The Effect of Temperature on the Application of Chemical Solutions to Rock

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ABSTRACT. Certain chemical solutions have been shown to reduce the degradation effect of water on the material properties of rock and increase the strength and cuttability of clay-bearing rock. Consequently, there is potential for the application of chemical solutions to enhance the cutting performance of mechanical excavators and for maintaining ground stability in clay-bearing rocks that exist surrounding coal formations. A study investigated the effect of temperature of chemical solutions on rock properties. The temperatures ranged between 5°C and 40°C. It was found that temperature effect varied with different solutions. In the case of potassium chloride, there were changes in abrasivity, weatherability and cuttability of rock with temperature whereas the results were less consistent with magnesium chloride and copper sulphate solutions.

INTRODUCTION

A challenge encountered by drag pick mechanical excavators is that cutting rates reduce significantly in clay bearing rock due to swelling of clay minerals by in some cases over 50% (Bilgin et al., 2004). In the presence of groundwater, clay softens and consequently reduces its strength and increases its deformability (Brady and Brown 2004). Underground coal mining operations can be adversely affected by clay swelling where the floors of coal seams are comprised of shales with bogging of machinery resulting in productivity losses and unsafe working conditions (Anwar et al., 1998). The slaking and collapsing behaviour of certain clay bearing rocks also reduces the stability of the roof and sidewalls of underground excavations.

Research over the past decade has found that certain chemical solutions can reduce the degradation effects of water, and increase strength and cuttability of clay bearing rock (Morkel and Saydam 2008 and Hagan et al., 2012). Therefore, there is potential for chemical solutions to be used to enhance the cuttability of rock and stabilise excavations. These changes have been attributed to the exchange of cations in solution with those in clay minerals as was demonstrated by a reduction in the cation concentration in solution after treatment of rock (Elias 2010).

Summersby (2012), Deramore-Denver (2010) and Elias (2010) reported on studies into the effect of immersion time and concentration on rock properties but there has been very limited research on how the temperature of chemical application affects rock. The only relevant finding in literature was that treating kimberlite with magnesium chloride at 40°C degraded more compared to when it was treated at room temperature (Morkel et al., 2007). It is understood that temperature is a factor that affects the rate of chemical reactions; hence temperature could impact on how quickly solutions will alter rock properties – the extent of which was investigated in this project.

PROJECT OBJECTIVES

The objective of this project was to determine if the temperature of chemical solution application affects various rock properties, namely strength, cuttability and weatherability. The chemical solutions examined in this study were potassium chloride, magnesium chloride and copper sulphate, which have been previously shown to cause significant changes to these rock properties. As the temperature of Australian underground mines varies considerably up to 40°C (Hassell et al., 2004), the temperature range investigated in this study was between 5°C and 40°C.
EXPERIMENTAL PROCEDURE

Sample preparation

Test specimens of Hawkesbury Sandstone were diamond cored from blocks sourced from Gosford Quarries on the Central Coast, NSW, and specimens of Althorpe Claystone were sourced from Bulga Underground Mine near Singleton, NSW. X-ray powder Diffraction (XRD) was used to identify the clay mineral composition of the rocks. The Hawkesbury Sandstone specimens contained 7% illite and 6% kaolinite, whilst Althorpe Claystone contained 20% illite and 3% palygorskite.

UCS, Brazilian tensile strength and core cuttability tests were performed on Hawkesbury Sandstone, whilst the slake durability test was conducted using Althorpe Claystone. The CERCHAR abrasivity test was carried out on both types of rocks. Different 1.5 mol solutions were prepared by dissolving potassium chloride, magnesium chloride and copper sulphate salts in water. This concentration was selected due to its proven effectiveness and to allow for comparison with past studies.

The core specimens were completely immersed in the chemical solutions as well as in pure water within a sealed container for a set amount of time. The container was placed in a temperature-controlled environment with the exception of the samples treated at room temperature. The 5°C environment was simulated in the laboratory’s industrial fridge, and the 30°C and 40°C environments were replicated in an industrial oven. The rocks treated at ambient room temperature in the laboratory were kept at a relatively constant temperature of around 20°C with thermometer readings ranging between 17°C and 22°C across the treatment period.

The treatment time was also controlled across the specimens for each test. The UCS, Brazilian tensile strength, CERCHAR and slake durability test specimens were immersed overnight for 17 hours, whilst the Core Cuttability test specimens were treated for six hours. The water-only treated specimens were also immersed for these periods, but only at room temperature. Following treatment, all test specimens were air-dried for an hour then wrapped in plastic film until testing.

Core cuttability test

The Invicta 6M linear rock cutting machine fitted with a tri-axial dynamometer, located in the UNSW Mining Engineering Rock Mechanics Laboratory, was utilised for the core cuttability test. The NQ (63 mm diameter) sandstone core specimens were cut to approximately 230 mm in length.

The mass and dimensions of the cores were recorded to determine the density prior to testing. Each core was secured in place in a vice and levelled so that a tungsten carbide pick would run along the axis of the core maintaining a constant depth of cut as shown in Figure 1. The depth of cut in each test remained unchanged at 5 mm. The total length cut, retained length and mass of rock cuttings mass were each measured and recorded before the core was repositioned for the second and subsequent cuts up to four cuts in total for each core. Between each cut, the core was rotated 180°, 90° and 270° from the first position. If the core broke during a cut, the following cut was performed using the largest remaining portion of core specimen.

Figure 1: Cut performed along the longitudinal axis of sandstone core
The triaxial dynamometer measured the transient changes in the directional strain during each test at a rate of $1 \times 10^3$ samples per second and the values stored on a data acquisition system. The carbide loss was determined by recording the mass of the carbide before and after each set of four cuts on a core specimen.

**Uniaxial compressive strength test**

The MTS 815 machine was used to conduct the UCS test. The test was carried out using sandstone specimens of approximately 57 mm diameter and 149 mm in length with a height to diameter ratio of 2.61. Three specimens were prepared and tested for each combination of chemical solution and temperature.

A constant force rate of 0.002 kN/s was applied to each specimen until failure (ASTM, 2010). The data acquisition system generated a plot of the force versus time and the peak force value was used to calculate the UCS if the sample had exhibited shear failure, which was the case for all but two samples.

**Brazilian tensile strength test**

The Brazilian or indirect tensile test was also performed using the MTS 815 machine. Sandstone specimens of approximately 57 mm diameter and 20 mm thickness were used for this test. Four specimens were prepared and tested for each combination of chemical solution and temperature.

In this case a constant force at a rate of 0.002 kN/s was applied (ASTM 2008). The data acquisition system generated a plot of the force versus time and the peak force value was used to calculate the indirect tensile strength. In this test, failure occurs when diametric cracks form between the platen contact points.

**CERCHAR abrasivity test**

The CERCHAR abrasivity test was performed in the method suggested by Alber et al., (2014) using the West (1989) design of testing apparatus. The test arrangement consists of a 7 kg vertical load applied to a sharpened steel pin applied to the top surface of the test specimen secured within a clamping vice. A dial gauge is used to measure the distance as the pin is made to traverse 10 mm across the rock surface as show in Figure 2. A microscope was then used to measure the length of resultant wear flat on the surface of the pin to an accuracy of ±0.01 mm. The test is replicated for each test specimen five times using five different pins. The sandstone and claystone specimens were approximately 60 mm in diameter and 50 mm in height. One specimen was tested for each combination of rock type, chemical solution and temperature.

![Figure 2: Pin scratching surface of CERCHAR specimen](image)

**Slake durability test**

This test was carried out using the slake durability device with steel drums comprised of 2 mm mesh and plastic troughs for holding water. Each set of specimens consisted of ten lumps of claystone weighing between 40 and 60 g, to give a total mass of between 450 and 550 g. Care was taken to randomly select
sets of rock samples that represented the variability of the Althorpe Claystone. One set of specimens was tested for every rock type, chemical solution and temperature. The mass of the steel drums with and without the claystone were measured before the test. The samples were dried overnight in the steel drums for 17 hours at 85°C, cooled at room temperature for 30 minutes and weighed before each cycle in the slake durability device. Each cycle involved rotating the steel drum in a water trough for 10 minutes at 20 rpm to expose the claystone to wetting and abrasion. Four cycles were performed to be consistent with the experiments of Summersby (2012), Deramore-Denver (2010), Elias (2010), and Morkel and Saydam (2008).

RESULTS AND ANALYSIS

Core cuttability test

Table 1 shows a summary of the core cuttability test results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cutting Force (kN)</th>
<th>Normal Force (kN)</th>
<th>Yield (m³/km)</th>
<th>Specific Energy (MJ/m³)</th>
<th>Carbide Wear (mg/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>1.215</td>
<td>0.938</td>
<td>0.0764</td>
<td>15.95</td>
<td>2.468</td>
</tr>
<tr>
<td>Water Treated</td>
<td>1.011</td>
<td>0.751</td>
<td>0.0661</td>
<td>15.33</td>
<td>2.481</td>
</tr>
<tr>
<td>KCl 5°C</td>
<td>1.135</td>
<td>0.912</td>
<td>0.0739</td>
<td>15.42</td>
<td>1.308</td>
</tr>
<tr>
<td>KCl 20°C</td>
<td>1.123</td>
<td>0.910</td>
<td>0.0717</td>
<td>15.63</td>
<td>1.070</td>
</tr>
<tr>
<td>KCl 30°C</td>
<td>1.079</td>
<td>0.715</td>
<td>0.0697</td>
<td>15.57</td>
<td>1.510</td>
</tr>
<tr>
<td>KCl 40°C</td>
<td>0.887</td>
<td>0.597</td>
<td>0.0687</td>
<td>13.04</td>
<td>2.719</td>
</tr>
<tr>
<td>MgCl₂ 5°C</td>
<td>1.031</td>
<td>0.795</td>
<td>0.0719</td>
<td>14.48</td>
<td>1.707</td>
</tr>
<tr>
<td>MgCl₂ 40°C</td>
<td>0.964</td>
<td>0.697</td>
<td>0.0743</td>
<td>13.00</td>
<td>2.025</td>
</tr>
<tr>
<td>CuSO₄ 5°C</td>
<td>1.014</td>
<td>0.738</td>
<td>0.0726</td>
<td>14.07</td>
<td>2.876</td>
</tr>
<tr>
<td>CuSO₄ 40°C</td>
<td>1.133</td>
<td>0.927</td>
<td>0.0681</td>
<td>16.65</td>
<td>2.108</td>
</tr>
</tbody>
</table>

Cutting and normal forces

The average cutting and normal forces for each chemical and the temperature along with the untreated and water treated controls are displayed in Figures 3 and 4 respectively. The percentage values shown in the following graphs indicate the measured parameter relative to the value of the water treated sandstone core. The error bars represent the variability with each set of test results.

![Figure 3: Core cuttability test results for cutting force](image-url)
While the forces do not vary significantly for the MgCl$_2$ treated samples, the difference between the forces for the CuSO$_4$ treated test specimens may be due to the lower concentration of the chemical at 5°C. At 5°C, the solubility of the chemical is between 231 and 275 g per litre (Dean and Lange 1999) which limited the concentration of the solution to 1 mol. It was observed that some of the CuSO$_4$ in solution had crystallised after the immersed samples were removed from the industrial fridge. Therefore, it is likely that rock samples treated with copper sulphate at 5°C were exposed to a concentration lower than 1.5 M.

From Figures 3 and 4, it can be observed that the cutting and normal forces for the KCl treated sandstone are similar at 5°C and 20°C, but that tend to decrease as temperature rises from 20°C to 40°C. These changes with temperature are plotted in Figure 5 showing the relationship between forces and temperature of KCl application can be represented by a bi-linear function.
Yield and specific energy

Figure 6 shows that yield slightly increased across the full range of chemical solution temperatures though generally, yield was greatest at the lowest temperatures. Figure 7 shows that there was a slight effect of chemical solution and temperature on specific energy and hence the efficiency of the cutting process though the results were not generally consistent.

![Figure 6: Core cuttability test results for yield](image)

![Figure 7: Core cuttability test results for specific energy](image)

There was a substantial decrease in the specific energy for the KCl 40°C samples, mainly due to the low cutting force. The difference in the specific energy for the CuSO₄ samples may also be attributed to the lower concentration of CuSO₄ at 5°C. The specific energy for both the low and high temperature MgCl₂ solutions.

Impact abrasivity

There is some variability in the results obtained for impact abrasivity as shown in Figure 8. This was determined from the difference in the carbide mass after the set of cutting tests for each specimen. There was only one data point for each treatment type with KCl 40°C being the one exception with two results. Therefore, it is recommended to carry out more experiments to allow for conclusions to about temperature to be drawn from this test.
Uniaxial compressive strength test

In Figure 9 the results show that UCS is mostly unaffected by the temperature of chemical application with differences of 7% or less relative to water treated samples.

In Figure 9, the UCS of the chemically treated samples is similar to that of the water treated samples. These results do not align with the outcomes of previous literature, which found that the UCS of samples immersed in KCl were higher than for samples immersed in water (Deramore Denver 2010; Elias 2010; Morkel and Saydam 2008). Elias (2010) also demonstrated that the UCS of samples immersed in CuSO4 was greater than the UCS of water treated samples.

The difference in results may be due to variation of the control variables between the tests, such as rock type, solution concentration and drying time. Deramore Denver (2010) and Elias (2010) performed UCS tests on siltstones sourced from Ravensworth North and Crinum Mines, whereas the results in Figure 9 are for sandstone from Gosford Quarry. The clay mineral constituents identified using XRD analyses are different for the two rock types with nacrite found in the siltstones, whilst the Gosford Sandstone consisted of kaolinite and illite. Although nacrite is polymorphous with kaolinite (Ruiz Cruz 2007) and both clay minerals are in the kaolin clay group (Velde 2012), comparison of the results show that KCl and CuSO4 may not have the same effect on the two different clay minerals. The presence of illite in the sandstone also limits the comparability of the results.

Morkel and Saydam (2008) found that submerging kimberlite specimens in 1.5 M KCl for 30 min before drying for 18 h resulted in UCS increasing above the value for water treated specimens. Aside from the
difference in treatment and drying times, the kimberlite contains smectite, which is a group of clay minerals known for their swelling behaviour. The contrast in results suggest that treatment and drying time have a significant impact on UCS and that KCl may be more effective on certain clay minerals than others.

Brazilian tensile strength test

The results (Figure 10) show that Brazilian tensile strength is largely unaffected by the temperature of KCl and MgCl₂ application with differences of 11% or less relative to water treated samples. The Brazilian tensile strength for sandstone treated at 5°C and 40°C differed by 26%, which may also be due to the lower concentration of CuSO₄ at 5°C.

![Brazilian Tensile Strength Test Results](image)

The chemically treated samples all yielded higher Brazilian tensile strengths compared to the water treated samples with KCl being the most effective; improving strengths to approximately the same level as untreated samples.

CERCHAR abrasivity test

Sandstone

The results in Figure 11 show that the CERCHAR Abrasivity Index (CAI) for the chemically treated samples were all significantly lower than both the untreated and water-treated specimens, which suggests that the application of KCl, MgCl₂ and CuSO₄ to sandstone reduces its abrasivity. This finding is consistent with most of the impact abrasivity results from the core cuttability test, although more core cutting experiments are recommended to improve the reliability of the test results. The reduction in the abrasivity of rock due to treatment with KCl, MgCl₂ and CuSO₄ has not been previously reported. Summersby (2012) found that the impact abrasivity of sandstone treated with these three chemicals was 123% to 309% of the value for an untreated, dry core. In that study, a treatment time of 24 h had been used for KCl, MgCl₂ and CuSO₄, but KCl was also tested after treatment for 5 min, 1 h and 8 h. The concentration of solutions used by Summersby (2012) was also 1.5 M. The inconsistency when comparing results may be due to the different drying times, which were not specified in that study.

Claystone

There was a significant reduction in the CERCHAR abrasivity of the claystone with chemical treatment in comparison to the plain water-treated specimen as shown in Figure 12. Interestingly the reduction was less significant when compared to the untreated specimen. Though the trends were less apparent, it would seem that a reduction in solution temperature enhanced the effect of the chemical treatment in terms of reduction in abrasivity.

Whilst the CAI did not vary significantly for claystone treated with MgCl₂ at 5°C and 40°C, it differed by 22% relative to the untreated sample for samples treated with CuSO₄ at the two temperatures. This difference may also be due to the lower concentration of CuSO₄ at 5°C.
Figure 11: CERCHAR abrasivity test results for Hawkesbury sandstone

Figure 12: CERCHAR abrasivity test results for claystone

It was demonstrated that the application of KCl, MgCl\textsubscript{2} and CuSO\textsubscript{4} to sandstone reduced its abrasivity relative to untreated and water treated samples. Figure 12 shows that this phenomenon is also generally true for claystone, with the exception of the KCl 40°C and CuSO\textsubscript{4} 40°C samples where the CAI values are only marginally greater than the untreated sample. Further CERCHAR abrasivity testing for claystone should be undertaken to improve confidence in these results.

**Slake durability test**

The Slake Durability Index (SDI) test results are provided in Table 2 and are plotted in Figure 13 showing the differences in the degradation rates.

**Table 2: Results for the Slake durability index test**

<table>
<thead>
<tr>
<th>Chemical solution</th>
<th>Temp (°C)</th>
<th>$I_{c1}$ (%)</th>
<th>$I_{c2}$ (%)</th>
<th>$I_{c3}$ (%)</th>
<th>$I_{c4}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>5</td>
<td>98.34</td>
<td>97.70</td>
<td>97.00</td>
<td>96.39</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>98.22</td>
<td>97.62</td>
<td>97.12</td>
<td>96.71</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>98.56</td>
<td>97.80</td>
<td>97.20</td>
<td>96.79</td>
</tr>
<tr>
<td>MgCl\textsubscript{2}</td>
<td>40</td>
<td>98.52</td>
<td>97.93</td>
<td>97.50</td>
<td>96.99</td>
</tr>
<tr>
<td>CuSO\textsubscript{4}</td>
<td>5</td>
<td>98.09</td>
<td>97.44</td>
<td>96.88</td>
<td>96.47</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>97.48</td>
<td>96.63</td>
<td>95.82</td>
<td>95.32</td>
</tr>
<tr>
<td>Untreated</td>
<td>5</td>
<td>96.16</td>
<td>94.94</td>
<td>94.11</td>
<td>93.51</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>97.29</td>
<td>96.38</td>
<td>95.67</td>
<td>95.25</td>
</tr>
</tbody>
</table>
It was observed that the claystone specimens treated with KCl over the range of temperatures from 5°C to 40°C performed consistently irrespective of the treatment temperature. The SDI of the KCl treated samples was very similar for all four cycles. However, there is a trend for the SDI to increase slightly as the KCl treatment temperature increases from 5°C to 40°C. The SDI of the KCl treated samples were significantly higher than the SDI of the untreated sample, which confirms that KCl is a strong degradation inhibitor for claystone irrespective of the temperature of the treatment solution.

The SDI for MgCl$_2$ and CuSO$_4$ treated samples differed significantly depending on whether treatment temperature was 5°C or 40°C. When treated with these two chemicals at 40°C, the SDI results were very similar to that of untreated claystone. However, when treated with MgCl$_2$ at 5°C, the SDI is similar to that of the KCl samples. Therefore, the effectiveness of MgCl$_2$ as a weathering inhibitor depends on temperature of application with 5°C being more effective than 40°C. These results align with the finding of Morkel et al., (2007) that disintegration of kimberlite increases by 27% when treated with MgCl$_2$ at 40°C compared to MgCl$_2$ at room temperature (~20°C).

The CuSO$_4$ 5°C sample had a considerably lower SDI than the CuSO$_4$ 40°C sample, which indicates that the application of CuSO$_4$ at the lower temperature increases degradation of claystone. Further testing should be carried out for claystone with MgCl$_2$ and CuSO$_4$ applied at temperatures between 5°C and 40°C to determine the effect of treatment temperature between these two points.

Summersby (2012) and Morkel et al., (2007) had found that cations have a strong effect on the weatherability of two types of clay bearing rock, kimberlite and Ulan Claystone, with the extent of weatherability increasing in the order: Cu$^{2+}$ > Mg$^{2+}$ > K$^+$. The slake durability test results in this study confirm that this trend is also exhibited in the Althorpe Claystone.

CONCLUSIONS

In general it was found that aside from the few exceptions noted below, the temperature at which KCl, MgCl$_2$ and CuSO$_4$ solutions are applied to rock did not affect cuttability, UCS, Brazilian tensile strength, abrasivity and weatherability.

The first exception is that the cutting and normal forces for sandstone decreased linearly as the temperature of KCl treatment increased from 20°C to 40°C.

Second, the CERCHAR abrasivity of sandstone and the weatherability of claystone also increased slightly as the temperature of KCl treatment increased from 5°C to 40°C.

Third, the temperature of the chemical solution significantly affects the weatherability of MgCl$_2$ and CuSO$_4$ treated claystone. When claystone was treated with either of these chemicals at 40°C, there were no changes in weatherability relative to untreated claystone. However, when treated with MgCl$_2$ at 5°C, the slake durability of the claystone improved to a similar level to that of the KCl treated samples. By contrast, the degradation of claystone increased substantially when treated with CuSO$_4$ at 40°C.
While the Slake Durability test results confirmed the findings of Summersby (2012) and Morkel et al. (2007), which was that cations have a strong effect on the weatherability of clay bearing rock, with the extent of weatherability increasing in the order Cu$^{2+} >$ Mg$^{2+} >$ K$^+$, the UCS and core cuttability results were not consistent with past literature. The UCS of the chemically treated samples was similar to that of the water treated samples, rather than higher in comparison as demonstrated by Elias (2010), Deramore-Denver (2010), and Morkel and Saydam (2008). Also, the cutting and normal force results in this study do not show that forces of the chemically treated samples are lower than the water treated sample as demonstrated by Summersby (2012) and Deramore-Denver (2010). The difference in results may be due to variation of the control variables between the tests, such as the type of clay mineral within the rock and drying time.

It was found that all three chemical solutions examined in this study reduced the abrasivity of rock when compared with water treated samples. The effect was most pronounced with the CERCHAR results for sandstone, which shows that the chemicals perform similarly to reduce the CAI by 36% relative to untreated sandstone.

Also, the chemically treated samples all had higher Brazilian tensile strengths compared to the water treated samples with KCl being the most effective, improving strengths to approximately the same level as untreated samples.

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