Characterisation of fly ashes for minimisation of acid mine drainage from coal mining waste rocks

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Abstract

Acid mine drainage (AMD) due to the oxidation of sulphide bearing waste rock (WR) is a common environmental problem associated with coal extraction. Therefore, WRs from a lignite producing coal field in Pakistan and Lignite (PK), bituminous (FI) and biomass (SE) fly ashes (FAs) were mineralogically and chemically characterised to i) estimate the potential of WRs for generating AMD ii) estimate their deteriorating effects on natural waters, and iii) evaluate the FAs for their potential to minimise the impacts of WRs by preventing and/or neutralising AMD.

The WRs were composed of quartz, pyrite, arsenopyrite, kaolinite, hematite and gypsum with traces of calcite, malladerite, spangolite, franklinite and birnessite. The major elements Si, Al, Ca and Fe were in the range (wt. %) of 8 – 12, 6 – 9, 0.3 – 3 and 1 – 10, respectively, with high S concentrations (1.94 – 11.33 wt. %).

All FAs contained quartz, with iron oxide, anhydrite and magnesioferrite in PK, mullite and lime in FI and calcite and anorthite in SE. The Ca content in SE was 6 and 8 times higher compared to PK and FI, respectively.

The WRs had considerable potential for generating AMD with net neutralisation potential corresponding to -70 to -492 kg $CaCO_3$ tonne^{-1}. FAs showed to have sufficient acid neutralisation potential corresponding to 20 – 275 kg $CaCO_3$ tonne^{-1}, SE being the most alkaline probably due to the higher Ca content.

The element leaching varied between the WRs due to their chemical and mineralogical composition and pH conditions during the weathering cell test for 28 weeks. However, in general, the leachates from the more acidic WRs were enriched about 3 to 4 orders of magnitude for certain elements compared to the less acidic WRs.

The concentrations of Ca, SO_4^{2-}, Na and Cl in the leachates were much higher compared to other elements from all FA samples. Iron, Cu and Hg were not detected in any of the FA leachates because of pH ranging from 9 to 13.

Overall, the WRs had considerable potential for AMD generation and element leaching, therefore, deteriorate natural waters within the mining area. FAs, on the other hand, possess potential to minimise the impacts of WRs on the environment, due to their buffering capacity. However, the FAs vary in chemical composition and buffering capacity depending on their source, which makes it a possible challenge for utilisation.

Key words: Coal, Mining waste, Acid mine drainage, Neutralization, Fly ash.

Introduction

Despite the latest developments for cleaner alternative fuels, coal still shares about 28% of the total world's primary energy supply (IEA 2015). It is a very large scale activity by which ca. 7.8 billion tonnes of coal were estimated to be extracted worldwide in 2013 (WCA 2014). Global increase in electricity demand is causing coal industry to expand further (IEA-CIAB 2010). However, coal mining raises particularly strong concerns e.g. it produces waste rock (WR) that often contains sulphides, principally high contents of iron sulphides such as pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$) with trace elements such as As, Cu, Hg, Zn, Ni, Co, Mo, Se and Cr.

The sulphide rich WRs are considered environmentally sensitive because the sulphide minerals are unstable when exposed to the surface atmospheric conditions. The sulphide minerals, in presence of water and oxygen, produce acidic leachates with elevated concentration of major and trace elements that one way or the other end up in natural water resources. Such a process is commonly referred to as acid mine drainage (AMD).

Utilisation of coal releases noxious gases (such as CO_2, SO_2 and NO_X; that are implicated in global climate change) and Hg (US EIA 2015). Burning coal generates fly ash (FA) containing ecologically harmful substances (including As, B, Cd, Cr, Cu, Pb, Se and Zn (ACCA 2014)). Additional to that, FAs also contain approx. $10 - 15$ % of particle size less than 10 μm (PM_{10}) that is breathable by humans and, therefore, is seriously harmful, causing damage to the human respiratory system (Medina et al. 2010). FA has been utilised in different ways such as concrete/concrete products, blended cement, road base/sub-base and soil modification/stabilization etc. (ACAA 2015) because of its physical (self-hardening) properties.

However, in recent years, several studies have shown that FA and its composites are effective in the neutralisation of AMD (Jia et al. 2014, Prasad and Mortimer 2011, Backstrom and Sartz 2011, Pérez-López et al. 2009, Pérez-López et al. 2007, Gitari et al. 2006).

The reviewed literature here indicates that the FAs are potential prevention and/or neutralisation agents for AMD. The FAs can be used as a dry cover material over WR dumps to isolate them from the surface atmospheric conditions and prevent AMD generation or the FAs can be mixed with WRs to backfill the underground coal mines and prevent or neutralise any AMD that might generate from the WRs.

Therefore, WRs from one of the large lignite producing coal field in Pakistan with an estimated reserves of 1.3 Bt and spread over 1309 km^2 (GoS 2012) and FA (PK) from a coal fired power station (utilising coal from the same field) were studied in this research. For comparative purposes, a bituminous coal FA from Finland (FI) and a biomass FA from Sweden (SE) were also included.

The main objectives of the study were to characterise WRs for determination of acid generating potential and FAs for acid neutralising potential. For this purpose, the mineralogical and chemical characterisation of WRs and FAs was performed. The acid generating and acid neutralising potentials of WRs and FAs were determined by acid-base accounting (ABA) and buffering capacity tests, respectively. The leaching of elements from WRs and FAs was also studied to estimate their deteriorating effects on natural waters.

Materials

Fly Ashes

Fly ashes were sampled from a lignite fired power plant in Pakistan (PK), bituminous coal fired power plant in Finland (FI) and a biomass FA from a pulp and paper industry in Sweden (SE). The selection of materials was based on their fuel source for a comparative study. PK (generated from fluidised bed combustor and captured using filter bags) was collected from a dumping pile and is, therefore, assumed to be cured to some extent, while FI (generated from boilers) was collected from an electrostatic precipitator and SE (generated from fluidised bed combustor) from multi-cyclone dry collectors.

Coal mine waste rocks

Samples were collected from four WR deposits near three underground coal mines (designated M1, M2 and M3) in a coal field, located 45 km NW of Hyderabad, Sindh province, Pakistan. The WR samples were designated WR1 and WR2 (collected from M1), WR3 (collected from M2) and WR4 (collected from M3). Each WR sample was composed of nine different sub-samples. WR1 was piled for about 2–3 months (therefore, weathering is assumed to have started), while the others were fresh, a few days to a few weeks old.

Methods

Mineralogical examination was achieved by X-ray diffraction (XRD) using a Siemens D5000 diffractometer (with CuKα radiation at 45 kV and 40 mA, and scanning range in Bragg–Brentano geometry from 5° to 90°).

The *Scanning Electron Microscope* (SEM) analyses were also carried out using a FEI Magellan 400 XHR SEM on the thin sections that were prepared by Vancouver Petrographics Ltd., Vancouver, BC Canada. The SEM was equipped with an INCA Energy 450 system with an X-MAX80 EDS detector. The detectors used were through-lens detector (TLD) and Everhart–Thornley detector (ETD), the operating voltages were set to 10 kV.

Chemical characterization was performed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES; (Martin et al. 1991)) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; (Long and Martin 1991)) at a SWEDAC-accredited laboratory (ALS Scandinavia, Luleå, Sweden). The ICP-AES analyses were performed using a Perkin Elmer Optima DV 5300 instrument following US EPA Method 200.7 (modified). The ICP-MS analyses were performed using a Thermo Scientific Element instrument following US EPA Method 200.8 (modified). LOI was determined at 1000 °C.

The determination of *chemical composition* was also realised by X-ray fluorescence (XRF) method using Olympus DELTA Premium Handheld XRF analyser to assess variation in composition within each WR deposit. ICP-AES and -MS analyses were performed on three subsamples of each WR, whereas, XRF was performed on all WR samples.

FAs were classified according to guidelines of ASTM C618 standard (ASTM 2012), which classifies FAs in two classifications, Class-F and Class-C. FAs having the sum of SiO_2, Al_2O_3 and Fe_2O_3 concentrations $\geq$70 wt. % and maximum LOI of 12 wt. % are classified as Class-F, which means that the FAs should have pozzolanic properties. Whereas, Class-C FAs have sum of SiO_2, Al_2O_3 and Fe_2O_3 <70 wt. % with maximum LOI of 6 wt. % are supposed to have cementitious properties in addition to pozzolanic.

Particle size distribution of FAs was determined by laser diffraction analysis using a CILAS 1064 laser granulometer (CILAS, Orléans, France). Prior to analysis, the sample was suspended in distilled water and the particles dispersed in the water by sonication. The particle size distribution was calculated using the CILAS software (de Boer et al. 1987).

A *batch leaching* test of the FA samples was performed with a liquid–to–solid (L/S) ratio of 10 (mL/g) following the procedure (modified) outlined in the Swedish standard SS-EN 12457-4 (SIS 2003).

The *Acid neutralisation potential* (ANP) of FAs was determined by the buffering capacity of FAs following a modified version of the batch titration method described by Wyatt (1984). The ANP was calculated as the $CaCO_3$ equivalent in kilograms per tonne (Eq. 1) required to neutralise the AMD and maintain a near-neutral pH of the solution.

$$CaCO_3 + 2\,H^+ \rightleftarrows Ca^{2+} + H_2CO_3 \tag{1}$$

A modified procedure of the Swedish standard SS-EN 15875 (SIS 2011) for *acid base accounting* (ABA) analysis was applied to evaluate the acidifying and neutralisation potentials of WR samples.

To evaluate the sulphide reactivity, oxidation kinetics, metal solubility and overall leaching behaviour of the sampled materials, WRs were subjected to kinetic testing using *weathering cells* and procedures similar to those described by Cruz et al. (2001). The samples were subjected to 28, 7-day, cycles (192 days) consisting of exposure to ambient air for 2 days, leaching on the third day, followed by a further 3 days of exposure to air and a further leaching on the seventh day.

Results and Discussion

Mineralogical, chemical and physical composition of the materials

The mineralogical composition determined by XRD is shown in Table 1. The minerals detected by XRD were also confirmed by SEM.

Table 1 Mineralogy of FAs and WRs determined by XRD.

Sample	Minerals
PK[a]	Quartz (SiO_2), iron (III) oxide (Fe_2O_3), anhydrite ($CaSO_4$) and magnesioferrite ($Mg(Fe^{3+})_2O_4$)

FI[a]	Quartz, iron (III) oxide, mullite ($Al_6Si_2O_{13}$) and quicklime (CaO)
SE[a]	Quartz, calcite ($CaCO_3$) and anorthite ($CaSi_2Al_2O_8$).
WR1[b]	Dominated by arsenopyrite (FeAsS), quartz (SiO_2) and kaolinite ($Al_2Si_2O_5(OH)_4$), with variable amounts of pyrite (Fe_2S), calcite ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$)
WR2[b]	Dominated by kaolinite ($Al_2Si_2O_5(OH)_4$), Hematite (Fe_2O_3) and gypsum ($CaSO_4 \cdot 2H_2O$), with variable amounts of quartz (SiO_2)
WR3[b]	Dominated by pyrite (FeS_2), quartz (SiO_2) and kaolinite ($Al_2Si_2O_5(OH)_4$), with variable amounts of malladerite (Na_2SiF_6), spangolite ($Cu_6Al(SO_4)(OH)_{12}Cl \cdot 3(H_2O)$), franklinite ($ZnFe_2O_4$)
WR4[b]	Dominated by pyrite (FeS_2), kaolinite ($Al_2Si_2O_5(OH)_4$), quartz (SiO_2) and TiO_2, with variable amounts of birnessite ($(Na_{0.3}Ca_{0.1}K_{0.1})(Mn^{4+},Mn^{3+})_2O_4 \cdot 1.5\ H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$)

[a]after Qureshi (2014), [b]after Qureshi et al. (2016)

The XRD analyses revealed that, besides the organic material, only quartz was common in all three FAs. The SEM, however, helped to determine two more minerals (mullite and albite) in PK. FA particles usually consist of three distinct regions, namely a core composed of amorphous aluminosilicate glass, an inner layer composed of a network of mullite crystals and an outer layer of deposits (Kukier and Summer 2004). The particular conditions created during the melting, evaporation and condensation of a coal mineral admixture determine the specific structure of the formed FA. For instance, thermal transformation of phyllosilicates present in coal particles commonly leads to the formation of glass and mullite (Kukier and Summer 2004).

The WRs examined here were rich in pyrite (the main acid generator), hematite, quartz, calcite, lime, gypsum and kaolinite, in accordance with findings for coal mining wastes in South Africa (Bell et al. 2001, Equeenuddin et al. 2010). In addition, in WR1, As is bound in arsenopyrite, as previously observed by Hower et al. (2008) in Kentucky. Some of these minerals (hematite and kaolinite) additional to pyrite may also contribute in weathering reactions, depending on the pH. Notably, sulphate minerals may contribute to acid generation (Nordstrom 1982), especially Fe[II] or Fe[III] sulphates, which hydrolyse Fe upon dissolution to form $Fe(OH)_3$ (Jennings et al. 2000). While the others (such as calcite and gypsum) may make important contributions to the self-neutralisation potential of WRs.

The mineralogy and chemistry of FAs is mainly governed by the fuel type, burning processes, storage and handling processes (Baker 1987) along with adsorption, condensation and chemical transformation (Jones 1995, Ratafia-Brown 1994), whereas, the mineralogy of WRs varies on the type of mineral or metal being extracted.

The chemical characterisation (Table 2) showed that the FAs were completely dry when sampled, while WRs contained some moisture content varying from 10 to 30 wt.%. Obvious differences in major and trace element composition of FAs and WRs were observed. The principle reason for such differences is their source of production. The FAs were produced from three different fuels and processes and WRs were sampled from different mines. Overall, the FAs were enriched in Si, Al, Ca and Fe mainly. The WRs were enriched in Si, Al and Fe mainly, additionally Ca in WR1. The WRs contained significantly high S content varying from 1 to 11 wt.%, which may indicate high enrichment of sulphide minerals.

Table 2 Chemical composition of FAs and WRs (Mean ± standard deviation, n=9).

		PK[a]	FI[a]	SE[a]	WR1[b]	WR2[b]	WR3[b]	WR4[b]
TS	%	98.7 ± 0.1	100 ± 0	100 ± 0	90.53 ± 5.38	77.33 ± 0.12	83.93 ± 0.23	80.73 ± 2.39
Si	Wt %	26.6 ± 0.9	42.2 ± 1.4	28.35 ± 0.4	8.33 ± 5.79	11.14 ± 2.04	9.54 ± 3.97	12.47 ± 1.94
Al	Wt %	17.9 ± 0.7	20.1 ± 1.3	6.65 ± 0.5	6.84 ± 4.7	9.24 ± 1.72	6.26 ± 2.35	9.35 ± 1.13
Ca	Wt %	5.49 ± 0.2	3.5 ± 0.3	33.35 ± 0.1	3.69 ± 5.64	0.44 ± 0.1	0.36 ± 0.06	0.33 ± 0.03
Fe	Wt %	31.2 ± 2	5.51 ± 0.08	2.53 ± 1	3.9 ± 4.26	1.57 ± 0.42	10.07 ± 3.88	5.63 ± 2.91
K	Wt %	0.51 ± 0.01	1.94 ± 0.02	5.56 ± 0.01	0.4 ± 0.25	0.41 ± 0.11	0.33 ± 0.16	0.35 ± 0.03
Mg	Wt %	2.02 ± 1	1.52 ± 0.01	3.63 ± 0.4	0.51 ± 0.09	0.54 ± 0.01	0.28 ± 0.04	0.26 ± 0.01
Mn	Wt %	0.07 ± 0	0.04 ± 0	1.72 ± 0	0.05 ± 0.07	0 ± 0	0.01 ± 0	0.02 ± 0.01

Na	Wt %	1.6 ± 0.04	1.13 ± 0.08	1.62 ± 0.03	0.16 ± 0.09	0.21 ± 0.04	0.21 ± 0.02	0.14 ± 0.01
P	Wt %	0.06 ± 0.01	0.57 ± 0.02	3.25 ± 0.01	0.02 ± 0.01	0.02 ± 0	0.02 ± 0.01	0.03 ± 0
Ti	Wt %	1.85 ± 0.1	0.71 ± 0.06	0.2 ± 0.02	0.41 ± 0.31	0.57 ± 0.13	0.69 ± 0.34	0.87 ± 0.19
LOI	Wt %	7.93 ± 0.1	4.45 ± 0.07	9.9 ± 0.03	n.d	n.d	n.d	n.d
S	Wt %	2.38 ± 0.2	0.12 ± 0.0014	1.40 ± 0.15	10.79 ± 12.05	1.94 ± 0.15	11.33 ± 4.73	7.43 ± 0.68
$SiO_2+Al_2O_3+Fe_2O_3$	Wt %	75.7 (Class-F)[c]	67.8 (Class-C)[c]	37.53 (n.c)[c]	n.d	n.d	n.d	n.d
As	mg/kg TS	7.49 ± 0.6	17.3 ± 0.1	28.7 ± 0.3	8.15 ± 8.13	0.3 ± 0.08	3.88 ± 0.73	2.06 ± 0.41
Ba	mg/kg TS	211 ± 8	1330 ± 0	2550 ± 5	98.53 ± 61.46	123 ± 22	83.33 ± 36.15	101 ± 18
Be	mg/kg TS	7.25 ± 0.4	3.91 ± 0.05	0.72 ± 0.3	2.3 ± 1.48	3.48 ± 0.42	1.84 ± 0.32	2.01 ± 0.78
Cd	mg/kg TS	0.97 ± 0.1	0.35 ± 0.02	13.05 ± 0.04	0.3 ± 0.04	0.22 ± 0.07	0.25 ± 0.12	0.45 ± 0.37
Co	mg/kg TS	88.6 ± 8	22.6 ± 0.28	9.88 ± 6	40.23 ± 26.07	15.43 ± 4.55	43.5 ± 21.88	75.37 ± 35.54
Cr	mg/kg TS	168 ± 7	70.1 ± 7.9	143 ± 1	67.63 ± 52.6	111 ± 20	101 ± 37	102 ± 38
Cu	mg/kg TS	119 ± 12	55.7 ± 0.99	100.05 ± 8	73.43 ± 53.26	101 ± 30	24.97 ± 2.04	68.13 ± 24.55
Hg	mg/kg TS	0.49 ± 0.1	0.19 ± 0	0.44 ± 0.04	0.22 ± 0.07	0.14 ± 0.02	0.1 ± 0.02	0.12 ± 0.05
Ni	mg/kg TS	155 ± 15	57.4 ± 0.99	61.95 ± 10	87.83 ± 38.94	50.27 ± 14.26	61.1 ± 30.57	107 ± 28
Pb	mg/kg TS	18.9 ± 2	27.7 ± 0.21	84.75 ± 1	14.54 ± 9.14	20.27 ± 5.02	8.88 ± 3.57	13.01 ± 3.69
Sr	mg/kg TS	1510 ± 61	1235 ± 21	875 ± 28	302 ± 103	241 ± 10	126 ± 18	167 ± 34
V	mg/kg TS	339 ± 7	102 ± 9	33.3 ± 1	178 ± 139	256 ± 38	139 ± 47	153 ± 38
Zn	mg/kg TS	218 ± 24	94.4 ± 1.56	2585 ± 16	70.6 ± 7.6	50.1 ± 3.9	49.67 ± 15.15	105 ± 109
Zr	mg/kg TS	277 ± 5	252 ± 5	95.55 ± 0.01	75.03 ± 56.56	119.7 ± 22	135 ± 50	135 ± 33

[a]after Qureshi (2014); [b]after Qureshi et al. (2016); [c]Classification of FAs (ASTM 2012); n.c, not classified; n.d, not determined

The classification of FAs revealed that the PK was a Class-F and FI was a Class-C FA, whereas, SE could not be classified according to the ASTM C618 guidelines. Therefore, PK and FI can be potentially used as cover or mixture material for WR dumps or mine backfilling, respectively.

FA particle surfaces are often enriched in highly environmentally reactive elements (such as As, Se, Mo, Zn and Cd (Hansen and Fisher 1980, Jones 1995)). As a result, these elements readily react when the FA particle is exposed to water and release into the environment. However, the release of the elements from FAs is controlled by precipitation or dissolution mainly, and possibly by desorption.

The classification of fine (≤63 μm) and coarse (>63 μm) particles in FAs (Table 3) was carried out in accordance with current guidelines in ISO 14688-1 (ISO 14688-1 2002); however, results for the < 1 μm size fraction are associated with some uncertainty because of the instrumental limitations. The high proportions of fine particles suggest that all three FAs have large surface areas (Pathan et al. 2003) that provide more chance for enrichment of many elements. This can play an important role in the context of AMD remediation but may also elevate the concentration of elements in leachates if proper pH conditions are not controlled and maintained.

Table 3 Proportion of coarse and fine particles in FAs.

Fly Ash	Fine (%)	Coarse (%)
PK[*]	75	25
FI[*]	87	13
SE[*]	99	1

[*]after Qureshi (2014)

AMD situation

Materials with neutralisation potential ratio (NPR) values <−20 kg $CaCO_3$ tonne[-1] and >20 kg $CaCO_3$ are usually regarded as acid producing and not-acid producing, respectively, and uncertain otherwise

(Miller et al. 1991, SRK 1989). Alternatively, AMD potential of WRs can also be determined using neutralisation potential ratio (NPR). A material is typically considered not-acid producing if NPR > 2.5, uncertain if 2.5 > NPR > 1, and acid-producing if NPR < 1 (Adam et al. 1997).

The ABA test (Table 4) showed that the WRs possess significant potential for producing AMD. Kinetic leaching tests indicate deteriorating effect of WRs on water quality by leaching elements (Table 5) in excess quantity compared to WHO standards (WHO 2011).

Table 4 *AMD generation potential of the WRs (mean ± standard deviation, n=3).*

Measured as kg CaCO$_3$ tonne^{-1} (except NPR)	WR1*	WR2*	WR3*	WR4*
Acid potential (AP)	123 ± 93	61 ± 5	354 ± 148	245 ± 4
Neutralisation potential (NP)	-21 ± 19	-9 ± 3	-138 ± 30	-107 ± 1
Neutralisation potential ratio (NPR)	-0.15 ± 0.03	-0.15 ± 0.05	-0.42 ± 0.11	-0.43 ± 0.01
Net neutralisation potential (NNP)	-144 ± 112	-70 ± 6	-492 ± 178	-352 ± 5

*after Qureshi et al. (2016)

The physicochemical characterisation of leachates from weathering cell test of WRs showed that the WRs were consistently producing acidic leachates throughout the test duration (i.e. 192 days). WRs 3 and 4 were identified as the most acid producing WRs, confirming ABA test results. However, WR1 (which produced near neutral leachates) probably contains some acid neutralising agents (such as calcite indicated by XRD) that were depleting with time as shown by decreasing pH trend in Figure 1. WR2 possesses the moderate AMD potential as indicated by the ABA results and its behaviour in kinetic leaching tests but may contribute to acidity with time.

Table 5 *Concentrations of selected elements in leachates from WRs 1 – 4 in the kinetic leaching tests compared to WHO (2011) drinking water standards.*

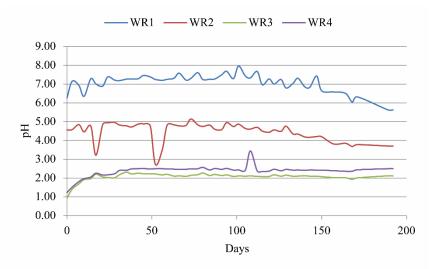|	WR1* Min – Max	WR2* Min – Max	WR3* Min – Max	WR4* Min – Max	WHO
Al (µg/L)	2 – 1,145	58.7 – 2,715	5,600 – 1,525,000	7,285 – 1,310,000	900
As (µg/L)	0.5 – 1	0.5 – 1	2.9 – 1,009.5	1.08 – 708	10
B (µg/L)	422 – 12,250	244 – 23,000	280 – 15,750	186 – 10,450	2400
Cd (µg/L)	0.05 – 6.9	0.07 – 3.36	0.6 – 233	3.25 – 327.5	3
Co (µg/L)	6.7 – 3,050	37.35 – 1,050	157 – 32,350	105 – 57,700	Not specified
Cr (µg/L)	0.5 – 1.3	2.36 – 42	92.5 – 6,590	247.5 – 4,425	50
Cu (µg/L)	1 – 17.3	1 – 34.4	89.3 – 2,640	137 – 26,750	2000
Mn (µg/L)	1,980 – 59,550	305 – 8,125	355 – 54,350	319 – 75,700	400^P
Ni (µg/L)	6.36 – 3,040	36.2 – 951.5	133 – 33,050	182 – 57,150	70
Pb (µg/L)	0.2 – 3.16	0.2 – 7.5	4 – 130	1.41 – 20	10
Zn (µg/L)	6.87 – 2,500	44.3 – 1,030	139 – 45,150	148 – 74,350	10 – 50
Ca (mg/L)	346 – 513	31.85 – 372	2.68 – 469.5	4.11 – 404	Not specified
Fe (mg/L)	0.004 – 140	0.3 – 4.8	391.5 – 36,450	221 – 17,900	0.5 – 50
K (mg/L)	6.7 – 32.4	8.83 – 26.8	1.25 – 20	0.7 – 13.7	Not specified
Mg (mg/L)	9.14 – 1,370	15.9 – 1,380	0.6 – 1,255	0.5 – 695.5	Not specified
Na (mg/L)	2.27 – 556	0.6 – 801	0.6 – 928	0.7 – 336	<20
Cl (mg/L)	3.88 – 1,030	3.1 – 1,130	2.3 – 524.5	1.5 – 136.5	5
SO$_4^{2-}$ (mg/L)	777 – 8,625	189 – 7,240	985 – 101,940	548 – 91,510	500^P
pH	5.6 – 7.3	2.7 – 4.9	0.945 – 2.3	1.2 – 2.5	Not specified
EC (mS/cm)	1.2 – 10	0.4 – 11.18	3.5 – 58.2	1.8 – 34.85	Not specified

*after Qureshi et al. (2016), ^{P} Preliminary

Figure 1 pH trends over the complete duration of weathering cell test.

AMD neutralising potential of FAs

The ANP of FAs is mainly determined by its total calcite content (Gitari et al. 2006), although it is also affected by the particle size of the FA. Finer FAs perform better than coarser FAs, because the larger total surface area of finer FAs increases the area of interaction with the surrounding water (Vadapalli et al. 2007).
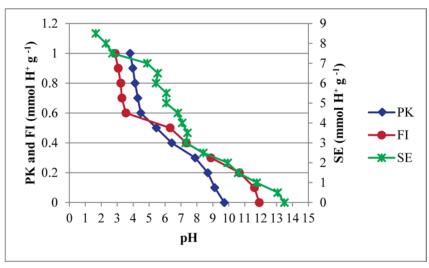

Figure 2 Acid titration curves of FAs against 1M HCl.

In the present study, significant differences in the ANP of the FAs were observed. The ANP calculations, based on Figure 2 and Eq. 1, showed that the SE FA had the highest ANP of 275 kg $CaCO_3$ tonne^{-1}, because of its higher calcite content and larger proportion of fine particles. The PK and FI possess an ANP of 20 and 25 $CaCO_3$ tonne^{-1}, respectively. Therefore, all FAs possess potential to neutralise AMD but larger quantities of less reactive FAs would be required than SE to do the same amount of work. However, due to the fact that the SE comes from a biomass source and that sometimes the coal producing and utilising countries produce significantly large quantities of coal FAs (requiring environmentally safe disposal) than biomass FAs, the less reactive coal FAs might be the only available option for mining companies. Furthermore, the coal fired power stations are usually situated near the coal mines, therefore, ease of availability of coal FAs makes them an economically promising solution as well.

The physicochemical composition of FAs contributed to leaching of some major and trace elements during batch leaching tests (Table 6). The most abundantly leached elements in FAs were Ca, K (in SE), Na, Al, Ba, Cr and Mo. Due to the strongly alkaline nature of FAs, mobility of some elements (such as Fe, Mg, As, Co, Cu and Hg) was restricted to minimum levels. However, probably the smaller

grain size of the SE FA contributed to a small increase in the leaching of some major elements, compared to the other two FAs.

Table 6 Physicochemical characterisation of FA leachates (mean ± standard deviation, n = 3).

		PK[*]	FI[*]	SE[*]
pH		9.55	12.25	13.48
Eh	mV	-145	-296	-155
EC	µS/cm	3.07	2.25	23.09
Ca	mg/L	497 ± 20	222 ± 4.27	644 ± 38
Fe	mg/L	<0.004	<0.004	<0.004
K	mg/L	8.86 ± 0.28	5.16 ± 0.09	1835 ± 106
Mg	mg/L	57.87 ± 6.24	<0.09	<0.09
Na	mg/L	364 ± 7	21.43 ± 0.54	319 ± 26.16
DOC	mg/L	1.18 ± 0.29	1.03 ± 0.05	2.50 ± 0.57
Cl	mg/L	53.67 ± 11.96	2.65 ± 2.56	401 ± 16
F	mg/L	4.10 ± 0.36	1.375 ± 0.13	0.90 ± 0.14
SO_4	mg/L	2123 ± 141	132 ± 7	1630 ± 212
Al	µg/L	131 ± 26	118 ± 21.75	2.53 ± 0.38
As	µg/L	1.83 ± 0.37	<0.5	<0.5
Ba	µg/L	78.23 ± 5.13	288 ± 10.61	257 ± 2.12
Cd	µg/L	0.36 ± 0.03	0.39 ± 0.02	0.21 ± 0.013
Cr	µg/L	1.13 ± 0.26	139 ± 1.71	600 ± 38.89
Mo	µg/L	330 ± 8	360 ± 4	265 ± 2.83
Pb	µg/L	<0.2	<0.2	19.7 ± 0
Zn	µg/L	2.11 ± 0.21	20.01 ± 23.74	135 ± 3.54

[*]after Qureshi (2014)

Conclusions

The mineralogical and chemical characterisation of the FAs and WRs showed large variations in composition and elemental concentrations. The principle reason for that is the source of sampled materials and their storage and handling processes.

The results from ABA tests along with weathering cell tests performed over WRs showed that the studied WRs possess considerable potential for producing AMD and leaching elements in excess concentrations that may end-up in natural water resources and deteriorate their quality.

The physicochemical composition of FA leachates indicates their potential for deteriorating ecosystem quality. However, their ANP is advantageous, making them a possible and potential solution for AMD.

Therefore, utilisation of FAs and WRs together (as cover or mixture material for WR dumps or mine backfilling, respectively) may potentially result in better environmental conditions. However, methods for utilisation must be investigated by scaled-up laboratory experiments due to the fact that the chemical composition of both materials contains elements of concern. Mixed utilisation may or may not contribute towards reduction in mobility of those elements, which also, to some extent, depend on pH conditions of the final mix.

Acknowledgements

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