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CHANGES IN ROCK PROPERTIES FOLLOWING IMMERSION IN VARIOUS CHEMICAL SOLUTIONS

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ABSTRACT: Many clay-bearing rocks will undergo changes in material properties after immersion in water. This is often accompanied by a reduction in strength and cuttability properties associated with increased degradation. In extreme cases such as with water active shales, it can lead to complete collapse or sloughing of the material. This can have important implications for Australian coal mining operations in terms of maintaining ground stability where clay-bearing rocks are in close proximity to coal formations.

Previous research has examined whether chemical solutions containing potassium chloride and copper sulphate could arrest these changes in rock properties. While they provided encouraging results, they did not fully explore the effects of altering the exposure times or concentrations of chemical solutions. The purpose of this paper is to outline the effect of changes in the concentration and exposure times of potassium chloride, magnesium chloride and copper sulphate solutions on clay-bearing rock.

The Slake Durability Index Test was used to examine the degradation of a claystone after immersion in a range of chemical solutions at different concentrations. There was little quantitative change due in part to the low permeability of the rock. Qualitatively it was found however that degradation was exacerbated following immersion in a copper sulphate solution and to a lesser extent with magnesium chloride. Conversely, potassium chloride at all concentrations was found to reduce the degradation effects of water.

Immersion of the test specimen in each of the solutions of potassium chloride, magnesium chloride and copper sulphate improved rock cuttability relative to dry, untreated rock.

INTRODUCTION

Clay minerals are found in most of the sedimentary rocks that make up the strata in coal formations (Hall, 1987). When clay comes into contact with water, it undergoes changes including swelling or dispersion (Ghazali, 2012). Certain clay minerals are more susceptible to swelling including smectitie, illite, kaolinite and chlorite. Such changes can lead to wall instability due to internal stresses generated by the swelling (Morkel, 2006). Moist clay-bearing materials will also experience lower strength, elastic modulus, cutting forces and pick wear (Mammen, *et al.*, 2007).

This phenomenon has posed particular problems in the oil and gas drilling industry where various chemical agents have been developed to mitigate the problems. In the case of mining, it can be particularly detrimental to the performance of machinery that uses drag picks such as roadheaders, longwall shearers and continuous miners. It has been reported for example that clay swelling can decrease the net cutting rate of these types of machines by up to 50% due to "sticky"faces (Bilgin, *et al.*, 2004).

Potassium cations in the form of potassium chloride were found to reduce the severity of this effect in rocks containing the clay mineral smectite (Morkel and Saydam, 2008; Nasr-El-Din, Al-Mulhem and Lynn, 1998). Research undertaken into another clay mineral, nacrite, showed similar results following immersion for 24 hours in potassium chloride. Interestingly immersion for only 6 h seemed to have magnified the degradation effects compared to the longer immersion time (Hagan, *et al.*, 2011).

These findings prompted further investigation into whether a treatment regimen could be optimized in terms of chemical selection, immersion time and solution concentration. The key parameters measured

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in the study were changes in degradation of the sample, forces of cutting, specific energy, yield, abrasivity and coarseness index.

EXPERIMENTAL PROCEDURE

Slake durability index test

Degradation of a rock sample following immersion in a chemical solution were assessed using the slake durability index test. This particular test is a measure of the resistance to degradation by subjecting material to four cycles of wetting, agitation and drying.

The solutions used in the test program included:

- pure water;
- KCl at concentrations of 0.5, 1.5 and 3 Molar;
- $MgCl_2$ at 1.5 M; and
- $CuSO_4$ at 1.5 M.

The 1.5 M solution was selected as the standard concentration in order to allow comparison with previously reported results by Deramore Denver (2010). These solutions were used as the slaking fluid in the test. The 0.5 M and 3.0 M solutions were selected to examine whether if there exists some critical salt concentration and whether changes in concentration have any effect on the extent of degradation.

A claystone sample from Ulan Coal Mine was used in the test. The main clay-bearing mineral in the sample is kaolinite. This mineral has a similar composition and clay chemistry to nacrite (Ghazali, 2012). Test specimens were prepared by crushing a sample into fragment sizes each weighting within the range of 40 to 60 g with the rough edges and corners removed to create rounded lumps of rock as per the suggested method of the ISRM (1981). Ten lumps having a combined mass of between 480 and 500 g were then placed into a steel mesh drum and oven dried at 105 °C to remove all inherent moisture before being weighed. The drum containing the rock fragments was placed within a tank and filled with the test solution as shown in Figure 1.

Figure 1 - Slake durability index test apparatus

The drum was rotated within the solution at 20 rpm for 10 min afterwhich the drum and its contents were removed and oven dried for 16 h before again being weighed. This set of processes comprise one slaking cycle. The results were calculated according to Equation 1:

$$I_{d2} = \frac{C-D}{A-D} \times 100\% \quad (1)$$

where:

I_{d2}: Slake durability index value;

C: mass of the drum plus retained sample portion after slake cycle;

A: initial mass of the sample;

D: mass of steel mesh drum.

The cycle was repeated four times and the results graphed.

Diffusion test

To determine the rate of diffusion of a solution within rock, a test was devised where 30 mm diameter specimens of rock core were submerged in a tank containing a solution of water and disodium a-[4-(N-ethyl-3-sulfonato benzyl amino) phenyl]-a-[4-N-ethyl-3-sulfonato benzyl amino) cyclohexa-2,5-dienylidene] toulene-2-sulfonate, a commonly found blue-coloured food dye. The methodology was modelled after experiments conducted by Mammen, *et al.* (2007). The test is based on the assumption that a chemical solution will diffuse into a rock mass at approximately the same rate as the dye molecules.

The test involved cores immersed in the dye solution at time intervals of 1, 2, 4, 8, 16 and 24 h. After a specimen had been immersed for the nominated time, it was cut open and the depth of dye penetration measured.

Core cuttability index test

The core cutting tests utilised a tri-axial dynamometer rock cutting rig as shown in Figure 2.

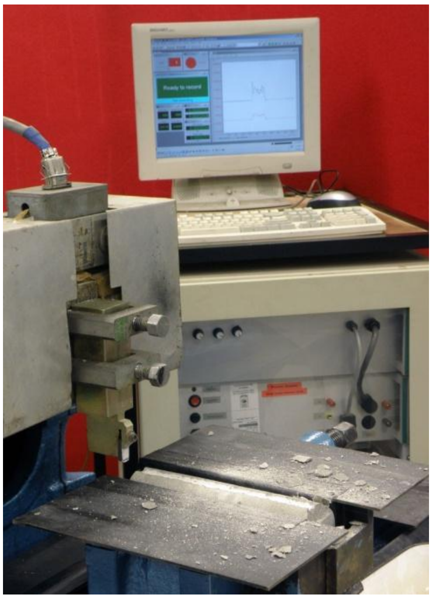

Figure 2 - Instrumentation used in the core cuttability test procedure at UNSW

The diffusion test revealed a treatment time of 24 h was required to obtain a penetration equivalent to the cutting depth of 5 mm.

In this test, diamond cored specimens of Hawkesbury Sandstone were used. The cores were first oven dried at 105 °C before being treated with a chemical solution.

Seven test scenarios were examined with solutions of different chemical composition and immersion times. The results were compared against dry untreated rock, the control specimen. The test solutions included pure water, KCl, $MgCl_2$, $CuSO_4$ where the test specimens were immersed for 24 h. A further three tests were conducted using a solution of KCl where the immersion times were 5 min, 1 h and 8 h. The concentration of each solution was held constant at 1.5 M.

In addition to measuring cutting forces and specific energy, the particle size distribution of the cutting debris was determined. This was based on the coarseness index procedure using sieve sizes of 4.75, 1.70, 0.50 and 0.125 mm.

RESULTS

Slake durability index test

The results for the slake durability index test are shown in Table 1.

Table 1 - Results of slake durability index test

slaking fluid	slake durability			
	I_{d-1} (%)	I_{d-2} (%)	I_{d-3} (%)	I_{d-4} (%)
water	100.0	100.0	98.7	98.7
KCl (0.5 M)	100.0	100.0	99.6	99.2
KCl (1.5 M)	100.0	100.0	100.0	98.8
KCl (3.0 M)	100.0	100.0	100.0	98.8
$MgCl_2$ (1.5 M)	99.6	99.2	98.3	97.9
$CuSO_4$ (1.5 M)	99.7	99.3	98.3	95.1

The magnitude of the mass change relative to the mass of the steel drum was small thus limiting quantitative analysis. However, the results indicated the degree of degradation was greatest using the $CuSO_4$ and $MgCl_2$ solutions while it was more limited with the KCl solution.

Diffusion test results

It was found that the penetration of solutions into the Hawkesbury Sandstone specimens could be modelled by a linear relationship for exposure times up to 24 h. This relationship is shown in Equation 2.

$$y = 0.117x + 1.45 \qquad (2)$$

where:

y: penetration (mm);

x: exposure time (h).

With respect to the claystone, due to its very low permeability only surface staining was observed for all treatment times.

Cuttability index test

The results of the cutting tests are summarised in Table 2. They indicate there was a significant reduction in the cutting parameters of the test specimens that had been immersed in a solution whether it was pure water or any of the chemical solutions as compared to the dry, untreated rock specimen.

When considering immersed for 24 h, the reduction in forces and specific energy were all greater with the three chemical solutions than pure water. The greatest reductions of 56.5% and 25.2% was attained with the magnesium chloride solution compared to the dry and the water-only treated specimens respectively.

Unexpectedly, the abrasivity of the specimens was found to have increased substantially with all chemical solutions in comparison to the dry sample having more than doubled after immersion in the copper sulphate solution.

With respect to the series of tests that examined immersion times in a potassium chloride solution, there was a significant reduction in forces and specific energy even after the shortest immersion time of 5 min. This is consistent with the results reported by Mammen *et al.* (2007).

Interestingly the greatest reduction in cutting parameters was obtained with the potassium chloride solution after immersion for 8 h. This is consistent with the results reported by Hagan *et al.* (2011). As noted earlier, immersion for 8 h was unlikely to have allowed sufficient time for the solution to diffuse into the rock to a distance equivalent to the full cutting depth. The reductions in cutting parameters were of a similar magnitude to that achieved with the magnesium chloride solution after 24 h immersion.
A possible mechanism to explain this is that despite the immersion times being of relative short duration, it nevertheless allowed for sufficient penetration of the solution causing rupture of the clay sheets thus

improving cuttability. By contrast, an immersion time of 24 h would allow for penetration to the full depth of cut thus strengthening the rock within the entire cutting zone.

All treatments reduced the coarseness index by a small amount indicating only a minor decrease in cutting efficiency. Overall, the results achieved with an immersion time of 24 h are consistent with the results observed in smectite with a less exaggerated result for KCl (Morkel, 2006).

Table 2 - Results of core cuttability index test

solution & immersion time	force		specific energy (MJ/m^3)	impact abrasivity (mg/m)
	cutting (kN)	normal (kN)		
dry untreated	1.19	0.94	17.7	1.8
water (24 h)	0.74	0.59	10.3	2.2
KCl (24 h)	0.72	0.61	8.9	2.7
$CuSO_4$ (24 h)	0.62	0.37	8.4	4.2
$MgCl_2$ (24 h)	0.57	0.39	7.7	3.1
KCl (5 min)	0.79	0.63	11.2	6.8
KCl (1 h)	0.76	0.62	11.4	5.3
KCl (8 h)	0.55	0.38	7.9	3.2
KCl (24 h)	0.72	0.61	8.9	2.7

CONCLUSIONS

The results from the Slake Durability Index tests using Ulan claystone indicate the cations have a strong effect on durability of rock with the strength of the effect following the order: $Cu^{2+} > Mg^{2+} > H2O > K^+$.

It was found that the penetration rate of chemical solutions could be modelled using a linear relationship for exposure times up to 24 h for the Hawkesbury Sandstone. Furthermore, it was found that Hawkesbury Sandstone underwent a minor decrease in density following all treatment regimens with the exception of $MgCl_2$ where a slight increase was measured.

The results showed that treatments in solutions of KCl, $MgCl_2$ and $CuSO_4$ for 24 h improved cuttability relative to pure water and even more so when compared against dry, untreated rock (the control specimen). Prolonged immersion in KCl tended to stabilise the material to a level where the results similar to that achieved with pure water. When considering the results of Deramore Denver (2010), the optimum immersion time seems to be between 6 h and 8 h.

A possible mechanism behind these results is that while the shorter immersion times only allows for limited diffusion into the rock, it can cause rupture of the clay sheets which thereby improves cuttability. By contrast, a treatment time of 24 h allows penetration equivalent to the full depth of cut, strengthening the rock within the cutting zone. The results achieved from the 5 min and 1 h immersion intervals with KCl were likely attributable to the low level of diffusion resulting in values nearer that of the control. None of the chemical solutions improved stability to an extent comparable to the control specimen. Higher impact abrasivity was seen with all treatments. Overall, the 24 h results conform to the reactions observed in rocks containing smectite with a less exaggerated result for KCl (Morkel, 2006).

These findings will assist in the development of treatment regimens both for improving stability in excavations and improving cuttability in specific mining operations that contain kaolinitic clays.

REFERENCES

Bilgin, N, Dincer, T, Copur, H and Erdogan, M, 2004. Some geological and geotechnical factors affecting the performance of a roadheader in an inclined tunnel, *Tunnelling and Underground Space Technology,* 19: 629-639.

Deramore Denver, L, 2010. Enhancing the cuttability of rock using chemical solutions, Honours thesis (unpublished), University of New South Wales, Sydney.

Ghazali, 2012. Clay Chemistry [online]. Available from: <http://www.scribd.com/doc/56573987/Clay-Chemistry> [Accessed: 22 April 2012].

Hagan P, Saydam S, Elias E, Deramore Denver L and Hebblewhite B, 2011. The effect of certain chemical solutions on some material properties of clay bearing rocks, in *Harmonising Rock Engineering and the Environment - Proceedings of 12th ISRM International Congress on Rock Mechanics*, Beijing, 18-21 October, (Taylor and Francis Inc., United States).

Hall, P L, 1987. Clays: their significance, properties, origins and uses, *A Handbook of Determinative Methods in Clay Mineralogy*, pp 1-26 (Chapman and Hall: New York).

ISRM, 1981. Rock characterization, testing and monitoring: ISRM suggested methods, pp 92-121 (Pergamon Press: Oxford).

Mammen, J M, Saydam, S and Hagan, P, 2007. The study of the effect of moisture content on rock cutting performance, in *Proceedings 2009 Coal Operators' Conference*, Wollongong, Australia, pp 340-347 (The AusIMM Illawarra Branch).

Morkel, J, 2006. Kimberlite Weathering: Mineralogy and Mechanism, PhD thesis (unpublished), University of Pretoria, Pretoria.

Morkel, J and Saydam, S, 2008. The influence of potassium on the weathering properties of kimberlite and the information provided by different testing methods, *International Journal of Rock Mechanics and Mining Sciences,* 45:1187-1194.

Nasr-El-Din, H A, Al-Mulhem, A A and Lynn, J D, 1998. Evaluation of clay stabilizers for a sandstone field in central Saudi Arabia, in *Proceedings International Symposium on Formation Damage Control*, Lafayette, United States of America, pp 613-629 (Society of Petroleum Engineers).