ALKALINITY PRODUCING COVERS FOR MINIMISATION OF ACID MINE DRAINAGE GENERATION IN WASTE ROCK DUMPS

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ABSTRACT

Cover systems constructed over potentially acid forming (PAF) waste rock overburden dumps with a blend of low-permeability cement kiln dust (CKD) and weathered granite reduces atmospheric oxygen transfer into underlying acid-producing material, reducing the rate of pyrite oxidation, leading to a decrease in the severity of acid mine drainage (AMD). The focus of this paper is quantifying the secondary benefit of CKD-blended cover systems from an alkalinity generation perspective. CKD has an inherent alkalinity content of ~650 kg CaCO₃ eq. t⁻¹, which is steadily dissolved by the percolation of rainfall through the CKD/granite cover system, buffering acid generation in the underlying PAF material.

A small scale leaching trial was undertaken at the Stockton Mine on the West Coast of New Zealand, replicating generation of alkalinity in leachate through a 300 mm thick cover system, composed of 1 part CKD to 4 parts granite (by volume). Initially high leachate alkalinity rates (3000 – 4000 mg CaCO₃ eq. L⁻¹) were released that stabilised at approximately 500 mg CaCO₃ eq. L⁻¹ after 31 weeks. This corresponded to a long-term alkalinity yield of 10.9 t CaCO₃ eq. ha⁻¹ yr⁻¹. A net present value (NPV) calculation showed covering a waste rock dump with a CKD blended granite cover system and treating a reduced acid load had a breakeven of 8 years, compared to not covering and treating a higher acid load. Thallium is a major constituent of concern derived from CKD application as a cover system material, with the potential to adversely affect receiving ecosystems. The leachate thallium concentration rapidly decreases to less than 0.002 mg L⁻¹ following a first flush.

1.0 INTRODUCTION

Acid mine drainage (AMD) is one of the major environmental impacts of coal mines that disturb pyritic overburden on the West Coast of the South Island of New Zealand (Pope et al., 2010). Pyrite oxidation generates AMD through Eqn. [1].

\[
\text{FeS}_2(s) + \frac{7}{2} \text{H}_2\text{O} + \frac{15}{4} \text{O}_2 \rightarrow \text{Fe(OH)}_3(s) + 2\text{SO}_4^{2-} + 4\text{H}^+ \tag{1}
\]

The total sulphur content at the Stockton Mine varies, with some rock dumps having an average of up to 1.75 wt.% total sulphur (Elder et al. 2011), and this sulphur is predominantly present as pyrite. With a disturbed area of ~1000 ha at the mine, AMD management is a significant issue.

A key aspect of mine closure is the design of final engineered landforms (ELFs) and cover systems to minimise long-term maintenance liabilities (Bonstrom et al. 2012). Rehabilitation of waste rock overburden dumps at Stockton Mine is a three-step process. First, the surface of the dump is reshaped from the tip-head angle of repose (~38°) to a final landform slope of around 22°, with construction of benches at regular intervals to control surface water runoff.
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velocity and reduce erosion. Second, a 300 mm thick layer of blended cement kiln dust (CKD) and granite gravel (at a ratio of 1 part CKD to 4 parts granite by volume) is placed over the reshaped waste rock dump surface and compacted, producing a permeability of $\sim 10^{-4}$ to $10^{-5}$ cm s$^{-1}$. Finally, the dump is re-vegetated to provide a long-term stable cover system, either through vegetation direct transfer (Rogers et al. 2011) or by top-soiling (400 mm layer) and replanting.

The aim of engineered cover systems is to limit influx of atmospheric oxygen and water (Bonstrom 2012; O’Kane and Ayres 2012), impeding the oxidation of pyrite (Equation 1) and minimising the transport of oxidation products from the overburden. The primary reason for CKD addition is to increase the finer fraction of the CKD:granite material, filling voids in the relatively coarse, weathered granite and reducing rainfall net percolation. This has benefits for oxygen transfer rates as the diffusion coefficient decreases with lower porosity. The low water permeability also means the cover system holds moisture, further reducing oxygen transfer, as the effective oxygen diffusion coefficient decreases with an increasing degree of saturation (Aubertin et al. 2000).

Conceptually, alkalinity generating cover systems work by reducing oxygen transfer and percolation into a waste rock dump and ensuring water that does seep into underlying reactive materials is alkaline (Taylor et al. 2006). Miller et al. (2003) showed that placing an alkaline cover (with 2m of limestone) over a failed PAF/limestone blended dump resulted in leachate recovery from pH 3 to pH 4-6 after 2.5 years. After stabilisation at pH 6 in the field trial the leachate alkalinity stabilised at around 100 mg CaCO$_3$ eq. L$^{-1}$. These results were replicated in the laboratory using column leach tests (Smart 2010). By maintaining alkaline leachate, the oxidation of sulphides in ARD wastes was reduced by 90% (Smart et al. 2010). Taylor et al. (2006) has recommended using magnesium alkaline materials with superior solubility and dissolution kinetics for construction of alkaline covers to minimise short-, medium-, and long-term acid discharges, especially in environments with lower annual rainfall for which there would be an insufficient load of alkalinity produced by carbonate-based cover systems.

This paper focuses on the secondary benefit to be derived from using alkalinity generating cover systems from an acid-base accounting perspective, rather than from oxygen exclusion. This benefit had not yet been quantified in the field for the cover system investigated. The work was undertaken at the Stockton Mine where CKD is used as the alkaline amendment. The locally sourced CKD has a typical ANC of $\sim$650 kg CaCO$_3$ eq. t$^{-1}$. The generation of alkalinity in water seeping through such covers adds alkalinity to the system, reducing the net amount of acid generated by a PAF waste rock dump. Thallium (Tl) was considered the major constituent of concern with the potential to leach from CKD at the Stockton mine. The Tl content of CKD used at the Stockton Mine is typically 10 mg kg$^{-1}$. Thus, leachate Tl concentrations were also measured to determine the potential effect of the use of CKD-based covers on the receiving environment as part of future work (e.g. ecotoxicity studies).

2.0 METHODS AND MATERIALS

A small scale leaching trial was set up at the Stockton Mine to determine the alkalinity yield from the standard CKD:granite cover system used for rehabilitation on site. The top was cut off two 200 L plastic drums, with a 600 mm diameter. Both drums were then filled with approximately 18 L (26 kg) of CKD and 72 L (130 kg) of granite gravel (blended in a wheelbarrow), resulting in a 300 mm deep layer across the base of both drums. This ratio of CKD to granite was used to replicate the 1 part CKD to 4 parts granite ratio (by vol.) used to cover engineered landforms at the mine. A further 114 L (180 kg) of topsoil was added to one of the drums (CKD cover + Topsoil) to simulate a 400 mm topsoil layer, while the other drum
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The drums were set up on racks about 800 mm off the ground at the mine site and left open to be naturally irrigated by rainfall. Five overflow holes were drilled in the side of each drum at the height of the topsoil or CKD:granite surface to prevent ponding of water within the drum. Thus, only water which would naturally infiltrate through the cover system reported as leachate. Leachate was collected through a hole in the base of the drum. The drainage hose was bent into a ‘U’ shape to create an air lock, preventing oxygen ingress into the drums from the outlet. The hose drained into collection buckets with an up to 43 L storage capacity for each drum.

The trial was monitored weekly over a period of 31 weeks. The pH and total volume of water collected in the bucket was measured in the field. An unfiltered and unpreserved 1 L sample was then taken from the collection buckets for each drum and sent to an external lab for alkalinity and Ti analysis, as the analytes of interest to the project. The alkalinity was determined by titration using the APHA method 2320B. The Ti concentration was determined by Inductively Coupled Plasma – Mass Spectrometry (ICP MS) using the APHA 3030B method.

3.0 RESULTS AND DISCUSSION

3.1 General

The weekly volume of leachate collected from each drum is shown on Figure 1.

The weekly volume collected ranged from 0 L (weeks with no rain) to 43 L. The average leachate volume collected over the 31 week trial period was 10.3 and 11.7 L per week for the CKD cover + Topsoil and CKD cover drums, respectively. Water storage and release by

Fig. 1. Leachate volume (L) collected for CKD cover + Topsoil (blue bars) and CKD cover (red bars) drums over the 31 week trial
evaporation in the soil layer is expected to cause the difference in leachate production between the two drums. Over the 31 week trial period the site experienced rainfall at rates 8% lower than average, which was slightly lower than would normally be expected.

The leachate pH steadily decreased from pH ~13 to ~11 over the 31 week trial period for both trials, as shown in Figure 2.

![Fig. 2. Leachate pH for CKD cover + Topsoil (blue diamonds) and CKD cover (red squares) drums over the 31 week trial](image)

X-ray diffraction testing has shown the ANC is predominantly from oxides (e.g. CaO, MgO, etc.), which explains its ability to produce leachate at pH 11-13.

### 3.2 Leaching Trial Alkalinity

The weekly leachate alkalinity is shown on Figure 3a. The leachate alkalinity from the CKD cover + Topsoil drum dropped from 4000 to ~500 mg CaCO$_3$ eq. L$^{-1}$ over the 31 week trial. The CKD cover alkalinity decreased from 3000 to ~500 mg CaCO$_3$ eq. L$^{-1}$. The alkalinity data from each drum were fitted by a power function (Table 1) and the continuous fitted lines produced by these functions (Fit. CKD cover + Topsoil and Fit. CKD cover) are overlayed on Fig 3a. The stabilised CKD leachate alkalinity of around 500 mg CaCO$_3$ eq. L$^{-1}$ is significantly higher than the 100 mg CaCO$_3$ eq. L$^{-1}$ expected from limestone (Smart et al. 2010). Thus, CKD is showing a higher alkalinity yield than limestone, which is likely to be due to the CKD alkalinity being present as more soluble oxides and hydroxides of calcium and magnesium as opposed to carbonates in limestone.

It is postulated, although not confirmed, that the difference between the two trials and elevated alkalinity from the CKD cover + Topsoil drum is due to the soil layer excluding atmospheric CO$_2$, thus limiting the formation of CaCO$_3$, and enabling higher, ongoing oxide and hydroxide dissolution when a soil cover is in place compared to the CKD cover drum.
The cumulative alkalinity loading (Figure 3b) was derived from the product of the weekly leachate volume and the corresponding alkalinity concentration derived from the fitting function in Table 1. The $R^2$ values of the fitting function are low, due to the variability of weekly alkalinity and leachate volumes collected. The objective of the fitting function is to allow further analysis of an idealised dataset without this variability. Figure 3b shows the CKD cover + Topsoil drum is continuing to release more alkalinity than the CKD cover drum. However, the fitted leachate alkalinity curves on Figure 3a show the alkalinity released from the two drums is converging at around 500 mg CaCO$_3$ eq. L$^{-1}$. Therefore, eventually the two cumulative alkalinity loading curves may become parallel.

The fitted cumulative alkalinity loading was determined as the product of the fitted weekly leachate alkalinity and the average weekly volume of leachate generated (10.3 and 11.7 L per week for the CKD cover + Topsoil and CKD cover drums, respectively), and extrapolated out to the end of the first year. The fitted cumulative alkalinity curve aligned with the actual data relatively well for both drums. The fitted data were used in further discussion as it evens out weekly fluctuations in alkaline load.

![Fig. 3. Leachate alkalinity (mg CaCO$_3$ eq. L$^{-1}$) (a) and cumulative alkalinity loading (g CaCO$_3$ eq.) (b) for CKD cover + Topsoil (blue diamonds) and CKD cover (red squares) drums over 31 week trial.](image)
### Table 1. Alkalinity decay rate fitting functions for CKD cover + Topsoil and CKD cover

<table>
<thead>
<tr>
<th>Drum</th>
<th>Alkalinity decay (mg CaCO₃ eq. L⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CKD cover + Topsoil</td>
<td>Y=7398.4w^{0.666}</td>
<td>0.5562</td>
</tr>
<tr>
<td>CKD cover</td>
<td>Y=4013.7w⁻^{0.581}</td>
<td>0.4545</td>
</tr>
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</table>

### 3.3 Theoretical acid treatment offset – CKD cover + Topsoil

Ongoing discussion has been restricted to the CKD cover + Topsoil scenario as this represents final cover systems at the Stockton Mine. The Mangatini catchment at the Stockton Mine has been significantly disturbed by both historic and more recent mining, with 232 ha of the total 319 ha catchment disturbed. The catchment produces 6600 t CaCO₃ eq. yr⁻¹ of acidity, which is currently neutralised by ultrafine limestone dosing (Elder et al. 2011). This value provides an estimated acid generation rate of 28.4 t CaCO₃ eq. ha⁻¹ over the disturbed area.

The surface area of the drums used in this trial was 0.25 m². The cumulative 671 g CaCO₃ eq. of alkalinity released from the CKD cover + Topsoil drum over the first year was extrapolated to 27.2 t CaCO₃ eq. ha⁻¹. Thus the alkalinity generation from the CKD cover system over the first year is approximately equal to the acid generation rate of the unamended catchment area.

Figure 3a shows the alkalinity generated from the CKD cover + Topsoil drum declines and then stabilises at around 500 mg CaCO₃ eq. L⁻¹ after one year. This corresponds to a lower alkalinity yield of 10.9 t CaCO₃ eq. yr⁻¹, which is just over a third of the pre-cover acid generation rate estimated from the catchment analysis above.

The acid neutralising capacity (ANC) of the CKD used at the Stockton Mine is approximately 650 kg CaCO₃ eq. t⁻¹, as determined using the method described in the AMIRA P387A Project ARD Test Handbook (IWRI and EGi 2002). Given 26 kg of CKD was used in each drum, the total alkalinity of each drum would be 16.9 kg CaCO₃ eq. The fitted cumulative alkalinity loading showed that for the first year, a cumulative 671 g CaCO₃ eq. of alkalinity was collected from the CKD cover + Topsoil drum, corresponding to leaching of 4.0 wt.% of the total alkalinity. Provided long term leachate alkalinity remains stable at 500 mg CaCO₃ eq. L⁻¹, the CKD cover + Topsoil drum would produce 268 g CaCO₃ eq. yr⁻¹, corresponding to leaching of 1.6% of the total ANC. Thus, at this rate it would take approximately 60 years for exhaustion of the alkalinity in the CKD.

Planning for mine closure requires consideration of the capital and operational costs associated with managing acid mine drainage in both the short- and long-term. Many mine operators choose to minimise capital expenditure early in a project and actively treat AMD drainage towards the end of mine operation and post closure in perpetuity, creating operational expenses over time frames in the order of 100 years or more. Such an approach will deliver significant savings from a net present value (NPV) perspective. While effective cover systems and rehabilitation of waste rock dumps is capital intensive, the decrease in acid production and subsequent treatment cost reduces longer term operational expenses and the ongoing risk of environmental harm.
Net present value (NPV) analysis methods essentially discount the future costs associated with treating acid mine drainage to a value in today's terms. The various parameters and assumptions used in the NPV analysis for this paper are shown on Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cover Capital expenditure</td>
<td>$55,000 ha⁻¹ Pers. Comm. (Nathan Thompson)</td>
</tr>
<tr>
<td>Cover Operational expenditure</td>
<td>0</td>
</tr>
<tr>
<td>Limestone treatment Capex</td>
<td>0</td>
</tr>
<tr>
<td>Acidity decay rate after covering</td>
<td>40% over first 7 years 0.62% pa thereafter Pers. Comm. (Phil Lindsay)</td>
</tr>
<tr>
<td>Acidity decay rate without covering</td>
<td>0.62% pa Pers. Comm. (Phil Lindsay)</td>
</tr>
<tr>
<td>Inflation rate</td>
<td>2.03% Pers. Comm. (Dave Thomas)</td>
</tr>
<tr>
<td>Discount rate</td>
<td>4.76% Pers. Comm. (Dave Thomas)</td>
</tr>
<tr>
<td>Ultra-fine Limestone treatment cost</td>
<td>$337.60 t⁻¹ CaCO₃ eq. neutralised Pers. Comm. (Dave Thomas)</td>
</tr>
<tr>
<td>Alkalinity yield</td>
<td>27.2 t CaCO₃ ha⁻¹ in first year 10.9 t CaCO₃ ha⁻¹ yr⁻¹ thereafter</td>
</tr>
</tbody>
</table>

The results of the NPV analysis are shown on Figure 4.

Two breakeven points are shown on Figure 4. The first occurs at year 8 where the NPV of not covering and treating the full acid load of the catchment is equal to the cost of covering and treating the residual acid load of the catchment once the leachate alkalinity has been deducted from the total acid load. The second breakeven point occurs at year 25 where the NPV of not covering and treating the full acid load is equal to the NPV of covering and treating the residual acid load of the catchment without deducting the leachate alkalinity from the total acid load. The difference in the two breakeven points is due to the long-term
alkalinity generation rates of the CKD:granite cover system. If the long-term alkalinity generation rate is less than 500 mg CaCO\textsubscript{3} eq. L\textsuperscript{-1} the break-even point will be pushed out beyond 8 years, but will not reach 25 years unless alkalinity generation from the cover system ceases abruptly after year one.

3.4 Leaching Trial Thallium concentration

The weekly leachate thallium concentration is shown on Figure 5a.

![Graph showing leachate thallium concentration over 31 weeks trial](image)

The leachate Tl concentration from the CKD cover + Topsoil drum decreased from 0.04 to ~0.002 mg L\textsuperscript{-1} over the 31 week trial. The CKD cover leachate Tl concentration decreased from 0.018 to ~0.0005 mg L\textsuperscript{-1}. The Tl concentration decay is consistent with a first flush type
scenario with Tl concentration decreasing by over an order of magnitude before stabilising 7
to 12 weeks after cover system construction. A power trendline was fitted to the Tl data from
each drum with the equations shown on Table 3. These equations were used to generate the
curves (Fit. CKD cover + Topsoil and Fit. CKD cover) shown on Figure 5a.

Table 3. Thallium concentration decay rate fitting functions for CKD cover +
Topsoil and CKD cover

<table>
<thead>
<tr>
<th>Drum</th>
<th>Thallium decay (mg L⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CKD cover + Topsoil</td>
<td>Y=0.0558w⁻¹.173</td>
<td>0.7794</td>
</tr>
<tr>
<td>CKD cover</td>
<td>Y=0.0293w⁻¹.399</td>
<td>0.7726</td>
</tr>
</tbody>
</table>

The cumulative Tl loading (Figure 5b) was derived from the product of the weekly leachate
volume and the corresponding Tl concentration. Figure 5b shows the CKD cover + Topsoil
drum is continuing to release more Tl than the CKD cover drum.

The cumulative Tl loading was determined as the product of the weekly leachate Tl
concentration produced by the fitting function and the average weekly volume of leachate
generated, and extrapolated out to the end of the first year. The derived cumulative Tl loading
curve matched the actual data relatively well for both drums.

One year after construction the cumulative Tl leached from the fitted CKD cover + Topsoil
drum was 2.0 mg. Extrapolating from the 0.25 m² drum results in a per hectare yield of 80.7 g
Tl ha⁻¹ in the first year for the CKD cover + Topsoil scenario. Conservatively assuming the
long term Tl leaching rate is 0.002 mg L⁻¹ results in a long term Tl yield of 43.5 g Tl ha⁻¹ yr⁻¹.
Evaluating whether this Tl leaching rate is acceptable would require a site specific risk
assessment to be done, including consideration of extant water quality guidelines and the
extent of attenuation before relevant compliance monitoring points. There were insufficient
data for the Australian and New Zealand Environmental Conservation Council (ANZECC) to
recommend a threshold value for Tl concentration for protection of aquatic ecosystems in its
2000 guidelines (ANZECC 2000). However, actual discharge Tl concentrations from the site
(when combined with surface water runoff) are likely to be below the current Tl consent limit
of 0.04 mg L⁻¹.

The CKD used for covers at the Stockton Mine generally has a total recoverable Tl content
(determined by acid digestion) of 10 mg Tl kg⁻¹ CKD. 26 kg of CKD was used in each drum
bringing the total recoverable Tl per drum to 260 mg. Therefore, 0.8% of the total recoverable
Tl leached from the CKD cover system to occur. Beyond year 1, a long term Tl yield of 0.5% per
year would be expected. Thus, based on the current Tl yield, it would be approximately 200
years for Tl exhaustion of the CKD cover system to occur.

4.0 CONCLUSIONS

Construction of alkaline cover systems using alkalinity amendments such as CKD results in
the generation of alkaline leachate with the potential to buffer acid generation from
underlying PAF material. A small scale leaching trial using components of the cover system
has shown the alkalinity generation rate stabilised at 500 mg CaCO₃ eq. L⁻¹ from a 1 part
CKD to 4 parts granite blend. This alkaline leachate would offset the acid production of PAF
waste rock dumps from an acid-base accounting perspective, with alkalinity generated at approximately one third the current acid generation rate in the Mangatini catchment on an area basis. While cover systems are expensive from a net present value perspective, the reduction in AMD treatment costs for the Mangatini catchment with an alkaline cover system results in a breakeven point of 8 to 24 years after cover construction, depending on long-term alkalinity generation rates, which is a viable and achievable alternative to treatment in perpetuity. Initially high leachate Thallium concentrations rapidly decay. Determining whether these stable TI leachate concentrations are acceptable would require a site specific risk assessment to be done.

5.0 REFERENCES


