DEVELOPMENT OF AN ACID RESISTANT TREATMENT GROUT UTILISING MODIFIED BAUXITE REFINERY RESIDUES

de Boer S[1], Clark M[1*], Basheer PAM[2] and McConchie D[1]

[1]*School of Environmental Science and Management,*
Southern Cross University, Lismore, NSW, Australia
[2]*School of Planning, Architecture, and Civil Engineering,*
Queen's University Belfast, Northern Ireland

Abstract

Alumina production by the Bayer Process creates large volumes of caustic refinery residues (red mud) and currently there is a need to find sustainable uses for refinery residues. The Basecon^{TM} neutralisation process results in soluble alkalinity being converted into solid alkaline hydroxide, carbonate and hydroxy-carbonate minerals. The resulting neutralised red mud (Bauxsol^{TM}) has a high acid neutralisation capacity, as well as a high metal binding capacity. Contrary to this ARD waters are acidic, metal-rich water that are typically treated by addition of lime. However, this is a short-term solution, which does not treat the source of the problem, the excavated and exposed sulphidic rock. Consequently, a novel approach is to incorporate Bauxsol^{TM} into an otherwise acid susceptible ordinary Portland cement (OPC) grout and to inject this into the broken rock and bind it back as a coherent mass. By sealing a waste rock dump by means of injecting a grout with an acid-neutralising and metal-binding capacity, ARD production is treated at source by preventing, or severely reducing the rate of production.

This paper details preliminary work in the development of Bauxsol^{TM}-based treatment grouts for such an application. Presented are the results for the fluidity, based on a factorial analysis design, that has allowed the determination of 9 mixes that are potentially suitable for injection into waste rock material. These 9 mixes are then exposed to high concentration sulphate solutions to determine the sulphate expansion characteristics.

Keywords: ARD, Bauxsol^{TM}, grout, treatment

1. Introduction

Acid rock drainage (ARD) is the largest environmental problem facing the mining industry. ARD occurs wherever sulphidic bearing rock is exposed to atmospheric conditions (Evangelou, 1995), primarily due to the oxidation of pyrite (FeS_2) with a subsequent release of acid that mobilises many toxic trace metals into a leachate. The formation of ARD occurs from most copper, lead, zinc, nickel, molybdenum, antimony, arsenic, silver and many coal mining and beneficiation operations, and most gold recovery operations with the exception of placer deposits. As such, a potential environmental hazard exists wherever human activities involve exposing sulphide minerals to the atmosphere. Consequently, suitable strategies to prevent and control acid formation must be considered wherever sulphide exposure may occur. Such strategies include: treatment of the solid and liquid wastes with lime or other chemical reagents, isolation of the sulphidic material from atmospheric oxygen by placing the material in sealed and capped disposal dumps (Congdon *et al.*, 1995), treatment with antibiotics to prevent accelerated sulphide oxidation caused by bacteria such as Thiobacillus thioxidans or Thiobacillus ferroxidans (Kleinmann *et al.*, 1981), and the impoundment of contaminated waters. Most of the current ARD treatment strategies are either very expensive or require long-term management (Congdon *et al.*, 1995; Kleinmann *et al.*, 1981).

Basecon^{TM} is a relatively recent technology developed to treat the red mud residue of alumina refining via the Bayer process. Basecon^{TM} technology is similar to the sea-water neutralisation of bauxite refinery residues, and red mud neutralised by Basecon™ is Bauxsol™. On average, 1-1.5 tons of bauxite refinery residue that can be converted to Bauxsol™ by the Basecon™ technology is produced per ton of aluminium extracted. The complex mineralogy of Bauxsol^{TM} gives it a high acid neutralisation capacity (2.5 – 7.5 moles of acid per kg of Bauxsol^{TM}; depending on the caustic recovery efficiency of the plant) and a high metal trapping capacity (>1,000 meq of metal per kg of Bauxsol^{TM}) (McConchie *et al.*, 1998; McConchie *et al.*, 2000). The chemical properties exhibited by Bauxsol^{TM} make it excellent for the treatment of acid mine waters, as demonstrated during the treatment of 1.6 GL of waste water at the Mt. Carrington mine site, NSW, Australia where metals were removed by between 99.95 to 99.99% (McConchie *et al.*, 2000). These properties, combined with the fine-grained nature of Bauxsol (>80% w/w <10 um in size), indicate the potential to produce fine grouts, which may be injected or sprayed into ARD rocks for treatment.

Cement-based grouts are in common use within the construction and environmental management industries for slope stabilisation, groundwater containment, foundation and tunnel reinforcement, and earthen dam wall sealing and strengthening (Burge and Wombacher, 2000; Cornwell and Plunguian, 1982; Ranc *et al.*, 1992; Svermova *et al.*, 2003; Watanabe *et al.*, 1990)]. However, very little work has been done on grout application for the treatment or stabilisation of acid rock materials. Studies which have investigated the use of grouts for treatment of acid rock drainage have incorporated the addition of coal combustion by-products (CCBPs) (Bulusu *et al.*, 2007), pulverised fly ash (Jang and Kim, 2000; Jarvis and Brooks, 1996), and flue gas desulphurisation (FGD) material, with limited success. The materials investigated by these authors (Bulusu *et al.*, 2007; Jang and Kim, 2000; Jarvis and Brooks, 1996) have tended to be of very low strength (< 2 MPa compressive strengths). Moreover, OPC grouts require additives when in an acidic environment, because cement is susceptible to acid, sulphate, and chloride attack (Al-Kadhimi *et al.*, 1988; Marchand *et al.*, 2002).

The two most important factors affecting a grout in the treatment of a sulphidic waste rock dump are grout fluidity and sulphate resistance. Firstly, grout fluidity must be considered for the development of a suitable treatment grout, because a grout should be suitably fluid to be pumped and injected into cavities and pores in the acid generating waste dumps. Fluidity, therefore, needs to be high enough to access the vast majority of pores, allow the neutralisation of pre-existing acid, bind the existing mobile metals, and prevent oxygen diffusion, which is central to the formation of ARD. However, the consistency should be viscous enough so that suspended cement and other components do not settle and create untreated void when excess water evaporates, and are able to coat the sulphide bearing material.

Secondly, given the high concentrations of sulphates in ARD, the grout must be resistant to sulphate expansion. Sulphate may be continually replenish as sulphides oxidise, only where oxygen and water have free access, and although pre-existing sulphate may be incorporated into the grout as ettringite, further sulphate supplies may further weaken the grout. Grouts, mortars, and concretes made with OPC are susceptible to internal sulphate attack, also known as delayed ettringite formation (DEF). Sulphates react with the hydration products of cement resulting in the deterioration of the strength providing calcium silicate hydrate (C-S-H) gel, and the formation of gypsum and ettringite (Santhanam *et al.*, 2002). These two compounds lead to the expansion, and ultimate failure, of cement-based structures.

The development of a Bauxsol™-based cementitou grout may provide a new strategy for the stabilisation and treatment of ARD generation in sulphidic waste-rock dumps. A Bauxsol™ –based grout may neutralise acidic water whilst simultaneously binding trace metals into a non-leachable form, thereby giving the grout adequate protection from chemical attack and improving strength and longevity. This paper presents the findings of studies into the fluidity and sulphate expansion of Bauxsol™-based grouts.

2. Materials and Testing Procedure

The grouts investigated were prepared with Bauxsol™ from Sardinia, Italy. Typical Bauxsol™ has a grading of 80% w/w passing 10 µm, whereas the ordinary Portland cement had a grading of 98% w/w finer than 45 µm (McConchie *et al.*, 2005). Chemical analysis of the OPC and the Bauxsol™ was performed using standard XRF analyses.

The experimental design employed a three-level factorial design. Based on preliminary results, values for Bauxsol™ replacement of OPC, water-to-binder ratios (W/B), and superplasticiser (SP) dosages (as a percentage weight of dry matter) were set at 0.30, 0.50, and 0.65 replacement; 0.35, 0.40, and 0.5 W/B; and 0.00, 0.50, and 1.00% SP. Each different dose rate was given a coded value of -1, 0, or 1, corresponding with an actual value, as can be observed in Table 1. Upon completion of mixing, the fresh properties of the grout mix were tested in order of: Lombardi plate cohesion, mini-slump, and Marsh cone. Following this, six 100 mm^3 concrete moulds were cast. Three each were tested at 7 and 28 days for uniaxial compressive strength.

Table 1. Mix proportioning of grout for fluidity tests

Mix	Coded Values			Actual Values		
	Bauxsol™	W/B	SP	Bauxsol™	W/B	SP (%)
1	-1	-1	-1	0.30	0.35	0.00
2	-1	-1	0	0.30	0.35	0.50
3	-1	-1	1	0.30	0.35	1.00
4	-1	0	-1	0.30	0.40	0.00
5	-1	0	0	0.30	0.40	0.50
6	-1	0	1	0.30	0.40	1.00
7	-1	1	-1	0.30	0.50	0.00
8	-1	1	0	0.30	0.50	0.50
9	-1	1	1	0.30	0.50	1.00
10	0	-1	-1	0.50	0.35	0.00
11	0	-1	0	0.50	0.35	0.50
12	0	-1	1	0.50	0.35	1.00
13	0	0	-1	0.50	0.40	0.00
14	0	0	0	0.50	0.40	0.50
15	0	0	1	0.50	0.40	1.00
16	0	1	-1	0.50	0.50	0.00
17	0	1	0	0.50	0.50	0.50
18	0	1	1	0.50	0.50	1.00
19	1	-1	-1	0.65	0.35	0.00
20	1	-1	0	0.65	0.35	0.50
21	1	-1	1	0.65	0.35	1.00
22	1	0	-1	0.65	0.40	0.00
23	1	0	0	0.65	0.40	0.50
24	1	0	1	0.65	0.40	1.00
25	1	1	-1	0.65	0.50	0.00
26	1	1	0	0.65	0.50	0.50
27	1	1	1	0.65	0.50	1.00

A ‘3rd generation’ superplasticiser (polycarboxylic polymer in solution) acts through a steric repulsion, unlike other superplasticisers, such as the melamine and naphthaline sulphonates, which operate through electrostatic repulsion mechanisms. This steric repulsion mechanism allows for greater particulate dispersion to provide a higher workability and slump retention, whilst avoiding retardation effects (Spiratos *et al.*, 2003). As these characteristics are important for ARD treatment grouts, polycarboxylic polymer was added to the grout mixtures. Superplasticiser was added to water and mixed in a shear mixer. The remaining dry reagents were added and mixed for 5 minutes, removed and hand-scraped to remove any dry matter stuck to the sides, before undergoing a further 2 minutes of mixing.

The Lombardi plate cohesion meter measures the cohesiveness of the grout. A clean dry steel plate (100 mm x 100 mm x 1 mm in dimension) was tared on a set of electronic scales before submersion in the grout mix. The plate was then withdrawn and held until dripping of grout had ceased. The plate was weighed again giving the weight of grout stuck to the plate (Svermova *et al.*, 2003).

The mini-slump test is essentially a smaller version of the slump cone. However, instead of recording slump, the mini-slump records the spread of the flowable grout to give an indication of workability. It has a bottom diameter of 38 mm, a top diameter of 19 mm, and a height of 57 mm. The cone is placed on a level plexiglass square and filled level with grout to the top rim. The cone is lifted and the spread diameter measured once the grout has stopped flowing or after one minute has passed (Koehler and Fowler, 2003).

The Marsh cone test measures the time taken for a particular volume of grout through a flow-cone. Marsh cones are not currently standardised, but in this case, a plastic funnel was filled with 1000 ml of grout, and the time recorded for 700ml to pass through the 5 mm opening. The top of the cone contained a sieve to prevent large particles blocking the funnel. The funnel was wetted with water before each test (C939-02, 2002).

The compressive strength cubes were de-moulded one day after casting and were then cured in water for a further 3 days. The moulds were then removed and patted dry for excess water before being wrapped in air-tight polythene. These were stored in a constant temperature and humidity room at 20 ± 1°C and 40 ± 1% relative humidity, until the 7 or 28 day test was carried out. The strength was determined on a Samuel Denison compressive strength machine (C109/C109M-05, 2005).

The fluidity data were analysed with the statistical software program Design-Expert® (Stat-Ease Inc., 2007). However, to obtain a more normal distribution, the plate cohesion data are transformed using natural logarithms. The statistical analysis indicated that 9 mixes had adequate fluidity and were further tested for sulphate expansion, a control grout containing no

Bauxsol™ was also included. The mix proportions for the control grout were ones that gave similar fluidity properties to the other 9 mixes. The mix proportions of the grouts tested for sulphate expansion are provided in Table 2.

Table 2. Mix proportioning of grout for sulphate expansion tests

Mix	Coded Values			Actual Values		
		W/B	SP		W/B	SP
c	-2	-1	0	0.00	0.35	0.50
1	-1	-1	1	0.30	0.35	1.00
2	-1	0	0	0.30	0.40	0.50
3	-1	0	1	0.30	0.40	1.00
4	-1	1	-1	0.30	0.50	0.00
5	-1	1	0	0.30	0.50	0.50
6	0	1	0	0.50	0.50	0.50
7	0	1	1	0.50	0.50	1.00
8	1	1	0	0.65	0.50	0.50
9	1	1	1	0.65	0.50	1.00

The sulphate expansion test procedure followed a standard test method for length change of hydraulic-cement mortars exposed to a sulphate solution (C1012-95A, 1995). Six bars for each mix were cast in a mortar bar mould 285 x 25 x 25 mm in dimension and left to set for 24 hours before de-moulding. The bars were cast with a ball bearing embedded in each end, for measuring purposes and cured in water for 28 days. At the conclusion of curing, each bar was measured in a comparator relative to a standard steel bar, to an accuracy of ± 1 μm, and then placed in a 10% sodium sulphate (Na_2SO_4) solution. Grout bars were measured relative to the same standard steel bar at 1, 2, 4, and 8 weeks of submersion; the Na_2SO_4 solution was replaced at 2, 4, and 8 weeks (C1012-95A, 1995).

Table 3. Chemical composition of OPC and Bauxsol™

Composition	Cement	Bauxsol™
SiO_2	20.8	16.59
Al_2O_3	5.0	23.26
Fe_2O_3	3.2	30.12
CaO	63.7	3.17
Na_2O	0.39	7.40
MgO	2.6	0.70
K_2O	-	0.13
MnO	-	0.04
TiO_2	-	6.66
P_2O_5	-	0.17
S	-	0.09
C	-	0.81

The chemical composition of Bauxsol™ and OPC as determined by XRF are presented in Table 2. These data indicate that Bauxsol™ contains substantial concentrations of aluminium oxides and the presence of aluminium oxides is highly likely to have detrimental effect on the sulphate expansion test work. This is because sodium sulphate attack is based on the generation of secondary ettringite (Eqs. 1, 2 & 3). Since ettringite ($C_6A\overline{S}_3H_{32}$) is a low density mineral (1.73g/cm^3) compared to the other products of hydration (2.50g/cm^3), its formation will lead to expansion and cracking of cement mortar bars during the Na_2SO_4 attack. The ettringite formation (Eqs. 1, 2 & 3) all require aluminate phases (i.e., monosulphate, hydrated aluminate and/or anhydrous C_3A) and the increased expansion due to Na_2SO_4 attack in the samples with higher Bauxsol™ contents is most likely because of the high alumina content in Bauxsol™.

$$C_4A\overline{S}H_{12} + 2C\overline{S}H_2 + 16H \rightarrow C_6A\overline{S}_3H_{32} \quad (1)$$

$$C_4AH_{13} + 3C\overline{S}H_2 + 14H \rightarrow C_6A\overline{S}_3H_{32} + CH \quad (2)$$

$$C_3A + 3C\overline{S}H_2 + 26H \rightarrow C_6A\overline{S}_3H_{32} \quad (3)$$

Where C = Calcium, A = Al_2O_3, S = SO_4, and H = H_2O.

3. Results and Discussion

3.1 Fluidity

The results of testwork are presented in Table 4 and show the Mini-slump, Marsh time, Plate cohesion, and 7 and 28 day compressive strength tests. In 15 of the 27 mixes, the viscosity was too great for the grout to flow through a Marsh cone. Of the mix ratios 7 of the 9 mixes at both 65% Bauxsol™ and 7 of the 9 mixes with 0.0% SP were too viscous and could not pass through the Marsh cone (Table 4). In addition, 8 of the 9 mixes that had a 0.35 W/B were too viscous to pass through the Marsh cone. This suggests that grouts with the highest tested loadings of Bauxsol™ , or the lowest W/B, or the lowest loading of SP, are impractical as a grout.

The results obtained from the fluidity experiment allowed for the removal of two-thirds of the 27 potential grout mixes from consideration, because they were too viscous. Grouts with a marsh time of over 400s or those that did not flow at all were deemed too viscous for an injectable grout, with the exception of mixes 9 and 16. Mix 9 was too fluid resulting in segregation of the binder, which in turn resulted in bleeding of the mix. Mix 16, whilst having a Marsh time of 189 s indicating a reasonably low viscosity, also had a mini-slump of only 89 mm indicates a high yield stress (the force needed to get matter flowing). The 9 remaining mixes also correlated strongly to the isoresponse plots displayed in Figure 1.

Table 4. Fluidity and strength results

Mix	Mini-slump	Marsh Time	Plate cohesion	Compressive strength (MPa)	
	(mm)	(s)	(g)	7 day	28 day
1	41	nf	70.2	44.3	52.5
2	95	nf	23.3	45.3	43.5
3	143	205	7.6	42.1	44.5
4	58	nf	17.6	39.4	46.4
5	105	350	14.2	40.8	42.8
6	151	103	3.5	38.7	40.8
7	98	145	11.1	23.8	32.4
8	138	53	5.1	27.1	31.2
9	182	41	3.2	30.0	33.0
10	40	nf	110.7	33.2	33.5
11	41	nf	74.6	34.6	37.4
12	65	nf	41.5	30.8	34.0
13	44	nf	30.6	29.3	29.3
14	86	nf	21.8	29.8	32.1
15	95	413	19.9	29.9	35.5
16	89	189	15.4	19.8	22.5
17	126	61	7.0	20.0	21.0
18	135	54	6.0	20.9	25.8
19	40	nf	151.8	19.6	23.2
20	40	nf	135.2	24.1	27.9
21	57	nf	21.2	21.8	26.1
22	41	nf	223.0	19.0	22.0
23	69	nf	24.3	21.0	23.8
24	73	nf	13.8	22.2	23.3
25	71	nf	26.7	12.1	14.3
26	106	98	11.7	13.4	15.6
27	121	87	11.8	13.0	15.0

Despite the poor flow characteristics of many mixes, all the mixes provided good strength with all in excess of 12 MPa, which is almost 6 times greater than other grouts used in the treatment of ARD systems (Jang and Kim, 2000; Jarvis and Brooks, 1996). However, strength developed is considerably lower than for grouts developed for dam stabilisation work (Ranc *et al.*, 1992).

Statistical analysis of the factorial design (Table 5) provides a comparison between the various measured parameters (e.g. plate cohesion) as well as the interactions of quadratic effects. These comparative data indicate the strength of the effect and the sign of the interaction. Missing data points in the table are because the effect of a response is not significant (i.e., the probability is greater than the F value for each response). For example, a probability >F greater than 0.10 implies that the response was not significant, and was consequently removed to give the model more precision. A positive value in the table signifies that an increase in the parameter results in an increase in the response, and vice-versa.

Table 5. Statistical modelling parameters

	Mini-slump (mm)	Marsh time (s)	Plate cohesion (g)	f'_c 7 days (MPa)	f'_c 28 days (MPa)
R^2	0.95	0.99	0.87	0.99	0.96
Transform	none	none	natural log	none	none
Intercept	73.30	647	3.06	30.84	32.88
BX	-21.83	297	0.61	-9.19	-9.78
W/B	28.00	-576	-0.85	-6.43	-6.22
SP	27.78	-283	-0.72	0.49	0.11
BX W/B	1.83	-271	-0.045	2.00	0.95
BX SP	-15.00	-	-	-	1.49
W/B SP	-	222	-	0.88	-

By presenting the estimate values from the statistical analysis, the model responses can be presented as an equation in the form:

$$y_1 = a_0 + a_1\,\text{BX} + a_2\,\text{W/B} + a_3\,\text{SP} + a_4\,\text{BX W/B} + a_5\,\text{BX SP} + a_6\,\text{W/B SP} \quad (4)$$

where y_1 is the response, a_0 the intercept value, and a_n the respective coefficient estimate of the various factors.

And so we get modelled equations for mini-slump, marsh time, plate cohesion, and 28 day compressive strength as follows in eqs. 5) - 8):

$$\text{Mini-slump (mm)} = 73.30 + 28.00\,\text{W/B} + 27.78\,\text{SP} - 21.83\,\text{BX} - 15.00\,\text{BX SP} + 1.83\,\text{BX W/B} \quad (5)$$

$$\text{Marsh time (s)} = 647 - 576\,\text{W/B} + 297\,\text{BX} - 283\,\text{SP} - 271\,\text{BX W/B} + 222\,\text{W/B SP} \quad (6)$$

$$\ln(\text{Plate cohesion})\ (\text{g}) = 3.06 - 0.85\,\text{W/B} - 0.72\,\text{SP} + 0.61\,\text{BX} - 0.045\,\text{BX W/B} \quad (7)$$

$$f'_c\ 28\ \text{days (MPa)} = 32.88 - 9.78\,\text{BX} - 6.22\,\text{W/B} + 1.49\,\text{BX SP} + 0.95\,\text{BX W/B} + 0.11\,\text{SP} \quad (8)$$

The high correlation coefficients of 0.95 for mini slump, 0.99 for 7 day strength and marsh time, 0.87 for plate cohesion, and 0.96 for 28 day strength, all imply the models fit very well and are robust. Further more the statistical analysis indicates that mini-slump values (Table 5) are influenced, in order of significance, by the additions of W/B, SP, and Bauxsol™. Both W/B and SP addition have a positive effect on the mini-slump, whereas Bauxsol™ addition has a negative effect. However, plate cohesion values are influenced, in order of significance, by W/B, Bauxsol™, and SP additions. On the other hand, the correlations are reversed with W/B and SP having negative effects, and Bauxsol™ dosages resulting in a positive effect.

Compressive strength should not be affected at all by SP addition, but data indicate a small positive influence as SP increases (Table 4). This increased strength is most likely because of less air entrainment caused by a decrease in grout viscosity as SP loading increase. However, Bauxsol™ content and W/B both have strongly negative effects on compressive strength at both 7 and 28 days. Bauxsol™ content has a significantly stronger effect on 7 and 28 day strength (-9.19 and -9.78 respectively) than increases in W/B (-6.43 and -6.22).

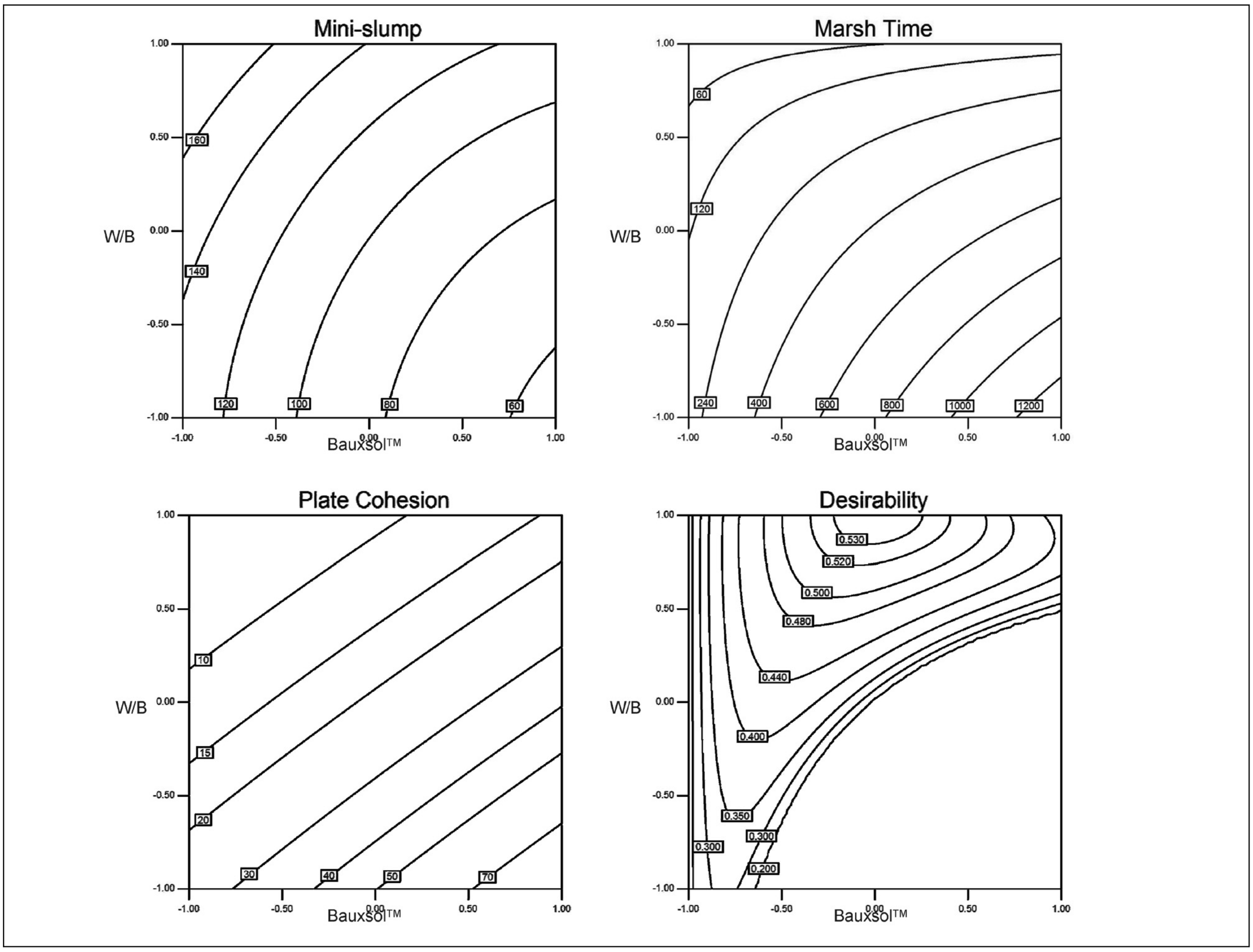

Figure 1. Isoresponse curves for mini-slump, marsh time, and plate cohesion, as well as optimization curve at SP = 1

The statistical models proposed in Table 5 also allow for the calculation of isoresponse curves (Figure 1), where all curves presented correspond to a coded superplasticizer value of 1 (ie. 1%). Thus, for any given W/B ratio and Bauxsol™ replacement level within the range tested, and at 1% addition of SP, the predicted response from the model can be determined easily by graphical observation. Furthermore, by setting goals for each response (on a scale of 1 to 5), the model can then optimise grout composition that best fits the desired out comes. In the case of the desirability (Figure 1), the maximisation of Bauxsol™ replacement was given a weighting of 5, whereas the maximisation of mini-slump, and marsh time, to ensure suitable fluidity, were weighted at 3. The maximisation of strength was for these grouts given that the very worst (Table 4) is nearly an order of magnitude stronger than previously reported ARD treatment grouts (Jang and Kim, 2000; Jarvis and Brooks, 1996). The resulting optimisation curve gives a maximum desirability value of 0.537 (desirability ranges from 0 poor, to 1 perfect). For Bauxsol™ based grouts at 1% superplasticiser, that is an optimisation that is only about 50% successful and that any mix will be compromised for some parameter. For example, it has already been shown in Table 4 that Bauxsol™ reduces mini-slump and strength, and increases marsh time, and by weighting for Bauxsol™ content to maximise metal reactivity and ARD neutralising capacity that flow will automatically suffer. However, the maximum desirability point on the optimisation curve sits almost directly over a design point (Mix 18). The fact that Mix 18 was one of the best grout mixes for fluidity (Table 4), supports the accuracy of the optimization model.

3.2 Sulphate Expansion

The results from the sulphate expansion test are shown in Table 6, and graphically in Figure 2. After 8 weeks with the grout bars submerged in a 10% Na_2SO_4 solution, 4 mixes (mixes 6-9) had failed completely, and three (mixes 2, 4, and 5) were visibly close to failure. On average, only three mixes (one of which was the control) had expanded less than 0.10% of the starting length, after 8 weeks. Missing values in Table 6 imply that the grout bars had failed. Moreover, there were two different failure mechanisms. Mixes 6 and 7 failed due to expansion, whereas mixes 8 and 9 (the only two containing 65% replacement of OPC by Bauxsol™) failed from dissagregation.

Table 6. Average length change (%) due to sulphate expansion

Mix	Week				
	0	1	2	4	8
C	0	0.05	0.05	0.06	0.07
1	0	0.02	0.02	0.03	0.05
2	0	0.02	0.02	0.04	0.13
3	0	0.01	0.01	0.02	0.07
4	0	0.04	0.05	0.25	0.40
5	0	0.06	0.05	0.09	0.16
6	0	0.06	0.05	0.08	-
7	0	0.06	0.13	-	-
8	0	0.11	-	-	-
9	0	0.06	-	-	-

Figure 2 shows an initial increase followed by a decrease between weeks 1 and 2. This may be because the grout bars were measured at weeks 1 and 2, whereas the sulphate solution was first replaced at week two. The proportion of Bauxsol™ in the system is likely to have buffered the effect of the Na_2SO_4 after only 1 week, resulting in a slight contraction of the grout bars; sulphate adsorption by Bauxsol™ has previously been made (Lin *et al.*, 2000). The data (Table 6) indicates that increases in Bauxsol™ increase susceptibility to sulphate attack, as predicted by equations 1-3, because of increase aluminium oxide contents. In addition, the increased addition of superplasticiser from 0.5 to 1.0% appears to halve the sulphate expansion experienced by mixtures with the same Bauxsol™ and W/B ratio (see mixes 2 & 3 and 4 & 5; Table 6).

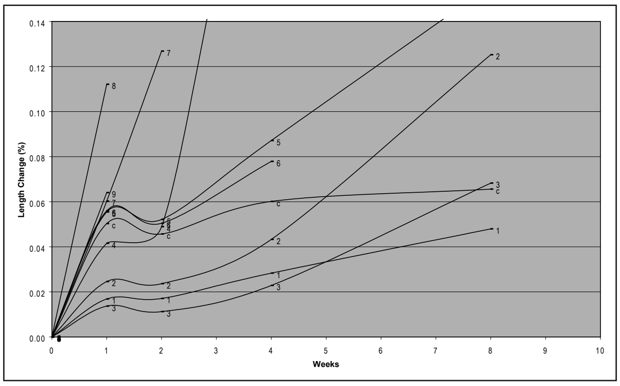

Figure 2. Graph of length change due to expansion in sulphate solution

Although most samples fail the sulphate exposure tests and give an expansion greater than 0.10% this does not mean that the grout is unusable, rather it means that the system is susceptible to degeneration and that service life will be compromised. In addition, the test assumes a continuous replenishment of sulphate in the exposed system. However, if the grouts are to be used to shut down sulphide oxidation in waste rock dumps and prevent ARD formation then the results of these engineering tests may be misleading. Although there may well be high sulphate in the pore fluids, during injection these sulphates will react with free alkaline materials and allow ettringite formation to occur before setting occurs, hence there will be few sulphates remaining in the system to initiate the delayed ettringite formation that causes the sulphate expansion. Hence, the data presented here do not, in the vast majority of mixes, comply with the ASTM standard C1012-95a. However, the context of application of the grouts developed in this work must also be considered, being the reduction in formation rate of ARD from waste rock dumps.

4. Conclusions

The test results of Bauxsol™ based grouts for the treatment of ARD waste rock stock piles indicate that suitably fluid grouts can be formulated that will penetrate voids. The strength of these grouts is much greater than those previously published, and suggest that not only can geochemical stabilisation potentially occur, but that physical stabilisation may also be achieved. For the fluidity of such Bauxsol grouts a factorial designed experimental plan provides statistically valid data that indicate Bauxsol™ content has a strong influence on fluidity and strength. The study shows that Mini slump is affected most by water/binder and superplasticiser rates, as was plate cohesion. Water/binder also had the greatest effect on Marsh time, with Bauxsol™ content and superplasticiser being the next most influential. Bauxsol™ has the greatest adverse effect on uniaxial compressive strength, with superplasticiser having little effect, as expected. Statistical optimization for fluidity, whilst maximising Bauxsol™ content, closely matched those grout mixes selected for further testing.

Sulphate expansion testing showed that two Bauxsol™-based grout mixes are more susceptible to sulphate attack than the control, but in some cases sulphate susceptibility is reduced. However, the data collected at this stage does not necessarily preclude high Bauxsol™ mixes, but may well limit their application to special application. Despite this, the data collected suggest that use of Bauxsol™ in injection grouts to stabilise ARD waste rock dumps to prevent ARD formation provides sustainable reuse option for red mud and provides an innovative solution to the biggest environmental problem in the mining industry.

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