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Leach Testing of Coal Fly Ash to Assess Its Applicability in the Closure of Abandoned Underground Coal Mines in Mpumalanga Province, South Africa

Supi Tlowana[1], Henk Coetzee[1], Viswanath Vadapalli[1], Mosidi Makgae[1], Richard Kruger[2]
1 Council for Geoscience 280 Pretoria street, Pretoria South Africa, stlowana@geoscience.org.za;
2 Richonne Consulting, 7173 Somerset Mall, South Africa, richonne@mweb.co.za

Abstract Coal mining in the Emalahleni area has raised concerns due to uncontrolled water pollution by acid mine drainage (AMD). Mine water treatment with coal fly ash (CFA) was considered as one of the passive treatment options. Batch leach experiments using different mine water and coal fly ash ratios were undertaken to assess neutralisation potential and quality of resultant treated water. Moreover, the mine water leach procedure was undertaken to establish leaching characteristics of CFA while in contact with AMD. Results confirmed that AMD can be treated with CFA and yield alkaline leachates. They also confirmed that leachate pH and contaminant attenuation can be controlled by varying CFA-AMD ratios. At an optimum ratio (5:1), CFA treatment produces circumneutral water and attenuates most of the metals dissolved in the AMD to below 1 mg/L levels. Mine water leaching protocol results indicated that at CFA:AMD ratio of 5:1, successive leaching of CFA can still generate alkalinity and sequestrate contaminants. However, risk of certain metals leaching into solution exists.
Keywords acid mine drainage, coal fly ash, batch leach, Mine Water Leach Procedure.

Introduction

South Africa's electricity generation is mainly from coal fired power stations. Eskom is the country's largest electricity utility and generates approximately 95% of power used in the country. Coal mining in South Africa and elsewhere in the world is associated with significant environmental impacts such as contamination of surface and groundwater resources. Coal mining is often associated with exposure of sulphide minerals such as Pyrite (FeS_2) to oxygen and water and subsequent generation of weak sulphuric acid popularly known as acid mine drainage (AMD). The oxidation of pyrite and AMD generation has been explained and illustrated by researchers elsewhere (Singer and Stumm, 1970).

Coal burning during electricity generation produces a substantial amount of coal fly ash (CFA). CFA is alkaline due to the presence of free lime. Other mineral phases of CFA include mullite, quartz and glass. Several researchers (Vadapalli et al, 2008 and Pérez-López et al, 2009) have studied AMD treatment using CFA and reported amelioration of AMD with significant contaminant attenuation. In this study, the treatment of AMD using CFA was investigated as part of a larger programme looking at the management of abandoned coal mines, which investigated the feasibility of using coal fly ash as a backfill for abandoned underground mines. In this regard, batch leach experiments were carried out using different CFA-AMD ratios to identify conditions for optimum contaminant removal. Moreover, the mine water leach procedure (Ziemkiewicz, 2005) was undertaken to assess the risk of leaching contaminants from CFA while in contact with AMD.

Materials and Methods

Coal fly ash samples were received from Kendal and Duvha power stations in air tight high density polyethylene (HDPE) containers. The mineralogy of the two CFA sample were determined by X-Ray Diffraction (XRD) spectrometry. Major and trace constituents in the samples were determined by X-Ray Fluorescence (XRF) Spectrometry. Acid mine drainage was collected from a decanting abandoned mine situated north-western of the town of Emalahleni. The mine water was appropriately preserved and analysed using Inductively

Coupled Plasma Mass Spectrometry (ICP-MS) and Ion Chromatography (IC) for dissolved metals and metalloids and anions respectively. The pH, electric conductivity (EC) and temperature of the mine water were recorded on site just after sampling. Initially, batch leach experiments were set up with different AMD:CFA ratios as required: 1:1, 2:1, 3:1, 4:1, 5:1, 10:1, 50:1 and 100:1 and agitated for 24 hours. The leachates were analysed for pH, EC, alkalinity and dissolved cations and anions. For the mine water leach experiment (MWLP), AMD:CFA mixtures at ratios of 5:1 and 10:1 were prepared. Control mixtures of deionised water and CFA aliquots at ratios of 5:1 and 10:1 were also prepared. Sealed containers were agitated on horizontal shaker for 18 hours. The sludge obtained from previous leaching cycle was saved for the next leach cycle and a total of 3 leaching cycles was carried out. The leachate samples were subjected to similar analysis as the batch leach experiments.

Results and discussions

XRD analysis indicated that CFA samples were predominantly composed of mullite (71% and 60% of wt. %) quartz (26% and 37% of wt. %) for Kendal and Duvha CFA respectively. XRF analysis confirmed the dominance of Si-Al matrix in Kendal and as well as Duhva CFA with a total wt. % of Si and Al almost reaching 85 wt. %. Other elements with considerable concentrations in both CFA types were observed to be Ba, Sr and Cu.

Batch leach experiments (table 1) indicated that AMD:CFA ratios from 1:1 to 10:1 yielded alkaline to circumneutral (pH 13-6) leachates for both Duhva and Kendal CFA types. However, ratios 50:1 and 100:1 produced leachates with pH < 4 for both CFA types indicating that the amount of ash was insufficient to neutralise the AMD. Leachate EC values increased with increase in AMD:CFA (except for 50:1 and 100:1) ratio indicating efficient contaminant removal for lower AMD to CFA ratios for both CFA types. The alkalinity of the leachates decreased with increasing AMD:CFA ratio, indicating that for higher AMD:CFA ratio, insufficient mass of CFA was added to the mixtures.

The treatment of AMD with CFA resulted in leaching of Na, K, Ca, Sr, Mo and Ba into the solution (table 1). Treatment of acidic waters with alkaline reagents results in leaching of monovalent ions into the solution. Elements such as Sr, Mo and Ba are usually adsorbed on to the surface of CFA particles and released into the solution as soon as the CFA comes in contact with AMD. From Table 1, it is evident that Fe, Al, and As were effectively removed from AMD using both CFA types. Immediately after the dissolution of CFA into the solution, Fe and Al in AMD are likely to undergo hydrolysis (Vadapalli et al, 2008) and form oxyhydroxides which will precipitate on the surface of the CFA particles. For AMD-CFA mixtures where the final solution pH >6, there was an effective removal of Mn, Co, Ni, Cu, and Zn. However, for higher AMD:CFA ratios these elements were leached from CFA into the solution. Mg was observed to be effectively removed for ratios with final pH>9, which agrees with previous findings (Vadapalli et al, 2008). Sulphate removal was significant at ratios yielding pH>6, however the final concentrations for all the AMD:CFA mixtures remained high, especially from 3:1 (AMD:CFA) ratio onwards. The final sulphate levels in CFA treated water is controlled by gypsum solubility and the competing Mg ion in the solution. Therefore, to reach acceptable sulphate levels, the Mg ion should be removed from the solution which is only possible at pH> 11(Vadapalli et al 2013). Further information on sulphate removal mechanisms whilst using CFA as reagent was critically discussed elsewhere (Vadapalli et al 2008).

Based on the preliminary analysis of the analytical data obtained using various AMD: CFA ratios, it was concluded that the optimum results were achieved using ratios of 5:1 and 10:1.

Therefore, the mine water leaching protocol tests were undertaken at these AMD:CFA to assess the risk associated with using CFA for passive AMD treatment underground. Successive leaching of two CFA samples indicated buffering of AMD after 3 cycles of leaching especially using the 5:1 ratio (table 2). Using the 10:1 ratio the pH of the leachates dropped to approximately 4 after the first leaching cycle. Furthermore, the 5:1 ratio was also effective in sequestering Al, Fe, Mn, Cr, Co, Ni, and Zn after 3 cycles of leaching. Species such as As, Ba, K, Ca, Na, Cu, Mo, Sr became more mobile as the number of leaching cycles increased. Sulphate also followed similar trend except it was reduced for the first leaching cycle.

Conclusions

Based on batch leach experiments results using different AMD:CFA ratios it was evident that CFA from both Kendal and Duhva power stations was efficient in raising pH and removing major contaminants from AMD. Preliminary analysis of analytical results indicated AMD:CFA ratio of 5:1 can be used to obtain desired results. Therefore, the ratio 5:1 can be used to obtain best results when CFA is slurried underground to counter AMD. The Mine Water Leaching Procedure (using AMD: CFA ratio 5:1) indicated continued buffering and sequestration of major chemical species by CFA in spite of 3 successive leaching cycles. However, elements such as Ba and Sr were leached from CFA into the solution and further interpretation is required to assess the significance of this leaching in the larger context of AMD treatment. Moreover, after leach cycle 1, sulphate was also observed to leach into the solution which needs further attention. Overall, considering the buffering and sequestration capacity and pozzolanic properties of CFA, it can be concluded that it can be used to backfill and closure of underground coal mines.

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Table 1 *AMD and leachates pH, EC, Alkalinity (Alk.), metals and sulphate concentrations results after neutralization of AMD with Kendal (K) and Duvha (D) CFA samples*

Ratio	AMD	K	D	K	D	K	D	K	D	K	D	K	D	K	D	K	D
		1:1		2:1		3:1		4:1		5:1		10:1		50:1		100:1	
pH	2.7	12.4	11.8	11.6	11.0	10.5	9.8	9.5	9.6	8.9	9.3	6.1	7.2	4.0	3.8	4.0	3.2
EC mS/cm	3.0	5.8	1.8	2.1	2.5	2.7	2.9	2.8	3.1	3.0	3.2	3.0	3.3	2.6	2.7	2.6	2.7
Alk. mg/L $CaCO_3$	0	1213	189.3	241.1	132.2	94.0	72.7	75.6	62.2	51.3	60.0	25.0	25.0	0	0	0	0
SO_4^{2-} mg/L	2282	1040	212	1626	1425	1860	2058	2035	2184	2174	2273	2147	1884	2322	2342	2342	2337
As mg/L	0.032	0.014	0.002	0.004	0.003	0.001	0.004	0.003	0.005	0.003	0.006	0.002	0.000	0.006	0.008	0.006	0.008
Al mg/L	276.0	0.260	1.80	1.00	0.900	0.330	1.30	0.880	1.20	2.40	0.700	0.620	0.021	177.0	196.0	216.0	256.0
Fe mg/L	348.0	4.25	0.110	0.550	0.082	0.250	0.060	0.140	0.050	0.490	0.061	36.40	1.80	2.10	1.60	7.30	16.10
Mn mg/L	8.40	0.006	8.60	0.009	0.005	0.006	0.005	0.049	0.007	0.700	0.057	5.00	3.60	8.60	8.10	8.60	7.80
Mo mg/L	0.001	0.820	1.30	0.425	0.869	0.305	0.644	0.235	0.478	0.171	0.407	0.041	0.141	0.001	0.006	0.001	0.002
Mg mg/L	47.80	0.160	0.550	0.410	0.290	12.70	8.30	54.60	28.40	60.90	47.10	105.0	83.30	101.00	71.90	84.80	60.00
Ca mg/L	61.70	974.0	180.0	751.0	717.0	782.0	863.0	810.0	816.0	855.0	741.0	808.0	751.0	278.0	314.0	213.0	228.0
Cr mg/L	0.077	0.188	0.049	0.126	0.096	0.129	0.115	0.090	0.098	0.136	0.071	0.012	0.008	0.021	0.034	0.051	0.069
Cu mg/L	0.049	0.026	0.005	0.007	0.003	0.053	0.047	0.003	0.004	0.015	0.002	0.007	0.002	0.064	0.104	0.060	0.091
Na mg/L	2.20	23.60	9.40	13.70	5.50	10.30	5.00	8.90	4.40	7.80	4.40	5.30	3.60	3.10	2.50	2.80	2.80
Ba mg/L	0.021	0.690	0.550	0.770	0.180	0.450	0.150	0.290	0.150	0.230	0.130	0.210	0.120	0.190	0.120	0.230	0.180

Co mg/L	1.50	0.020	0.010	0.004	0.003	0.003	0.003	0.004	0.003	0.032	0.004	0.690	0.360	1.500	1.400	1.500	1.400
Ni mg/L	2.20	0.090	0.029	0.039	0.028	0.036	0.033	0.043	0.003	0.370	0.004	1.100	0.360	2.200	1.400	2.300	1.400
K mg/L	6.10	14.00	42.800	1.400	24.700	14.700	21.300	11.100	17.500	9.400	16.400	8.800	12.200	6.900	8.300	6.700	7.000
Sr mg/L	0.550	30.80	7.500	16.100	7.000	11.200	6.700	9.800	6.000	8.500	5.800	6.700	5.200	3.200	2.600	2.700	2.000
Zn mg/L	5.80	0.078	0.062	0.053	0.047	0.081	0.072	0.049	0.046	0.210	0.046	1.400	0.117	6.100	5.600	6.200	5.600

Table 2 *Leachates pH and load release amounts for the AMD- CFA ratio optimization for Kendal and Duvha samples. The amounts are for a 3 cycle mine water leach procedure experiment and are calculated as cumulative sum of kilograms of constituent per ton of CFA per cubic meter of AMD treated. Negative values highlight that the constituent has been imported into the CFA and positive ones that there is release from CFA into the leachate water.*

Constituent	AMD mg/L	Cycle	Kendal CFA								Duvha CFA							
			5:1Control		10:1Control		5:1		10:1		5:1 Control		10:1 Control		5:1		10:1	
			Load $kg/t/m^3$	pH	Load $kg/t/m^3$	pH	Load $kg/t/m^3$	pH	Load $kg/t/m^3$	pH	Load $kg/t/m^3$	pH	Load $kg/t/m^3$	pH	Load $kg/t/m^3$	pH	Load $kg/t/m^3$	pH
SO_4^{2-}	2282	1	-21669	11.9	-43239	12.2	-3462	6.4	-2217	4.6	-22283	12.2	-44296	12.2	-1610	9.0	-4695	8.3
		2	-43792	11.7	-87365	11.0	6997	7.1	6800	4.7	-44506	11.8	-88377	11.6	3314	7.5	4071	4.7
		3	-65844	11.6	-131554	11.6	11912	6.4	17255	4.5	-66663	11.4	-132548	11.1	6678	6.5	14779	4.1
As	0.032	1	0.310		0.716		0.338		0.693		0.310		0.710		0.387		0.669	
		2	0.721		1.5		0.748		1.5		0.738		1.6		0.816		1.6	
		3	1.1		2.4		1.2		2.4		1.2		2.5		1.2		2.5	
Al	276.0	1	-2796		-5592		-2783		-4434		-2810		-5580		-2804		-5622	
		2	-5579		-11143		-5594		-9070		-5600		-11129		-5615		-9812	
		3	-8340		-16682		-8395		-13358		-8377		-16672		-8419		-11836	
Fe	348.0	1	-3078		-6184		-3090		-6154		-3095		-6156		-3090		-6178	
		2	-6154		-12364		-6178		-12309		-6189		-12313		-6179		-12350	
		3	-9231		-18543		-9265		-18463		-9284		-18468		-9268		-18513	
Mn	8.39	1	-77.2		-155		-36.1		-27.7		-77.6		-154		-75.3		-71.0	
		2	-154		-310		-81.5		4.8		-155		-309		-118		31.3	
		3	-231		-465		-129		120		-233		-463		-102		143	

Mo	0.001	1	0.531	0.998	0.118	0.001	0.911	1.6	3.1	1.9
		2	0.893	1.6	0.884	-0.003	1.9	2.6	4.9	2.1
		3	1.3	1.9	1.0	-0.034	2.4	3.1	4.9	2.1
Mg	47.8	1	-490	-983	200	439	-492	-980	-64.7	310
		2	-979	-1967	925	1804	-984	-1959	450	1182
		3	-1467	-2950	1476	3689	-1476	-2937	1044	1677
Ca	61.7	1	1445	2690	5512	8952	1679	2173	5523	9466
		2	3556	4464	12158	19058	2372	2554	12928	19580
		3	4836	5732	18562	29889	2751	2879	19326	25986
Cr	0.077	1	-0.689	-1.3	-0.938	-1.6	-0.383	-0.722	5.4	6.5
		2	-1.6	-2.7	-1.3	-3.3	-0.272	-1.2	9.4	7.0
		3	-2.0	-4.0	-2.1	-5.1	-0.314	-2.3	9.0	5.7
Cu	0.049	1	-0.591	-1.2	4.8	13.9	-0.595	-1.2	-0.515	8.1
		2	-1.2	-2.4	5.8	33.9	-1.2	-2.4	0.775	37.7
		3	-1.8	-3.6	7.9	62.4	-1.8	-3.5	10.0	65.7
Na	2.23	1	5.6	-11.9	23.5	15.7	-14.4	-35.4	3.4	-1.5
		2	-9.7	-50.7	26.2	6.9	-32.8	-81.7	2.1	-10.3
		3	-28.6	-90.4	24.9	1.1	-51.5	-122.7	1.7	-20.4
Ba	0.021	1	14.2	19.9	0.63	1.5	8.6	10.5	0.557	0.762
		2	29.2	32.3	1.0	2.7	16.3	16.2	1.0	1.9
		3	40.2	43.0	1.6	3.9	20.7	21.2	1.6	3.0
Co	1.46	1	-14.0	-28.1	-8.7	-12.9	-14.0	-27.9	-13.9	-18.8
		2	-27.9	-56.1	-21.1	-19.6	-28.1	-55.9	-26.1	-16.0
		3	-41.9	-84.2	-32.4	-17.9	-42.1	-83.8	-30.3	-14.9
Ni	2.20	1	-22.5	-45.1	-14.3	-22.9	-44.9	-22.2	-29.7	-22.5
		2	-44.9	-90.2	-33.5	-37.5	-89.9	-40.9	-30.7	-44.9
		3	-67.4	-135	-51.8	-41.2	-135	-48.3	-34.3	-67.4
K	6.10	1	-47.6	-92.5	10.3	7.1	-16.8	-65.0	63.1	78.3
		2	-106	-210	5.2	-7.1	-48.7	-165	94.2	132
		3	-168	-334	1.5	5.2	-96.7	-280	125	157
Sr	0.545	1	52.4	72.9	64.1	100	13.8	13.8	44.4	86.4
		2	95.5	103	135	204	26.0	20.5	95.2	165
		3	125	131	210	327	35.1	28.7	157	234
Zn	5.78	1	-57.6	-116	-43.6	-61.3	-58.0	-115	-57.9	-116
		2	-115	-232	-101	-101	-116	-231	-116	-103
		3	-173	-347	-152	-108	-174	-346	-156	-99.6