INFLUENCE OF MINE WATER PH ON THE LEACH CHARACTERISTICS AND STRUCTURAL INTEGRITY OF TWO BACKFILL PRODUCTS

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ABSTRACT

As a component of its closure operations and to prevent future sinkhole formation, a colliery in Mpumalanga (South Africa) intends to backfill historical bord-and-pillar mining cavities underlying a river. Two backfill products, namely pulverised fly ash (PFA) and coal slurry product are under consideration. Both products were previously shown to have Department of Water Affairs waste characterisation hazard ratings (DWAF, 2005) of HR3 and HR4 respectively and classify as permissible backfill materials provided the maximum total load of contaminants is not exceeded. To understand the risks associated with underground backfilling, a series of investigations were carried out on these two materials to determine their structural integrity and leaching characteristics when exposed to geochemical and groundwater conditions ranging from highly acidic to alkaline.

The total analysis of the two backfill products indicated that the elemental composition of the PFA product is dominated by Si>Al> Ca>Fe> Ti> Mg> K> Na> P > SO_4 with minor amounts of other metals such as Pb, Zn, Ni, Cu, Cr, Ba and Sr. The composition of the coal slurry product was dominated by Si> Ca>SO_4> Fe >Mg with minor, but still significant, amounts of F, Ti, K, P, Mn, Sr, Ba, Na and Cr. For each of the two samples, independently, a 30g mass of crushed backfill material was agitated with 60ml of distilled water. The suspension was then titrated against 1M HCl to various pre-determined pH values, noting the volume of acid titrated in each instance. The pH end points for the PFA sample were 2.5, 3.5, 5.0, 5.5, 7.0 and 9.5 and end points for the coal slurry sample were 2.0, 3.5, 5.0, 7.0 and 9.5. The leachates were analyzed for major, minor and trace elements and major anions.

Leaching characteristics of both backfill products were shown to be similar, with concentrations of most contaminants in the leachates gradually increasing as leachate pH decreased, particularly at very low pH. The assessment further estimated the approximate timeframe required for acidic drainage conditions to develop in the backfilled workings. The findings provide an indication of the risk of net acid generation and leaching of metals/salts into the groundwater regime when the backfill materials are exposed to a range of drainage conditions from slightly alkaline to highly acidic. These risks, in turn, guide decisions regarding the suitability of the two candidate backfill products for use.

Keywords: Pulverised Fly Ash, Coal Slurry, Leaching Characteristics, Structural Integrity Backfilling.

1. INTRODUCTION

Mines are backfilled to avoid subsidence, provide support to pillars and walls to reduce the void volume in underground coal mines (Barret et al (1978) and Donovan (1999)). A colliery in Mpumalanga proposed to backfill historical bord-and-pillar mining cavities beneath a river to prevent future sinkhole formation and to comply with mine closure standards. Two candidate backfill products, namely pulverised fly ash backfill (PFA) and low ash coal (LAC) slurry backfill were considered. Moreover, two backfill options were under consideration: 1. To backfill the entire void volume with the pulverised fly ash (PFA) product; or 2. To backfill only the void directly beneath the river with the PFA backfill product and thereafter to pump the remaining volume with the slurry backfill product. A risk was identified that the backfill products, on placement underground, may undergo structural failure and/or unacceptable leaching of metals/salts if exposed to alkaline to highly acidic underground mine water.

The properties of fly ash and its derived products as backfill materials were studied by few authors (Palarski (1993) and Vadapalli et al. (2008)). However, not many studies were carried out on the coal slurry as a backfill material. The current study aims to investigate the leaching characteristics and structural integrity of PFA and LAC when they are placed underground and exposed to pH 2 to pH 10 water.

2. METHODOLOGY

Geochemical Assessment

Each backfill product was analyzed for mineralogy (by XRD) and total elemental composition (by acid digestion and ICP-MS/OES).

Subsamples of the crushed backfill products were then titrated against 1*M* HCl to determine the aqueous acidity required to neutralise the backfill alkalinity at each of pH 9.5; 7.0; 5.0; 3.5 and 2.5 (or pH 2.0 in the case of the coal slurry). The resultant supernatant solutions were then analyzed for major ions and metals.

Geotechnical Assessment

Shelby tubes were used to collect samples of both backfill products. Samples were also obtained of both backfill products after they had been contacted (for 48 hours on a rotary shaker) with sufficient 1*M* HCl to reduce the pH of the supernatant water to pH 9.5; 7.0; 5.0; 3.5 and 2.5 (or pH 2.0 in the case of the coal slurry). All collected samples were then analyzed for foundation and indicator / oedometer testing. The oedometer test is widely used in practice to provide the parameters that are required to estimate the settlement, and rate of settlement, of foundations on soils or substrates.

3. RESULTS AND DISCUSSION

Backfill Mineralogy and Chemical Composition

The elemental composition of the PFA backfill product is dominated by Si, Al, Ca, Fe and Ti. These elements are reflected in the mineralogy which is dominated by quartz (> 50 %), with lesser amounts of mullite, calcite, rutile and hematite. Table 1 provides a summary of the XRD analysis of the two backfill materials.

Table 1. XRD analysis of the two backfill materials

Mineral Phase	Formula	PFA backfill	Coal slurry backfill
Quartz	SiO_2	>50 %	>50 %
Mullite	$Al_6Si_2O_{13}$	20-50 %	Not detected
Calcite	$CaCO_3$	3-10 %	10-20%
Rutile	TiO_2	<3 %	Not detected
Hematite	Fe_2O_3	<3 %	Not detected
Kaolinite	$Al_2(Si_2O_5(OH)_4)$	Not detected	20-50 %
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$	Not detected	10-20 %
Bassanite	$CaSO_4.0.5H_2O$	Not detected	<3 %
Dolomite	$CaMg(CO_3)_2$	Not detected	<3 %

The total elemental composition of the coal slurry backfill product is dominated by Si, Ca, SO_4 and Fe (Table 2) whilst the mineralogy is dominated by quartz (> 50 %), calcite, kaolinite and ettringite. The concentrations of potentially toxic elements were generally between 70 to 90 % greater in the PFA backfill than in the coal slurry backfill (e.g. Mn, Cu, V, Pb and Zn) but less so for Fe and Cr (which were, respectively, 52 % and 30 % greater in PFA backfill than in coal slurry backfill).

Table 2**.** Total composition of the two candidate backfill products in order of abundance

Parameter	Units	PFA backfill	Coal slurry backfill
pH	-	10.4	11.1
Si	mg/kg	220 000	50 000
Al	mg/kg	120 000	28 000
Ca	mg/kg	52 000	33 000
Fe	mg/kg	21 000	10 000
Ti	mg/kg	11 000	800
Mg	mg/kg	9 400	8 500
K	mg/kg	6 300	680
Na	mg/kg	3 600	130
P	mg/kg	2 500	360
SO_4	mg/kg	2 000	11 800
Ba	mg/kg	1 400	160
Mn	mg/kg	1 100	290
Sr	mg/kg	730	160
F	mg/kg	500	1 100
Zr	mg/kg	470	46
Cl	mg/kg	250	250
Li	mg/kg	210	19
Cu	mg/kg	190	13
Cr	mg/kg	140	100
V	mg/kg	97	15
Pb	mg/kg	72	15

Zn	mg/kg	69	14
Ni	mg/kg	57	5
As	mg/kg	35	14
Sb	mg/kg	13	13
Co	mg/kg	11	5
Bi	mg/kg	10	10
Sn	mg/kg	10	10
Be	mg/kg	5	0.5
Cd	mg/kg	5	5
Mo	mg/kg	5	5
Se	mg/kg	3	3
NO_3	mg/kg	2	0.3
Hg	mg/kg	2	2
Ag	mg/kg	0.5	0.5

Influence of Drainage PH on Backfill Metal/Salt Leaching Potential

The titration curves for both backfill products showed good reproducibility (Figure 1 and Figure 2).

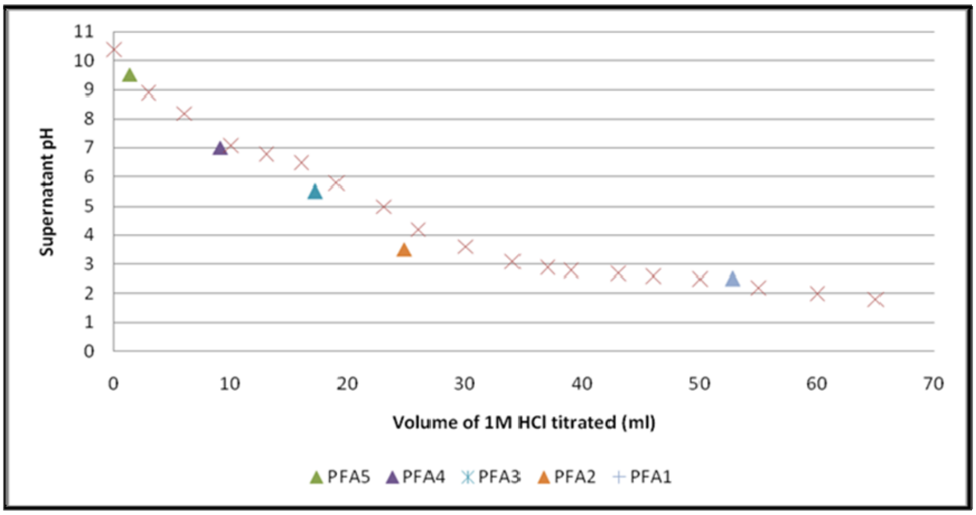

Figure 1. Titration of crushed PFA backfill product against 1*M* HCl. The positions of five supernatant samples collected for laboratory leach testing are also shown.

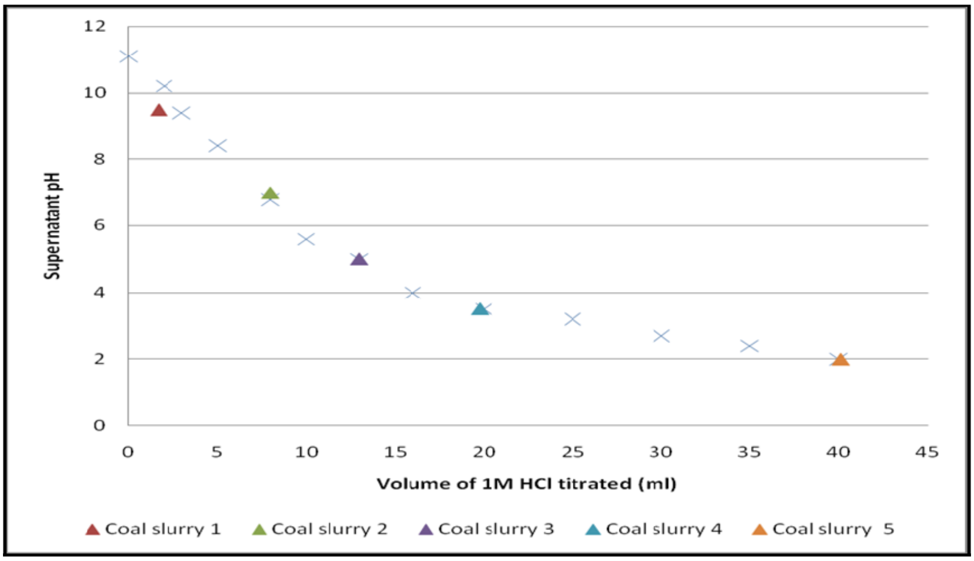

Figure 2. Titration of crushed coal slurry backfill product against 1M HCl. The positions of five supernatant samples collected for laboratory leach testing of the backfill product are also shown.

Table 3 and Table 4 provide the ICP analysis of the supernatants recovered at various pH levels for selected elements in the PFA and coal slurry products respectively. Both backfill products showed progressive increase in the leaching of most elements as pH decreased, particularly at pH 3.5 and below. At pH 2.5 there was moderate leachability (5 to 10 % weight percentage of the original solid) of Zn from both backfill products and of V from the PFA backfill. At this same pH there was high leachability (> 30 % by weight) of Mn from both backfill products and of Cu from the coal slurry backfill. Chromium and Pb remained relatively immobile (< 5 % by weight) from either backfill product at low pH, as was Cu from the PFA backfill and V from the coal slurry backfill. Considering the large volumes of mine water throughflow required to release these metals, the contribution of backfill leaching to regional groundwater concentrations of these trace metals is likely to be relatively small and of low risk to human health.

Table 3. Concentrations of selected elements at various pH levels in PFA supernatant.
All the concentrations are indicated in mg/kg.

Element	**Original solid**	**Element leachability at various supernatant pHs**				
		pH 9.5	**pH 7**	**pH 5.5**	**pH 3.5**	**pH 2.5**
Al	120,000	25	12	10	53	3,670
B	N/D	1.2	5.7	10.7	17.8	29.4
Cr	140	0.2	0.4	0.5	0.1	5.3
Cu	190	0.0	0.0	0.0	0.1	0.8
Fe	21 000	0.0	1.3	0.0	3.5	317
Mn	1 100	3	5	27	181	467
Ni	57	0.02	0.02	0.24	1.1	2.97
Pb	72	0.03	0.03	0.04	0.04	0.05
Si	220 000	53	136	200	771	12 346
V	97	0.0	0.0	0.0	0.0	8.7
Zn	69	0.0	0.0	0.0	1.6	5.7
SO4	2 000	142	386	660	860	1 080

Table 4. Concentrations of selected elements at various pH levels in coal slurry supernatant.
All the concentrations are indicated in mg/kg.

Element	**Original solid**	**Element leachability at various supernatant pHs**				
		pH 9.5	**pH 7**	**pH 5.5**	**pH 3.5**	**pH 2.5**
Al	28 000	1	1	0	90	2 569
B	N/D	0.1	1.3	2.4	5.6	10.7
Cr	100	0.1	0.1	0.1	0.1	2.4
Cu	13	0.0	0.0	0.0	0.2	5.0
Fe	10 000	0.0	0.0	0.0	3.7	434
Mn	290	0	1	29	114	400
Ni	5	0.02	0.02	0.02	0.7	1.8
Pb	15	0.03	0.03	0.04	0.04	0.05
Si	50 000	3	9	49	346	5 339
V	15	0.0	0.0	0.0	0.0	0.0
Zn	14	0.0	0.0	0.0	0.7	4.0
SO4	11 800	987	3 015	5 670	5 240	6 807

Geotechnical Testing

Table 5 presents the results of testing the particle size distribution and foundation/indicator parameters of both backfill products.

Table 5. Analysis of particle distribution and foundation/indicator parameters

Backfill product	**Treatment**	**Grading**	**Permeability (m/s)**	**Uniformity of coefficient**			**Coefficient of gradation**	
				D_{10}	D_{60}	C_u	D_{30}	C_g
Coal slurry	Undisturbed	Gap graded	10^{-9} to 10^{-7}	0.0160	0.160	10	0.046	0.83
	pH 9	Gap graded	10^{-9} to 10^{-7}	0.0030	0.180	60	0.044	3.59
	pH 2	Gap graded	10^{-9} to 10^{-7}	0.0024	0.090	38	0.042	8.17
PFA	Undisturbed	Well graded	10^{-9} to 10^{-7}	0.0060	0.035	6	0.016	1.22
	pH 9	Well graded	10^{-9} to 10^{-7}	0.0070	0.050	7	0.020	1.14
	pH 2	Well graded	10^{-9} to 10^{-7}	0.0070	0.047	7	0.020	1.22

It can be noticed from Table 5 that the PFA backfill is well graded whilst the coal slurry backfill is gap-graded. This implies that the coal slurry backfill will have a higher porosity than the PFA backfill. Moreover, the coefficient of gradation (C_g) for the coal slurry backfill increases with the addition of solution acidity, leading to a more gap-graded material. However, the permeability of both materials ranged between 10^{-9} and 10^{-7} m/s (Table 5).

The mean effective stress versus the confined modulus for the backfill products at various supernatant pH values are presented in Figure 4 and Figure 5. The coal slurry sample (Figure 4) at low stress showed only a slight variation in the confining modulus. Moreover, the undisturbed sample shows the highest confined modulus (57 MPa) at an effective stress of 1.1 MPa. At the same effective stress the confined modulus reduces to 30 MPa (± 47 % decrease from the original modulus) at pH 9 and to 20 MPa (± 63 % decrease) at pH2.

For the PFA sample from Figure 5 it can be noticed that at low effective stress there is only slight variation in the confining modulus. In general, there is a decrease in the confining modulus (as per the coal slurry backfill). At an effective stress of 1.2MPa, the undisturbed sample has a confined modulus of 40 MPa, compared to 35 MPa for the pH 9 sample (±12 % decrease in stiffness from undisturbed modulus).

To confirm the effects of acid solution on the structural integrity of each of the backfill materials it would be necessary to test undisturbed backfill samples in contact with acid solution under confined pressure for an extended period of time (≥ 1 year).

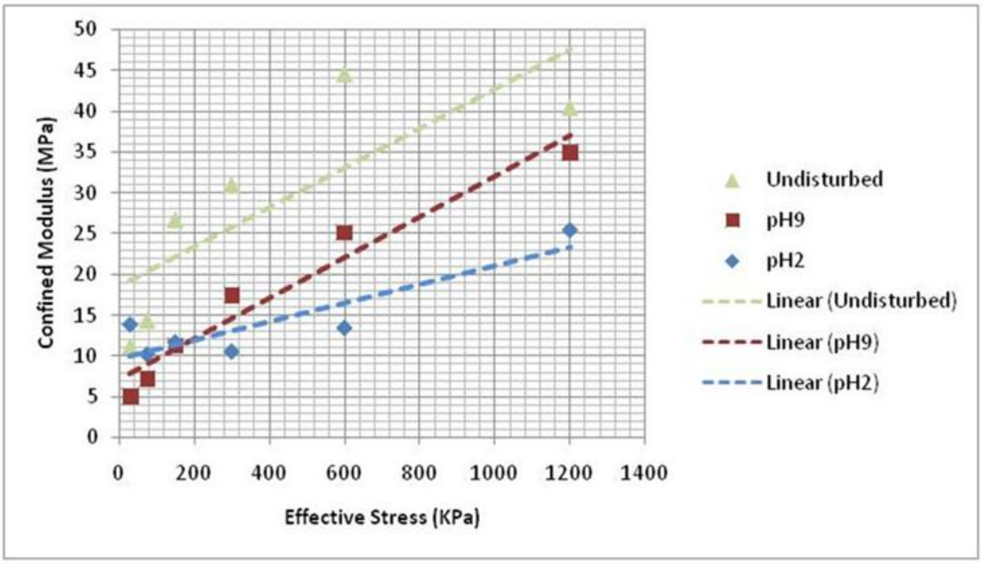

Figure 4. Coal slurry confined modulus versus effective stress

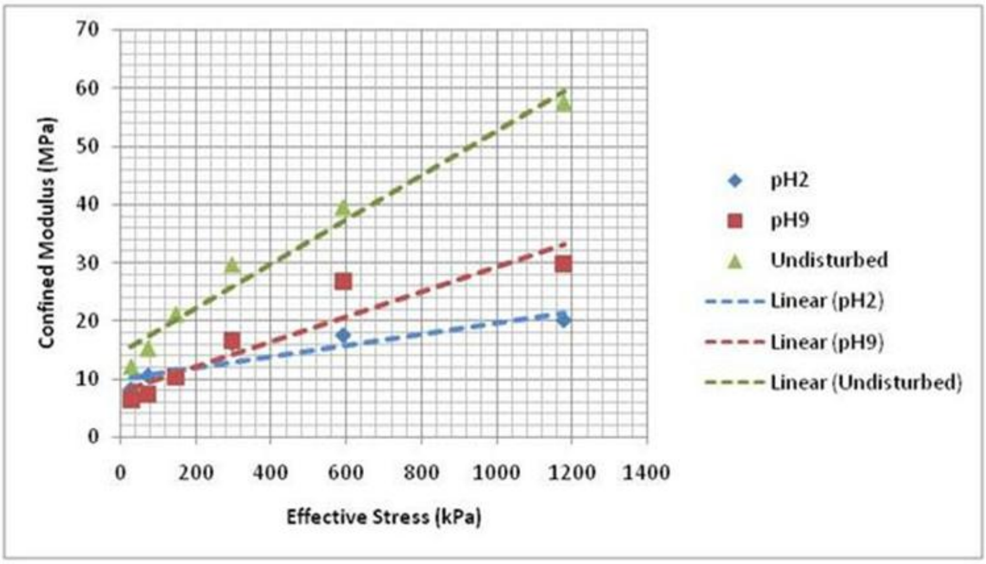

Figure 5 PFA confined modulus versus effective stress

The titration curves presented in Figure 2 and Figure 3 were used to quantify the acidity required to counteract the alkalinity within a unit m^3 of each backfill product at various pH levels. The equivalent volume of pH 2.5 groundwater required to supply this acidity was calculated, both for a unit m^3 of backfill and for the total volume of backfill product/s to be used in both proposed backfilling scenarios. The results of these calculations are presented in Table 6.

The volumes shown in Table 6 probably represent an underestimate as the calculations were based on crushed backfill products which would have a permeability and a surface area ratio (and therefore rate of reactivity) significantly greater than the undisturbed backfill placed in the mine voids. Assuming a hydraulic gradient of between 1:10 and 1:100 it would require several thousand to several million years for the groundwater volumes shown in Table 3 to pass through the backfilled workings over the transmissivity ranges measured for either backfill material.

Table 6. Volumes of pH 2.5 groundwater needed to neutralise backfill alkalinity at selected pH levels

Backfill	Leachate pH	g H^+ / m^3 backfill	m^3 groundwater (Scenario 1)	m^3 groundwater (Scenario 2)
PFA	9.5	76	2.2×10^5	1.4×10^5
	7	491	1.5×10^6	8.8×10^5
	5	1 242	3.7×10^6	1.7×10^6
	3.5	1 339	4.0×10^6	2.2×10^6
	2.5	2 851	8.5×10^6	2.4×10^6
Coal slurry	9.5	131	N/A	1.1×10^5
	7	617	N/A	5.1×10^5
	5	1 002	N/A	8.3×10^5
	3.5	1 527	N/A	1.3×10^6
	2	3 093	N/A	2.6×10^6

4. CONCLUSIONS

Based on the investigations it can be concluded that the elements leaching from both products increase as pH drops. The weight percentage of SO_4 leaching from both products increases progressively with decreasing pH, indicating the onset of acid rock drainage conditions. The progressive leaching of Ca and (to a lesser extent) Mg with decreasing pH suggests the progressive release of carbonate alkalinity to counteract this acidity. Mn and Zn release readily from both backfill products under highly acidic conditions as does V from the PFA backfill and Cu from the coal slurry backfill. Iron, Pb and Cr show low rates of leachability from either backfill even at low mine water pH. Mine water dilution effects are likely to ensure that the contribution of backfill leaching of elements to local groundwater concentrations remains relatively small.

The PFA backfill shows greater structural integrity than the coal slurry backfill. The PFA backfill does display a decrease in stiffness on exposure to acidic drainage but at a lower rate than that of the coal slurry backfill product. Neither product would be expected to fail structurally under the range of drainage conditions that were laboratory tested.

Large volumes of pH 2.5 groundwater throughflow would be required to supply sufficient acidity to neutralise the alkalinity contained within either of the backfill products. Assuming a hydraulic gradient of between 1:10 and 1:100 it would require several thousand to several million years for the groundwater volumes to pass through the backfilled workings over the transmissivity ranges measured for either backfill material.

The conclusion can be reached that the risk of either of the candidate backfill products failing either structurally or through metal/salt leaching to groundwater is low. The PFA backfill would be the preferred option from a structural and geochemical perspective, but either product would be suitable for use in the backfilled mine voids.

5. ACKNOWLEDGMENTS

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