testwork apparatus, illustrated in Figure 3-1A, was designed for the coarse grained MgO testwork. In this design, four (4) L of MgO is loaded into a five (5) L plastic beaker and water is supplied via gravity feed using a 25 L water container suspended above the beaker. Water from the 25 L container was funnelled into the beaker and directed through the coarse grained MgO matrix to the base of the beaker using a plastic pipe. After existing the pipe, water rose vertically through the MgO reactor bed and discharged at the surface via overflow of the plastic beaker, mimicking a potential caustic magnesia reactor described in Earth Systems (2022).

The second testwork apparatus, illustrated in Figure 3-1B, was designed for the fine grained MgO testwork. The major difference between the two apparatus designs was that water in the second apparatus was directed to the base of the MgO reactor bed using external pipping. This was done so that sufficient pressure head would be created to facilitate movement of water through the finer grained MgO. Similar to the first apparatus, water then moved vertically through the MgO reactor bed (housed in a PVC pipe) and discharged at the surface via overflow of the plastic beaker.

To create different residence times, the testwork apparatus design included a series of valves on the 25 L water containers to control the rate of water flow into the bed of MgO.

3.3.3 Data collection

pH, EC, oxygen reduction potential (ORP), temperature, and alkalinity were measured during the experiment. pH, EC, ORP and temperature were measured at ten-minute intervals during testwork using probes placed near the water overflow, and data was downloaded at the completion of each experiment. pH, EC, ORP and temperature

were also manually measured periodically throughout the trials. pH probes were calibrated daily with pH 4, pH 7 and pH 10 buffer solutions, and EC values were calibrated daily using a 1413 μ S/cm and 2760 μ S/cm standard solution. pH was temperature corrected using automatic temperature compensation (ATC).

Logger EC data was used to calculate alkalinity using linear regression modelling, and manual alkalinity measurements were made periodically using Merck Spectroquant[®] total alkalinity tests. All alkalinity measurements were performed in duplicate using two separate Spectroquant[®] spectrophotometers. Calibration of the spectrophotometers involved preparation of blanks daily using deionised (DI) water, and the blanks were used calibrate the spectrophotometers so that only alkalinity produced by the dissolution of MgO was measured (i.e., blanks were used to "zero" both spectrophotometers prior to analysis). Approximately once per week, a standard solution of 5.0 mmol NaOH (250 mg/L CaCO₃ equivalent) was prepared and used to cross check the accuracy and precision of alkalinity measurements.

The flow rate was determined between two and four times per day depending on the specific flow rate used (more frequent determination for higher flow rates). The multiple determinations of flow rate were performed before and after filling the 25 L tank, such that variations in the flow rate due to changing hydraulic head (i.e., as the vessel progressively emptied) were averaged out. The flow rate was measured by recording the time taken to fill a 500 ml volumetric cylinder using a stopwatch. Each flow determination was taken in duplicate, approximately five minutes apart and the average value used for subsequent calculations.

3.4 Laboratory Trials

Eleven discrete alkalinity load assessments were completed during the laboratory trials, and the assessments are summarised in Table 3-2.

МдО Туре	Run No	Sample Number(s)	Residence Time (mins)	Water Used*	Air Agitation
	1		63	Deionised	No
	2		30	Deionised	No
Coarse Grained	3	1&2	17	Deionised & Mains	No
	4		119	Mains	No
	5		30	Mains	No
	6	3	19	Mains	No
	7		69	Mains	No
Fine grained	8		14	Mains	No
Fine grained	9		25	Mains	No
	10		52	Mains	Yes
	11	- 4	22	Mains	Yes

Table 3-2: Summary of laboratory trial runs.

*The deionised water had a pH of 5.0-5.4 and an EC of ~3.0 μ S/cm. Mains water had a pH of ~6.9 and an EC of ~65 μ S/cm.

Distilled water was initially used for the testwork due to concerns about the precipitation of manganese oxides on MgO particles due to the presence of manganese in tap water. When it was established that this was not an issue, the trials were conducted with tap water.

3.4.1 Reagent Preparation

The trials commenced with coarse grained MgO (3-5 mm and -3 mm particle sizes). The coarse grained MgO was produced by sieving -5 mm Causmag MgO using a 3 mm screen. The residence time selected for the first run was 63 mins. Each subsequent run time was then selected based off the results of the previous run.

Selected water samples were sent to a NATA-accredited laboratory (ALS Melbourne) for alkalinity analysis. This was done to confirm the type of alkalinity being produced (e.g., bicarbonate, carbonate).

3.4.2 Reagent Characterisation

To confirm the composition of the coarse grained Causmag MgO selected for the testwork, material characterisation using quantitative X-ray diffraction (QXRD) was completed. The QXRD method is provided in Appendix A.



4. **RESULTS**

4.1 Caustic Magnesia Characterisation

The results of QXRD analysis of the coarse grained Causmag MgO are summarised in Table 4-1. Full QXRD results are provided in Appendix A.

The key findings include:

- Coarse grained MgO is comprised of predominantly periclase (MgO; 57.4 wt.%) and amorphous (22.1 wt.%) material (likely Mg- and Ca-bearing oxides), with minor amounts of magnesite (9.3 wt.%), calcite (6.7 wt.%), dolomite (2.5 wt.%), and quartz (1.1 wt.%).
- 9.8 wt.% of the coarse-grained MgO is comprised of minerals containing calcium (calcite, dolomite, portlandite, and quicklime).
- 18.5% of the coarse-grained MgO is comprised of carbonate minerals (magnesite, calcite, dolomite). This suggests that material is partially calcined (i.e., volatile components have only partially been removed).

Coarse-grained MgO			
Mineral/Phase	Amount (wt.%)		
Periclase (MgO)	57.4		
Amorphous (non-crystalline)	22.1		
Magnesite (MgCO ₃)	9.3		
Calcite (CaCO ₃)	6.7		
Dolomite (CaMg(CO ₃) ₂)	2.5		
Quartz (SiO ₂)	1.1		
Portlandite (Ca(OH) ₂)	0.5		
Rutile (TiO ₂)	0.2		
Brucite (Mg(OH) ₂)	0.2		
Quicklime (CaO)	0.1		

Table 4-1: Summary of QXRD results for the coarse grained Causmag Reagent.

4.2 Laboratory Trials

4.2.1 pH, EC, and temperature

The average pH, EC and temperature results for the laboratory trials are provided in Table 4-2 and Table 4-3, and more comprehensive data are provided in Appendix B.

The key findings include:

- Trials with the coarse grained MgO produced the highest average pH and EC values.
- For the coarse grained MgO assessments:



- Average pH and EC values were highest at the beginning of the trials (i.e., run 1 and 2) for both the -3 mm and 3-5 mm MgO assessments.
- Average pH and EC were similar for runs 3-5 for both the -3 mm and 3-5 mm MgO despite variation in the residence times.
- Average pH values for the 3-5 mm MgO are higher than the -3 mm MgO throughout the trials.
- $_{\odot}$ The highest average EC value was recorded for the -3 mm MgO (4112 μ S/cm) during run 1. Average EC values for the -3 mm MgO are higher than the 3-5 mm during runs 1 and 2 and lower from runs 3-5.
- Average temperature values for the 3-5 mm MgO are higher than the -3 mm MgO throughout the trials.
- For the fine grained MgO trials:
 - Average pH and EC are similar for runs 7-11 throughout the testwork, despite variations in grainsize, MgO compositions (i.e., minor vs negligible CaO component) and residence time.
 - \circ Run 6-100 μ m (Causmag) MgO has lower pH and temperature, and higher EC, than runs 7-11.

Run No	Residence time (mins)	Sample No	Sample Grainsize (mm)	Average pH	Average EC (µS/cm)	Average Temperature (°C)
1	63	1	-3	10.6 (±0.5)	4112 (±519)	24.8 (±4.7)
I	03	2	3-5	11.5 (±0.2)	3073 (±146)	30.3 (±5.8)
2	30	1	-3	10.0 (±0.3)	2386 (±1454)	21.0 (±0.5)
Z	30	2	3-5	11.6 (±0.2)	1669 (±778)	21.4 (±0.2)
3	17	1	-3	9.7 (±0.2)	496 (±97)	21.9 (±0.2)
3	17	2	3-5	11.1 (±0.2)	539 (±240)	22.0 (±0.1)
4	110	1	-3	9.8 (±0.2)	39 (±53)	21.8 (±0.0)
4	119	2	3-5	11.3 (±0.2)	803 (±167)	22.4 (±0.1)
5	30	1	-3	9.5 (±0.2)	310 (±52)	21.9 (±0.3)
J	50	2	3-5	11.2 (±0.2)	427 (±93)	22.3 (±0.2)

Table 4-2: Data logger average pH, EC, and temperature values for the coarse-grained testwork.

Table 4-3: Data logger average pH, EC, and temperature values for the fine-grained testwork.

Run No	Sample No	Sample Grainsize (µm)	Residence time (mins)	Average pH	Average EC (µS/cm)	Average Temperature (°C)
6	3	-100	19	9.3 (±0.3)	218 (±21)	20.5 (±0.2)
7	3	-100	69	10.1 (±0.3)	125 (±8)	22.1 (±0.3)
8	3	-100	14	10.6 (±0.0)	139 (±4)	22.4 (±0.1)
9	3	-100	25	10.2 (±0.1)	123 (±4)	22.1 (±0.1)
10	4	-100	52	10.6 (±0.2)	194 (±5)	21.0 (±0.1)
11	4	-100	22	10.9 (±0.0)	194 (±10)	21.2 (±0.1)



4.2.2 Alkalinity

The alkalinity results for the laboratory trials are provided in Table 4-4 to Table 4-6, and Figure 4-1 to Figure 4-4. Additional data are provided in Appendix B and external laboratory results are provided in Appendix C.

The key results include:

- Alkalinity loads only occasional exceeded the minimum average value of 300-400 kg CaCO₃/day. Such exceedances only occurred due to early dissolution of the more soluble CaO component of the coarse-grained reagents.
- Following on-going leaching of the CaO component of the reagents, alkalinity loads fell well below the minimum average load requirements for Big Swamp.
- None of the reagents sustained the minimum average alkalinity load requirement for treatment of Big Swamp water acidity.

Additional observations included:

- For coarse grained MgO trials:
 - The highest average alkalinity load was produced by the -3 mm MgO during run 2 (592 kg CaCO₃/day)
 - The -3 mm MgO produced higher alkalinity loads during runs 1-2 whereas the 3-5 mm MgO produced higher alkalinity loads during runs 3-5.
 - The average alkalinity loads during runs 1-2 ranged from 592 376 kg CaCO₃/day
 - The average alkalinity loads generated during runs 3-5 ranged from 271 27.6 kg CaCO₃/day
- For the fine grained MgO trials:
 - \circ The average alkalinity loads generated during runs 6-11 ranged from 105 35.5 kg CaCO₃/day.
 - For both fine grained MgO reagents, higher alkalinity loads were generated during shorter residence times (e.g., 14mins, 22 mins) compared to longer residence times (i.e., 52 mins, 69 mins).
 - \circ Formation of a compacted layer at the base of the PVC pipe occurred during the -100 μm Causmag testwork (runs 6-9). This was likely related to molar volume increases associated with hydration of CaO and possibly MgO. This caused water to be channelled up the centre of the PVC pipe, effecting alkalinity generation.
 - Water in the trials with -100 μm Calix MgO (runs 10 and 11) became cloudy and manual alkalinity measurements were significantly higher than alkalinity measurements calculated from logger EC (see Figure B-7 in Appendix B).
- Externally measured total alkalinity values for water samples collected during runs 6, 8, and 9 are lower than average alkalinity values collected during these runs. The alkalinity was present as carbonate and bicarbonate.

Run No	Residence time (mins)	Sample No	Sample Grainsize (mm)	Average Alkalinity (mg CaCO ₃ /L	Average Alkalinity Load (kg CaCO₃/day)
1	63	1	-3	934 (±116)	476 (±59)
	1 63	2	3-5	702 (±33)	376 (±17)
2	20	1	-3	548 (±326)	592 (±352)
2	30	2	3-5	387 (±174)	423 (±188)
3	17	1	-3	125 (±22)	238 (±42)
5	17	2	3-5	134 9±54)	271 (±108)

Table 4-4: Data logger average alkalinity values for the coarse grained MgO.





1	4 119	1	-3	103 (±12)	27.6 (±3.2)
4		2	3-5	193 (±38)	51.8 (±10.0)
5	5 20	1	-3	83.1 (±11.7)	88.3 (±12.4)
5	30	2	3-5	109 (±21)	117 (±22)

Table 4-5: Data logger average alkalinity values for the fine grained MgO.

Run No	Sample No	Sample Grainsize (µm)	Residence time (mins)	Average Alkalinity (mg CaCO₃/L)	Average Alkalinity Load (kg CaCO₃/day)
6	3	-100	19	62.4 (±4.7)	105 (±8)
7	3	-100	69	41.6 (±1.7)	19.4 (±0.8)
8	3	-100	14	44.7 (±0.9)	101 (±2)
9	3	-100	25	41.2 (±0.8)	53.0 (±1.0)
10	4	-100	52	57.0 (±1.0)	35.5 (±0.7)
11	4	-100	22	57.2 (±2.2)	84.5 (±3.2)

Table 4-6: Alkalinity results for fine grained MgO water samples analysed using an external laboratory.

Run No	Sample No	Residence time (mins)	Hydroxide Alkalinity (as CaCO ₃)	Carbonate Alkalinity (as CaCO ₃)	Bicarbonate Alkalinity (as CaCO₃)	Total Alkalinity (as CaCO₃)
6	3	19	<1	25	18	43
8	3	14	<1	14	19	34
8	3	14	<1	16	18	34
9	3	25	<1	12	20	32
11	4	22	<1	27	20	47



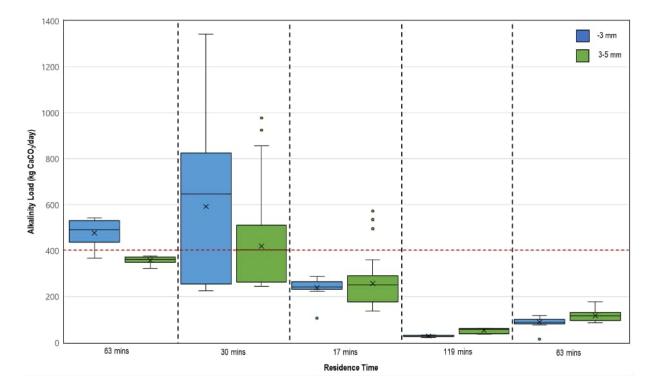


Figure 4-1: Box-and-whisker plot of alkalinity loads by residence time for the coarse grained MgO trials. The box-and whisker plot features include the mean (shown by "x"), median (line in the middle of the box), interquartile range (middle 50% of the values; represented by the box), the lower and upper 25% of the values (the whiskers), the minimum and maximum scores excluding outliers (lines at the end of the whiskers), and outliers (dot points). The dashed red line indicates the minimum average (indicative) alkalinity load required to treat Big Swamp.

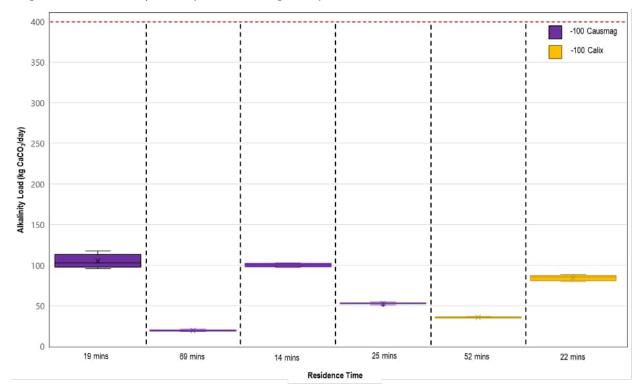


Figure 4-2: Box-and-whisker plot of alkalinity loads by residence time for the fine grained MgO trials. The box-and whisker plot features include the mean (shown by "x"), median (line in the middle of the box), interquartile range (middle 50% of the values; represented by the box), the lower and upper 25% of the values (the whiskers), the minimum and maximum scores excluding outliers (lines at the end of the whiskers), and outliers (dot points). The dashed red line indicates the minimum average (indicative) alkalinity load required to treat Big Swamp.





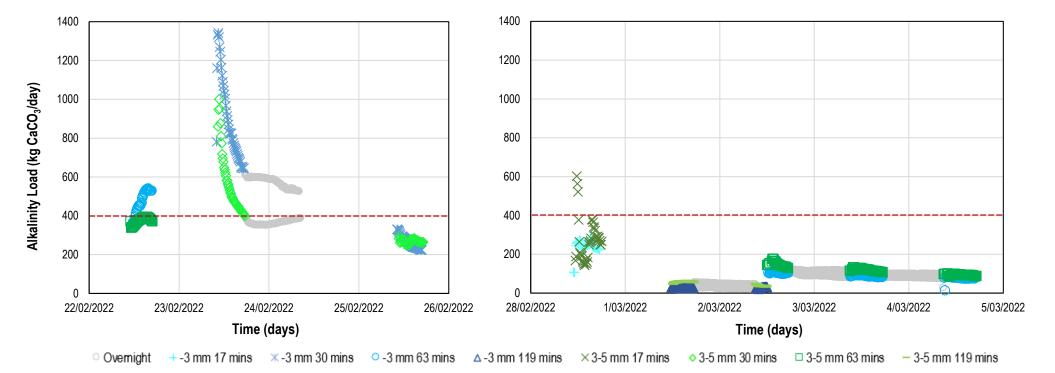


Figure 4-3: Variations in alkalinity load with time for the coarse grained MgO. The different residence times are shown by different symbols shapes/colours. Data that was collected overnight are shown in grey circles. The dashed red line indicates the minimum average alkalinity load required to treat Big Swamp.



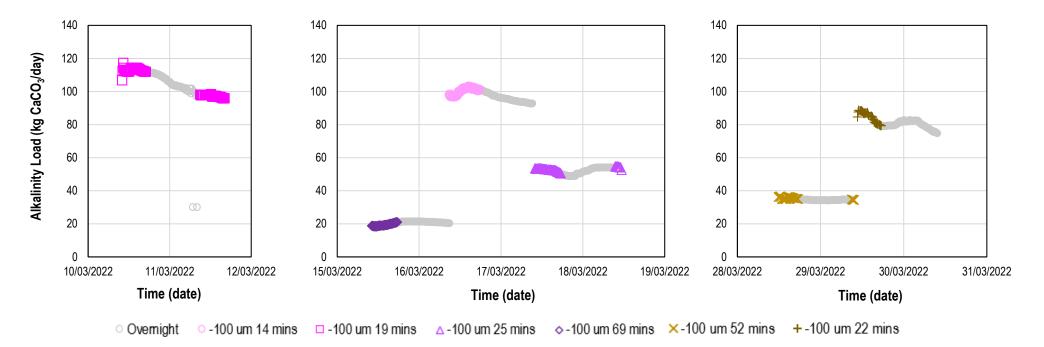


Figure 4-4: Variations in alkalinity load with time for the fine grained MgO. The different residence times are shown by different symbols shapes/colours. Data that was collected overnight are shown in grey circles.



5. CONCLUSIONS

The conclusions from the laboratory trials include:

- QXRD results confirm the presence of minor CaO in the coarse grained (Causmag) MgO.
- Soluble alkalinity in the coarse grained MgO rapidly decreased at all grainsizes and likely reflects depletion of more soluble CaO component rather an MgO.
- While the initial alkalinity load generated from the -3mm coarse grained MgO was > 400 kg CaCO₃, the rapid decrease in alkalinity with time for both coarse grained MgO materials makes them unsuitable for long term treatment of acidity loads being generated from Big Swamp.
- The presence of cloudy water coupled with higher alkalinity measurements suggests particulate alkalinity is being generated by the -100 μ m Calix MgO.
- Both soluble and particulate alkalinity loads for the fine grained MgO are too low to manage average daily acidity loads from Big Swamp under any of the conditions tested.
- MgO can likely generate no more than ~100 kg CaCO₃ alkalinity per day. While this is inadequate for water treatment atr Big Swamp, it may be useful for other alkalinity treatment applications at the site.

While alkalinity loads generated from the MgO tested are too low to treat Big Swamp, a more reactive reagent may be suitable. Success in the migration of water through -100 μ m powder encouraged out-of-scope testwork on passive dissolution of hydrated lime (Ca(OH)₂). This additional testwork is detailed in Section 6 and Attachment D.

• Ca(OH)2 has the potential to generate ~500-2,000 kg CaCO3 alkalinity per day.

📚 Barwon Water

6. ALTERNATIVE REAGENT – HYDRATED LIME

Hydrated lime (Ca(OH)₂) is a manufactured dry powdered reagent that can be used in powder or, more commonly, slurry form to produce dissolved or suspended (particulate) alkalinity, respectively. It has a saturation pH of 12.4 and is more soluble than MgO, having a solubility (at 20 °C) of 1,300-1,850 mg/L. It is typically utilised in active treatment systems.

To test whether Ca(OH)₂ could be utilised in a semi-passive or passive treatment system, five discrete alkalinity load assessments were completed on a sample of Ca(OH)₂. Residence times for the five runs are provided in Table 6-1. The assessments were completed using the same apparatus as the fine grained MgO trials (see section 3.3.2 and Figure 3-1B for details) and mains water was used.

A summary of the average alkalinities and average alkalinity loads produced during the five assessments is provided in Table 6-1 (and additional data is provided in Appendix D). Key results from the assessments included:

- The average alkalinity loads produced during the five assessments ranged from 580-1828 kg CaCO₃/day and thus exceeded the minimum average value of 300-400 kg CaCO₃/day required to treat the acidity present in water discharging from Big Swamp.
- The highest average alkalinity load (1828 kg CaCO₃/day) was produced using the shortest residence time (16 mins).
- Higher flow rates were observed to produce more turbidity compared to lower flow rates. This suggests
 that the alkalinity produced at higher flow rates is predominantly produced through particulate alkalinity
 whereas alkalinity produced at lower flow rates may be being produced predominantly through soluble
 alkalinity.
- The minimum and maximum alkalinity loads generated during the assessments were 507 kg CaCO₃/day (Run 2) and 2579 kg CaCO₃/day (Run 5).

Run No.	Residence time (mins)	Average Alkalinity (mg CaCO ₃ /L)	Average Alkalinity Load (kg CaCO₃/day)	Notes
1	59	1123 (±120)	612 (±66)	
2	48	875 (±146)	589 (±98)	
3	48	1870 (238)	1259 (158)	Reactor bed agitated to facilitate water circulation
4	45	1425 (±336)	1022 (±241)	
5	16	902 (±428)	1828 (±836)	

Table 6-1: Summary of hydrated lime laboratory assessment conditions and alkalinity results.

Based on the results, the alkalinity loads produced by Ca(OH)₂ are sufficient to treat average daily acidity loads being produced from Big Swamp.

However, several factors need to be considered / resolved before a treatment method using $Ca(OH)_2$ could be implemented including:

- Ca(OH)₂ saturation pH of 12.4 (water contacting the reagent will become highly alkaline).
- Ca(OH)₂ powder or solutions can react with CO₂ in the air, resulting in the precipitation of CaCO₃. Specialist management practices may be required to efficiently dose the reagent.

7. **RECOMMENDATIONS**

Key recommendations from this testwork include:

- MgO should not be regarded as a suitable reagent to meet the acidity loads being generated at Big Swamp.
- For immediate treatment of acidity loads at Big Swamp, a chemical dosing system downstream of Big Swamp should be considered. The use of an isotainer containing liquid caustic soda with a solar powered dosing valve should be assessed in detail. This would avoid the need for diesel or mains power but would still carry the OH&S and environmental risks inherent in the use of this highly caustic reagent (ie. saturation pH of 14).
- If a caustic soda dosing system is not regarded as acceptable, continue to assess the feasibility of treating acidity loads at Big Swamp using a semi-passive hydrated lime dosing system. Issues related to reagent carbonation need to be overcome.
- While MgO has been proven to be inappropriate for semi-passive water treatment, the low alkalinity loads that it can passively release could potentially be useful as a sediment remediation option. The release of low concentrations of alkaline water from an MgO based reactor into the fire trench could assist with immobilization of iron that is being generated via reductive dissolution of ferrihydrite within the swamp. The soluble iron would likely be immobilised as iron carbonate (ie. siderite). This needs to be considered as a remediation strategy, not a treatment strategy.

8. **REFERENCES**

- Barwon Water, 2021. *Hydro-Geochemical Modelling. Design of Contingency Measure. Boundary Creek, Big Swamp and surrounding environment.* Remediation and Environmental Protection Plan. July 2021.
- Earth Systems (2022). *Semi-Passive Treatment of Big Swamp. Desktop Review and Trial Treatment Plan*. January 2022.
- Sullivan, L. Ward, N. Toppler, N and Lancaster, G. 2018. *National Acid Sulfate Soils guidance: National acid sulfate soils sampling and identification methods manual*. Department of Agriculture and Water Resources, Canberra ACT.



Attachment A QXRD Method and Report

QXRD Method:

X-ray diffraction traces were obtained from the samples with a Panalytical Aeris Research Powder Diffractometer. Operating conditions were 40kV/15mA, Fe Kß filter, step scan 0.01/29 secs°20 at, 1/4° divergence and a 1.0° ant-scatter slit. Scan range was 5° to 90° 20. Phases were identified by computer search-match of the 2022 ICDD PDF4 Minerals Database. The amorphous components have been estimated by modelling the broadened background.

Sample Supplied:

One pulp:

Causmag Caustic Magnesia

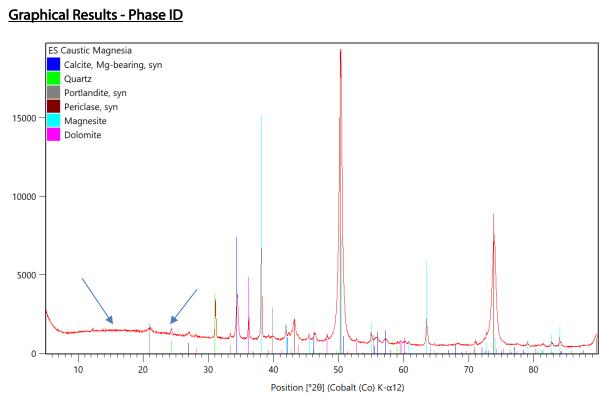
<u>Crystalline phases identified in the sample by search-match of the 2022 ICDD PDF4 mineral</u> <u>database:</u>

Periclase – magnesia, broad peaks indicate small diffracting particle (crystallite) size Magnesite Calcite Dolomite Quartz Portlandite

A broad swell in the low 20 portion of the XRD trace indicates the presence of amorphous or poorly diffracting phases. This has been modelled to quantify the amount present. The elevated background is not present on the trace where nano-particle sized magnesia (expected in caustic magnesia) would present.

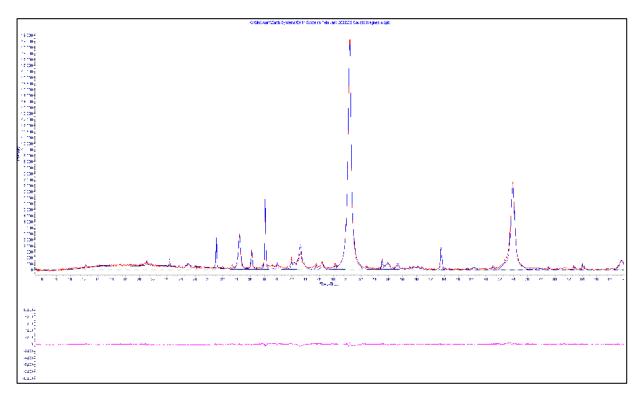
Results wt.% (semiquantitative normalised) DL ~0.4wt.% 0wt.% = not detected

Phase	Weight%
Periclase	57.4
Amorphous	22.1
Magnesite	9.3
Calcite	6.7
Dolomite	2.5
Quartz	1.1
Portlandite	0.5
Rutile	0.2
Brucite	0.2
Lime	0.1



Trace obtained from #BARW 2346 Caustic Magnesia, showing peaks for the main phases identified, indicated as shown at top left of the figure. The broad background feature due to non-diffracting components is arrowed.

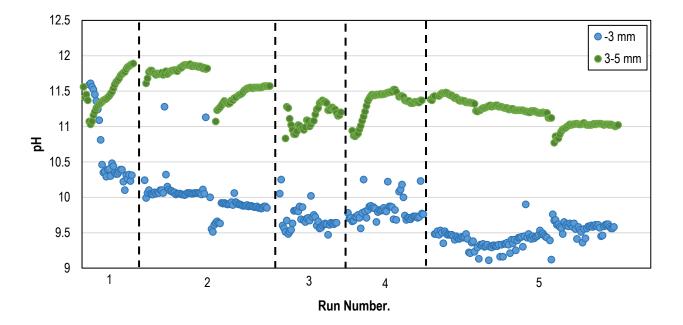
Graphical Results - Quantitative Refinement



XRD traces obtained for the sample supplied – red trace = instrumental, blue trace = computed, pink trace = difference.

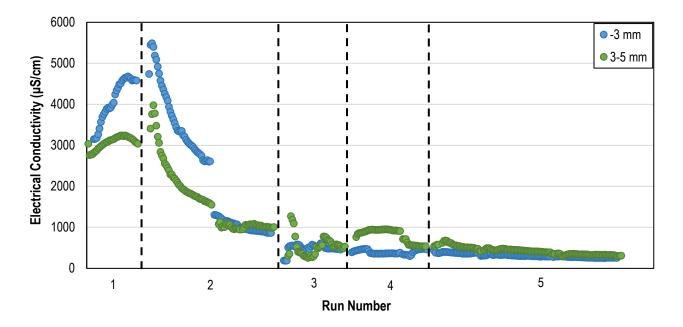
Attachment B Caustic Magnesia Laboratory Trial Figures





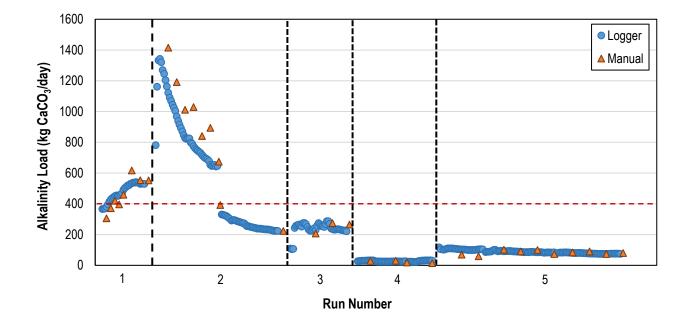
CAUSTIC MAGNESIA LABORATORY TRIAL FIGURES

Figures B-1: Plot comparing pH logger data collected during each run using the coarse grained MgO. Each run corresponds to a different residence time (i.e., contact time between the MgO and water) – Run 1: 63 mins; Run 2: 30 mins; Run 3: 17 mins; Run 4: 119 mins; Run 5: 30 minutes. Each run is demarcated by black dashed vertical lines and the width of each run reflects the number of data points collected during the run. Runs 1 and 2 used deionised water (pH 5.0-5.4), run 3 used deionised and mains water (pH 6.9), and runs 4 and 5 used mains water.

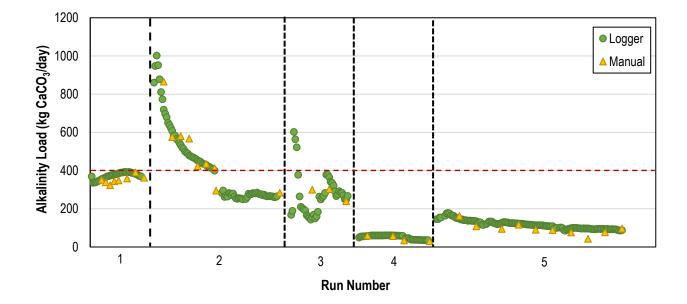


Figures B-2: Plot comparing electrical conductivity logger data collected during each run using the coarse grained MgO. Each run corresponds to a different residence time (i.e., contact time between the MgO and water) – Run 1: 63 mins; Run 2: 30 mins; Run 3: 17 mins; Run 4: 119 mins; Run 5: 30 mins. Each run is demarcated by black dashed vertical lines and the width of each run reflects the number of data points collected during the run. Runs 1 and 2 used deionised water (EC ~3 μ S/cm), run 3 used deionised and mains water (EC 67.1 μ S/cm), and runs 4 and 5 used mains water.





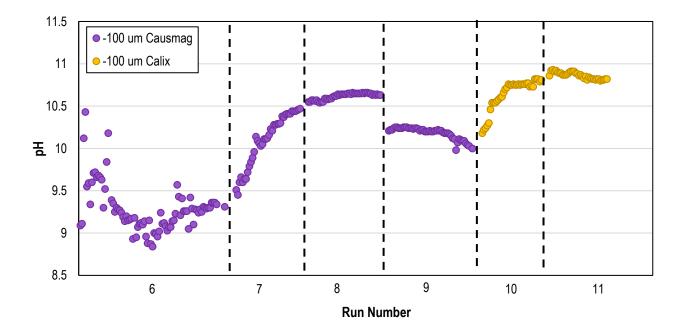
Figures B-3: Plot comparing data logger and manual alkalinity loads collected during each run using the -3 mm coarse grained MgO. Each run corresponds to a different residence time (i.e., contact time between the MgO and water) – Run 1: 63 mins; Run 2: 30 mins; Run 3: 17 mins; Run 4: 119 mins; Run 5: 30 mins. Each run is demarcated by black dashed vertical lines and the width of each run reflects the number of data points collected during the run. Runs 1 and 2 used deionised water, run 3 used deionised and mains water, and runs 4 and 5 used mains water.



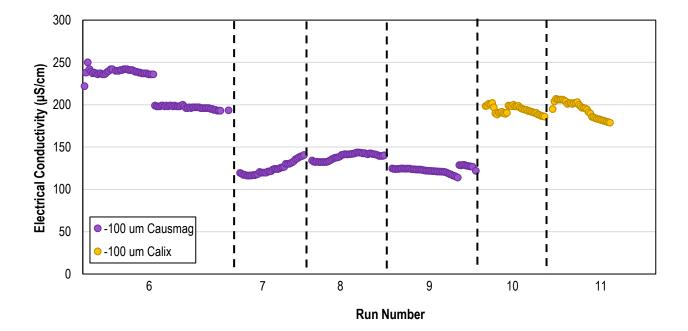
Figures B-4: Plot comparing data logger and manual alkalinity loads collected during each run using the 3-5 mm coarse grained MgO. Each run corresponds to a different residence time (i.e., contact time between the MgO and water) – Run 1: 63 mins; Run 2: 30 mins; Run 3: 17 mins; Run 4: 119 mins; Run 5: 30 mins. Each run is demarcated by black dashed vertical lines and the width of each run reflects the number of data points collected during the run. Runs 1 and 2 used deionised water, run 3 used deionised and mains water, and runs 4 and 5 used mains water.





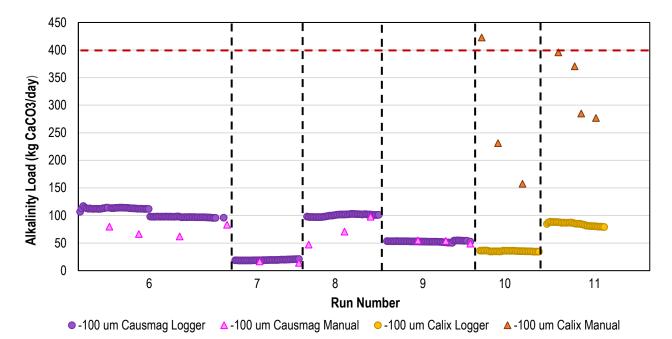


Figures B-5: Plot comparing pH logger data collected during each run using the fine grained MgO. Each run corresponds to a different residence time (i.e., contact time between the MgO and water) – Run 6: 19 mins; Run 7: 69 mins; Run 8: 14 mins; Run 9: 25 mins; Run 10: 52 mins; Run 11: 22 mins. Each run is demarcated by black dashed vertical lines and the width of each run reflects the number of data points collected during the run. Runs 6-11 used mains water (pH 6.9).



Figures B-6: Plot comparing pH logger data collected during each run using the fine grained MgO. Each run corresponds to a different residence time (i.e., contact time between the MgO and water) – Run 6: 19 minutes; Run 7: 69 minutes; Run 8: 14 minutes; Run 9: 25 minutes; Run 10: 52 minutes; Run 11: 22 minutes. Each run is demarcated by black dashed vertical lines and the width of each run reflects the number of data points collected during the run. Runs 6-11 used mains water (EC 67.1 μ S/cm).





Figures B-7: Plot comparing data logger and manual alkalinity loads collected during each run using the fine grained MgO. Each run corresponds to a different residence time (i.e., contact time between the MgO and water) – Run 6: 19 mins; Run 7: 69 mins; Run 8: 14 mins; Run 9: 25 mins; Run 10: 52 mins; Run 11: 22 mins. Each run is demarcated by black dashed vertical lines and the width of each run reflects the number of data points collected during the run. Runs 6-11 used mains water.

Attachment C External Laboratory Testwork Results



CERTIFICATE OF ANALYSIS

Work Order	EM2205310	Page	: 1 of 2	
Client	EARTH SYSTEMS PTY LTD	Laboratory	Environmental Division M	lelbourne
Contact	: MR JEFF TAYLOR	Contact	: Customer Services EM	
Address	: 14 Church St	Address	: 4 Westall Rd Springvale V	/IC Australia 3171
	Hawthorn VIC, AUSTRALIA 3122			
Telephone	: +61 03 9810 7500	Telephone	: +61 3 8549 9600	
Project	: BARW2346	Date Samples Received	: 25-Mar-2022 11:45	30000 m
Order number	:	Date Analysis Commenced	: 30-Mar-2022	
C-O-C number	:	Issue Date	: 01-Apr-2022 16:33	A NATA
Sampler	: Ashton Soltys			Hac-MRA NATA
Site	: Melbourne			
Quote number	: EN/222			Accreditation No. 825
No. of samples received	: 5			Accredited for compliance with
No. of samples analysed	: 5			ISO/IEC 17025 - Testing

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This Certificate of Analysis contains the following information:

- General Comments
- Analytical Results

Additional information pertinent to this report will be found in the following separate attachments: Quality Control Report, QA/QC Compliance Assessment to assist with Quality Review and Sample Receipt Notification.

Signatories

This document has been electronically signed by the authorized signatories below. Electronic signing is carried out in compliance with procedures specified in 21 CFR Part 11.

Signatories	Position	Accreditation Category
Dilani Fernando	Laboratory Coordinator	Melbourne Inorganics, Springvale, VIC



General Comments

The analytical procedures used by ALS have been developed from established internationally recognised procedures such as those published by the USEPA, APHA, AS and NEPM. In house developed procedures are fully validated and are often at the client request.

Where moisture determination has been performed, results are reported on a dry weight basis.

Where a reported less than (<) result is higher than the LOR, this may be due to primary sample extract/digestate dilution and/or insufficient sample for analysis.

Where the LOR of a reported result differs from standard LOR, this may be due to high moisture content, insufficient sample (reduced weight employed) or matrix interference.

When sampling time information is not provided by the client, sampling dates are shown without a time component. In these instances, the time component has been assumed by the laboratory for processing purposes.

Where a result is required to meet compliance limits the associated uncertainty must be considered. Refer to the ALS Contact for details.

Key: CAS Number = CAS registry number from database maintained by Chemical Abstracts Services. The Chemical Abstracts Service is a division of the American Chemical Society.

LOR = Limit of reporting

* = This result is computed from individual analyte detections at or above the level of reporting

ø = ALS is not NATA accredited for these tests.

~ = Indicates an estimated value.

Sodium Adsorption Ratio (where reported): Where results for Na, Ca or Mg are <LOR, a concentration at half the reported LOR is incorporated into the SAR calculation. This represents a conservative approach for Na relative to the assumption that <LOR = zero concentration and a conservative approach for Ca & Mg relative to the assumption that <LOR is equivalent to the LOR concentration.

Analytical Results

Sub-Matrix: WATER (Matrix: WATER)			Sample ID	MgO -5mm Fresh_F	MgO 100um Spent_F	MgO -3mm Spent_F	MgO 3-5mm Spent_F	MgO 100um Fresh_F
		Sampli	ng date / time	25-Mar-2022 03:50	25-Mar-2022 04:00	25-Mar-2022 04:10	25-Mar-2022 04:20	25-Mar-2022 05:10
Compound	CAS Number	LOR	Unit	EM2205310-001	EM2205310-002	EM2205310-003	EM2205310-004	EM2205310-005
				Result	Result	Result	Result	Result
ED037P: Alkalinity by PC Titrator								
Hydroxide Alkalinity as CaCO3	DMO-210-001	1	mg/L	608	<1	<1	<1	<1
Carbonate Alkalinity as CaCO3	3812-32-6	1	mg/L	52	360	486	374	60
Bicarbonate Alkalinity as CaCO3	71-52-3	1	mg/L	<1	162	178	150	8
Total Alkalinity as CaCO3		1	mg/L	661	522	664	523	68
ED093F: Dissolved Major Cations								
Calcium	7440-70-2	1	mg/L	82	2	1	2	4
Magnesium	7439-95-4	1	mg/L	<1	124	146	113	<1
Sodium	7440-23-5	1	mg/L	28	9	4	5	23
Potassium	7440-09-7	1	mg/L	1	4	1	1	1



CERTIFICATE OF ANALYSIS

Work Order	EM2204830	Page	: 1 of 2		
Client	EARTH SYSTEMS PTY LTD	Laboratory	: Environmental Division Me	elbourne	
Contact	: ASHTON SOLTYS	Contact	: Customer Services EM		
Address	: 14 Church St	Address : 4 Westall Rd Springvale VIC Australia 3171			
	Hawthorn VIC, AUSTRALIA 3122				
Telephone	:	Telephone	: +61 3 8549 9600		
Project	: BARW2346	Date Samples Received	: 17-Mar-2022 15:50	MUUUU	
Order number	:	Date Analysis Commenced	: 22-Mar-2022		
C-O-C number	:	Issue Date	: 23-Mar-2022 14:47	NATA	
Sampler	: Saskia Ruttor			HAC-MRA NATA	
Site	: Melbourne				
Quote number	: ME/016/19 V2			Accreditation No. 825	
No. of samples received	: 4			Accredited for compliance with	
No. of samples analysed	: 4			ISO/IEC 17025 - Testing	

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This Certificate of Analysis contains the following information:

- General Comments
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Additional information pertinent to this report will be found in the following separate attachments: Quality Control Report, QA/QC Compliance Assessment to assist with Quality Review and Sample Receipt Notification.

Signatories

This document has been electronically signed by the authorized signatories below. Electronic signing is carried out in compliance with procedures specified in 21 CFR Part 11.

Signatories	Position	Accreditation Category
Dilani Fernando	Laboratory Coordinator	Melbourne Inorganics, Springvale, VIC



General Comments

The analytical procedures used by ALS have been developed from established internationally recognised procedures such as those published by the USEPA, APHA, AS and NEPM. In house developed procedures are fully validated and are often at the client request.

Where moisture determination has been performed, results are reported on a dry weight basis.

Where a reported less than (<) result is higher than the LOR, this may be due to primary sample extract/digestate dilution and/or insufficient sample for analysis.

Where the LOR of a reported result differs from standard LOR, this may be due to high moisture content, insufficient sample (reduced weight employed) or matrix interference.

When sampling time information is not provided by the client, sampling dates are shown without a time component. In these instances, the time component has been assumed by the laboratory for processing purposes.

Where a result is required to meet compliance limits the associated uncertainty must be considered. Refer to the ALS Contact for details.

Key: CAS Number = CAS registry number from database maintained by Chemical Abstracts Services. The Chemical Abstracts Service is a division of the American Chemical Society.

LOR = Limit of reporting

^ = This result is computed from individual analyte detections at or above the level of reporting

ø = ALS is not NATA accredited for these tests.

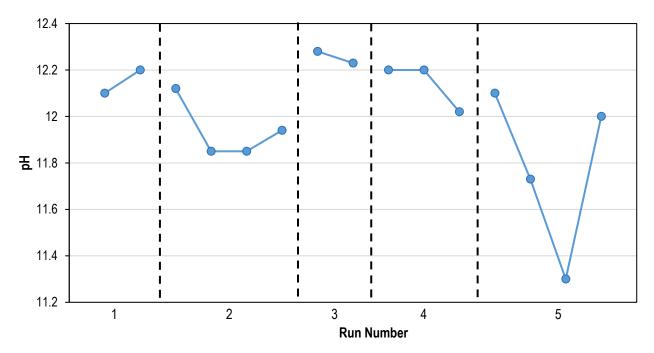
~ = Indicates an estimated value.

Analytical Results

Sub-Matrix: WATER (Matrix: WATER)			Sample ID	BARW_01	BARW_02	BARW_03	BARW_04	
		Samplii	ng date / time	17-Mar-2022 13:00	17-Mar-2022 13:20	17-Mar-2022 13:30	17-Mar-2022 13:40	
Compound	CAS Number	LOR	Unit	EM2204830-001	EM2204830-002	EM2204830-003	EM2204830-004	
				Result	Result	Result	Result	
ED037P: Alkalinity by PC Titrator								
Hydroxide Alkalinity as CaCO3	DMO-210-001	1	mg/L	<1	<1	<1	<1	
Carbonate Alkalinity as CaCO3	3812-32-6	1	mg/L	25	14	16	12	
Bicarbonate Alkalinity as CaCO3	71-52-3	1	mg/L	18	19	18	20	
Total Alkalinity as CaCO3		1	mg/L	43	34	34	32	

Appendix D Hydrated Lime Laboratory Trial Figures





HYDRATED LIME LABORATORY TRIAL FIGURES

Figure D-1: Plot comparing pH (based on manual measurements) collected during each run using powder hydrated lime. Each run corresponds to a different residence time (i.e., contact time between the Ca(OH)₂ and water) – Run 1: 59 mins; Run 2: 48 mins; Run 3: 48 mins; Run 4: 45 mins; Run 5: 16 mins. Each run is demarcated by black dashed vertical lines. Runs 1-5 used mains water (pH 6.9).

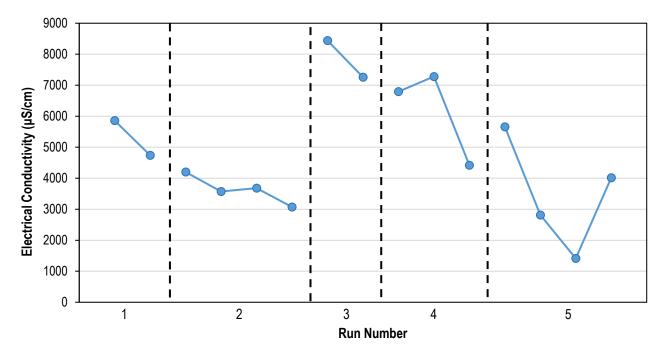


Figure D-2: Plot comparing electrical conductivity (based on manual measurements) collected during each run using powder hydrated lime. Each run corresponds to a different residence time (i.e., contact time between the Ca(OH)₂ and water) – Run 1: 59 mins; Run 2: 48 mins; Run 3: 48 mins; Run 4: 45 mins; Run 5: 16 mins. Each run is demarcated by black dashed vertical lines. Runs 1-5 used mains water (EC 67.1 µS/cm).



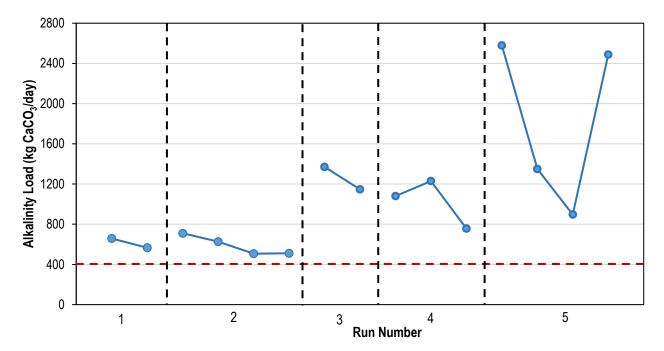


Figure D-3: Plot comparing alkalinity loads (based on manual measurements) collected during each run using powdered hydrated lime. Each run corresponds to a different residence time (i.e., contact time between the Ca(OH)₂ and water) – Run 1: 59 mins; Run 2: 48 mins; Run 3: 48 mins; Run 4: 45 mins; Run 5: 16 mins. Each run is demarcated by black dashed vertical lines. Runs 1-5 used mains water (pH 6.9).

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