Characterising the environmental risks of coal preparation wastes: A study of fine coal slurry waste and discards from South African collieries

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Abstract

In order to be effectively managed, the risks associated with wastes arising from the primary production of coal and other mineral resources first need to be well understood. This paper demonstrates the application of a combination of laboratory-scale tests and analytical methods to characterise the potential environmental risks associated with typical coal production wastes from South African collieries. The results indicate that the compositions and properties of these wastes are highly variable. The need to consider the time-related nature of the acid generating behaviour and the potential availability of metals and salts has also been highlighted.

Keywords: coal processing waste, environmental risks, acid rock drainage, metal contamination and salinization risks

Introduction

South Africa still relies heavily on its coal reserves for power generation, with around 70% of the country's primary energy consumption being based on coal. The preparation (also known as the cleaning or processing) of run-of-mine (ROM) coal, generates two different types of coal processing wastes: discards and ultra-fine slurry waste. These wastes are traditionally disposed of to landfill and pose a significant threat to the surrounding environment and local communities (Bosman and Kid 2009). Of particular concern is the long-term generation of acid rock drainage on exposure of the sulfide mineral, pyrite, to air and water in the presence of naturally-occurring microbial organisms (Oelofse 2008). The pollution risks associated with coal processing dumps are aggravated by the fact that coal wastes and associated environmental risks remain poorly characterised, making it difficult to identify and justify meaningful impact mitigation approaches. In particular, little attention has been given to the potential risks associated with metals and salts, or the role of microbial activity in the acid generating behaviour. To overcome these shortcomings, a generic protocol comprising a suite of laboratory-scale tests and analytical methods laboratory is proposed for characterising the risks typically associated with sulfidic mine wastes (Kotelo 2012; Opitz et al. 2015). This paper presents the key results derived from the application of such a protocol for characterising the environmentally significant properties of typical coal production wastes from South African collieries.

Methods

Application of the integrated characterisation protocol outlined in Figure 1 was demonstrated for the case of two fine coal slurry wastes and one coal discard, collected as fresh grab samples at collieries in the Witbank and Waterberg coalfields of South Africa. Environmentally significant properties investigated include: sulfur and its forms, total and available elements (including metals and semi-metals or metalloids), mineralogical composition, and the potential for acid rock drainage generation. Ash analysis was carried out using the SANS 131:2011 method, and analysis of inorganic elements was conducted by the University of Stellenbosch Central Analytical Facilities, using Wavelength-Dispersive X-Ray Fluorescence (WDXRF) and

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). Total sulfur analysis was conducted by means of the standard Leco combustion method at the external ALS laboratories, and sulfur speciation conducted in-house, using the protocol developed by the Australian Coal Association Research Programme (ACARP) C15034 (Miller 2008). Semi-quantitative mineralogical analysis was also conducted using the relatively new QEMSCAN instrument acquired by the Centre for Minerals Research at UCT, in order to support interpretation of the chemical analytical data. Characterisation of the acid rock drainage potential was carried out using acid base accounting (ABA) and net acid generation (NAG) static chemical tests, as well as the standard batch biokinetic test developed at the University of Cape Town. Sequential chemical extraction (SCE) tests were carried out to assess the partitioning and potential availability of inorganic elements for release to the environment under different weathering conditions (Broadhurst et al. 2009; Opitz et al. 2015). On this basis, elements were ranked and scored according to their potential environmental risks (eq.1), using the protocol developed by Broadhurst and Petrie (2010).

$$RPFi = \frac{(ACi)^2}{ARCi \times BCi} \qquad \text{[eq.1]}$$

Where: AC_i is available concentration (mg/kg); ARCi environmentally accepted concentration (mg/kg), represented by drinking water standards as a proxy; and BC_i the natural background concentration (mg/kg), represented by average crustal abundance as a proxy.

Results and Discussion

Chemical composition of mineral matter

The relatively high ash content for the Witbank discard sample (tab.1) is consistent with the higher content of ash-forming minerals, such as quartz (SiO_2) and kaolinite ($Al_4Si_4O_{10}(OH)_2.H_2O$), identified by means of mineralogical analysis as being the major contributors to mineral matter in all three samples. The higher SiO_2:Al_2O_3 ratios in the Waterberg slurry relative to the Witbank slurry (tab. 1) is also consistent with the higher quartz: kaolinite ratio. The Waterberg coal slurry also has a higher content of CaO and MgO than the Witbank waste samples (tab. 1), which can probably be attributed to the higher content of acid neutralising calcite ($CaCO_3$) and amphibole ($Ca_2Mg_5Si_8O_{22}(OH)_2$) minerals, as identified by mineralogical analysis.

A comparison of sulfur speciation results indicates that the Witbank slurry has a lower content of sulfur and sulfur forms (sulfide sulfur, total soluble sulfate and organic sulfur) than the Waterberg slurry and Witbank discard wastes (tab. 1). Sulfide sulfur accounts for more than 50% of the sulfur in all the coal wastes samples, and, in accordance with mineralogical analysis, is mainly in the form of pyrite. Sulfate sulfur accounts for 17-20% of the total sulfur in the slurry wastes, but only 12% of total sulfur in the Witbank

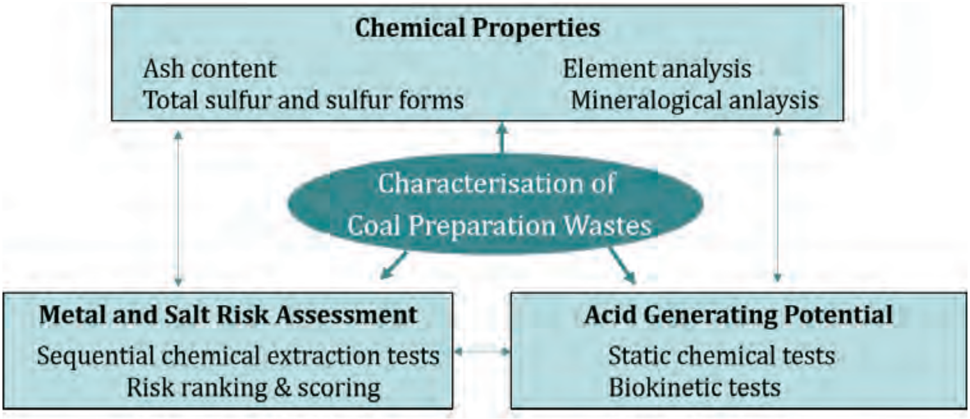

Figure 1 *Integrated characterisation protocol applied to the coal production wastes*

coal discards. Furthermore, whilst the soluble sulfate sulfur in the ultrafine slurry wastes is mainly in the form of non-acid generating minerals (e.g. gypsum, $CaSO_4.2H_2O$, and epsomite, $MgSO_4.7H_2O$), the majority of the sulfate sulfur in the Witbank discards is in the form of acid-generating sulfates (e.g. melanterite, $FeSO_4.7H_2O$). The contribution of the remaining sulfur, comprised mainly of organic sulfur, varies between 21% and 36%, with the proportion of organic sulfur being lower in the Waterberg slurry coal waste.

The concentration ranges of trace elements (< 100 ppm) were found to be similar across all the coal wastes, and also to those reported for the coal standard SARM 19. A comparison of trace element concentrations with average crustal abundance values indicated, however, that a number of trace elements are significantly enriched in the coal wastes relative to their average concentrations in the earth's crust. This pertains particularly to Bi and Se, the concentrations of which are more than 10 times higher than the average crustal abundance values. Other elements which are enriched by a factor of between 1 and 10 include Mo, In (discards only), Pb, Sn, As, Sb, Ge, Cs, Ce, U and Th.

Acid generating characteristics

MPA values obtained on the basis of acid-forming sulfur are significantly lower than those obtained on the basis of total sulfur, decreasing in the order Witbank discards ≥ Waterberg slurry >> Witbank slurry (tab. 2). On the other hand, the acid neutralising capacity (ANC) is significantly higher for the Waterberg coal slurry waste than for the Witbank coal wastes. This is consistent with the higher content of reactive neutralising minerals, calcite and amphibole, in the Waterberg slurry. Despite the relatively high sulfide sulfur content, the high ANC of the Waterberg slurry sample resulted in a negative net acid producing potential (NAPP), consistent with the circum-neutral final NAG pH. In contrast, the relatively low ANC of the Witbank discards resulted in positive NAPP values, consistent with the acidic NAG pH values. Although the Witbank slurry and discards wastes have similar ANC values, the lower MPA values for the slurry waste resulted in lower NAPP values, and a weakly acidic final NAG pH. Extended boiling of the NAG solution in the case of the Witbank slurry waste resulted in a decline in the final pH to 5.24, indicating that formation of soluble organic acids may be contributing to the acidity of the NAG solutions in the case of the standard single test (Stewart et al. 2009).

In accordance with universal classification criteria, the Waterberg sample is non-acid forming, regardless of whether the total or acid-forming sulfur contents are used to calculate NAPP (fig. 2). Similarly, the Witbank discards sample remains potentially

***Table 1** Major mineral components and sulfur forms in the coal processing wastes*

Characteristic	**Composition (mass %)**		
	Waterberg slurry	**Witbank slurry**	**Witbank discard**
Minerals matter			
Ash	49.20	40.90	63.00
SiO_2	28.49	22.58	47.21
Al_2O_3	3.83	13.16	15.39
Fe_2O_3	5.22	2.33	2.50
CaO	3.83	0.83	0.06
MgO	1.08	0.20	0.06
Sulfur speciation			
Sulfide sulfur	1.13	0.55	1.02
Acid soluble sulfur	0.00	0.01	0.23
Non-acid soluble sulfur	0.32	0.19	0.00
Organic sulfur	0.39	0.32	0.69
Total sulfur	1.84	1.06	1.94

Table 2 *Static acid rock drainage test results*

Sample	MPA (kg/t H_2SO_4)		ANC (kg/t H2SO4)	NAPP (kg/t H_2SO_4)		NAG pH	
	S(T)	S(AF)		S(T)	S(AF)	Single stage	Extended boil
Waterberg slurry	54.16	34.58	102.29	-48.12	-67.71	5.19	-
Witbank slurry	32.44	17.14	29.22	3.22	-12.39	3.97	5.24
Witbank discards	53.86	38.25	29.10	24.76	9.15	2.56	2.54

MPA = maximum potential acidity; ANC=acid neutralising capacity; NAPP = net acid producing potential; NAG=net acid generating; S(T)=Leco total sulfur; S(AF)=ACARP acid forming sulfur

acid-forming, even when only acid-forming sulfur is considered. In contrast, the classification of the Witbank slurry sample varies considerably, depending on whether the presence of non-acid forming sulfur compounds and formation of organic acids is taken into account.

The time-related pH profiles obtained in the biokinetic tests for the Waterberg slurry sample (fig. 3) confirm that this sample is net acid neutralising under the non-pH controlled biokinetic conditions, with the pH remaining above neutral for the duration of the test period. This is consistent with the NAF classfication in accordance with the static chemical tests.

The relatively low redox potentials (< 350 mV vs SHE) observed through the duration of this test are consistent with the absence of microbial catalytic activity. However, un-

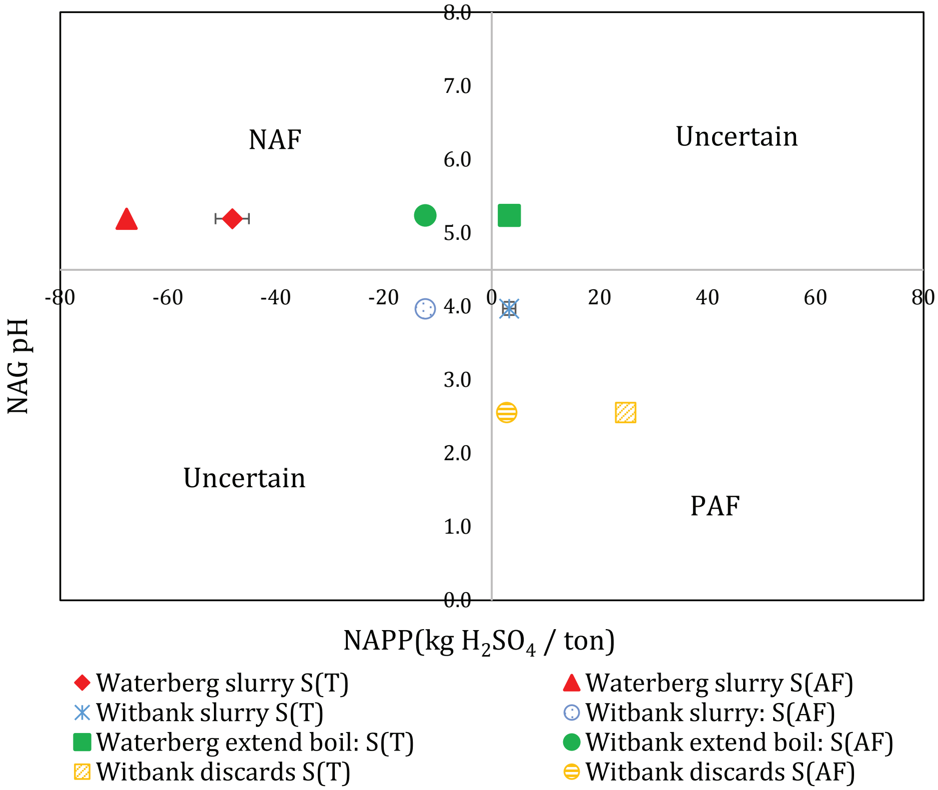

Figure 2 *Classification of acid generating potential of static test results (NAF=non-acid forming; PAF = potentially acid forming).*

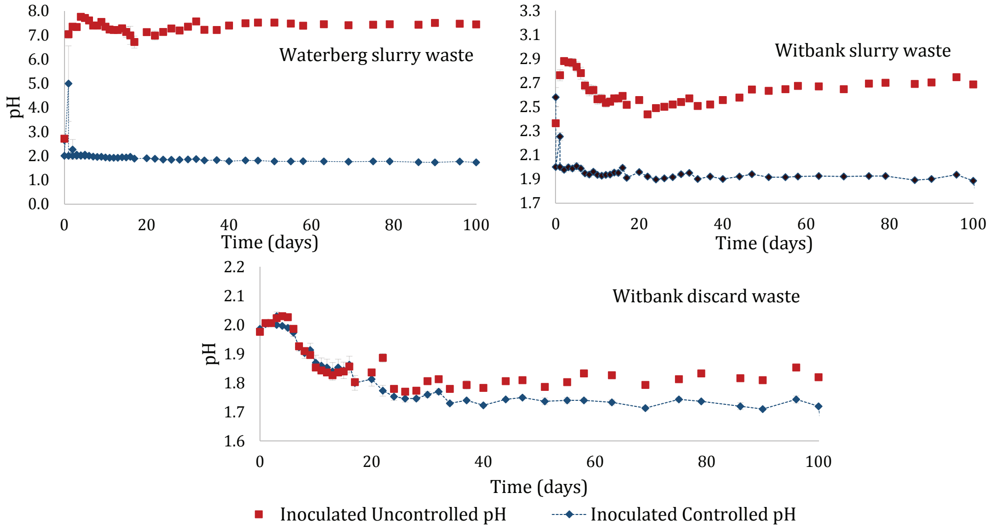

Figure 3 *Time-related pH profiles for the pH controlled and uncontrolled batch biokinetic tests.*

der conditions where the pH was controlled at a pH of 2.0, the acid neutralising capacity of the sample became depleted within 4 days, followed by an increase in the redox potential to 700 mV, indicative of microbial catalytic activity. This indicates that the sample could become net acid generating if exposed to acidic conditions. Consistent with the static tests, the time-related pH profiles for the biokinetic tests are indicative of the relatively low acid neutralising capacity of the Witbank coal wastes, with the pH increasing only slightly in the initial stages of the biokinetic tests (fig. 3). This neutralising capacity is, furthermore, rapidly depleted, with the sample becoming net acid generating over the 4-22 day period. A rapid increase in the redox potential to >700mV over this period is, furthemore, consistent with microbially assisted pyrite oxidation. In the case of the Witbank slurry, this was followed by a prolonged period (22-100 days) in which the pH gradually increased and the sample exhibited acid neutralising behaviour. These test results confirm that the acid generating behaviour of the Witbank slurry waste is likely to vary with time and be highly dependant on test conditions. In the case of the Witbank discards, there is very little evidence of long-term acid neutralising behaviour, with the pH remaining very acidic (<2) for the duration of the test period. This can be attributed to the higher content of acid-forming sulfur and is consistent with the potentially acid-forming (PAF) classification of the sample on the basis of static test results.

Potential metal contamination and salinization water-related risks

Ranking and scoring of the potential environmental significance of elements on the basis of sequential chemical extraction tests (tab. 3), indicates that no elements in the Witbank slurry waste are likely to pose a high risk under any leach conditions.

Iron poses a potentially high risk in the case of the Waterberg slurry and Witbank discard, and a moderate risk in the case of the Witbank slurry waste under oxidising conditions, as well as a moderate risk in all wastes under non-oxidising acid leach conditions. Other elements posing a moderate environmental risk include Mn (Waterberg slurry waste; all leach conditions), Pb (both non-oxidising and oxidising leach conditions for all coal waste samples), S (oxidising leach conditions for all coal waste samples), Sb (oxidising leach conditions for all coal waste samples); Al (Both coal slurry wastes; oxidising leach conditions) and Hg (Witbank coal slurry waste; oxidising leach conditions). Risks from Fe and Al relate largely to physical and aesthetic effects, whilst Mn, Pb, Sb and Hg are all potentially toxic to mammals and eco-systems. Salinization of water sources is mainly as a result of elevated concentrations of soluble sulphates.

***Table 3** Identification of significant elements on the basis of potential environmental risk under neutral, acid and oxidising leach conditions*

	Environmental risk potential (ERP)[1]		
	Low	**Moderate**	**High**
		Neutral leach conditions[2]	
Waterberg slurry	S, Ca, Sb, Pb	Mn	-
Witbank slurry	S, Sb	-	-
Witbank discards	S, Sb	-	-
		Acid leach conditions[3]	
Waterberg slurry	S, Sb, Ca, As, Ba, Se, Al	Mn, Fe, Pb	-
Witbank slurry	Mn, S, Sb, As, Al	Fe, Pb	-
Witbank discards	S, Sb, Al, Mo, Cr	Fe, Pb	-
		Oxidising leach condition[s4]	
Waterberg slurry	Se, Hg, Al, Ba, Ca, Ni, Mo, B, U, V, Cd	Mn, Pb, S, Sb, Al	Fe
Witbank slurry	As, Se, Ba, Mn, Ni, U	Fe, Pb, S, Sb, Al, Hg	-
Witbank discards	Hg, AS, Mo, Al, Se, Cr, Ni	S, Pb, Sb	Fe

1. Low= ERP/1000 of 0.1-1; Moderate= ERP/1000 of 1-10; High= ERP/1000 of 10-100
2. Accumulative concentration of elements in the water soluble and exchangeable fractions (1 and 2)
3. Accumulative concentration of elements in the water soluble, exchangeable, carbonate and oxide fractions (1-5)
4. Accumulative concentration of elements in all fractions except the residual fraction (i.e. 1-6)

Conclusions

The results of this study show that application of a combination of laboratory-scale tests and analytical methods is required in order to develop a comprehensive understanding of the key properties of coal preparation wastes on a case-by-case basis. In particular, biokinetic tests provide a rapid method for assessing the time-related behaviour of coal wastes under conditions of microbial activity, and can be used to compliment chemical static tests. Sequential chemical extraction tests can, furthermore, be combined with a relatively simple ranking and scoring method to identify elements of potential environmental significance under various weathering conditions. Elements identified as being of potential environmental significance under acid generating conditions for the wastes investigated include iron, sulfur, lead, antimony, and in certain cases arsenic, manganese and mercury. A more rigorous and quantitative analysis of mineralogical composition could provide further information on the components controlling the acid forming and neutralising reactions, thus further validating the outcomes of the static and biokinetic test results. It is also postulated that a flow-through biokinetic test would provide a more rigorous understanding of the acid generating behaviour under the type of conditions occurring in a disposal scenario.

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References

Bosman C, Kidd M (2009) Water Pollution, Chapter 17 of Fuggle and Rabie’s Environmental Management in South Africa. 2nd Edition. Juta Law Publishers

Broadhurst JL, Petrie J (2010) Ranking and scoring potential environmental risks from solid mineral wastes. Minerals Engineering 23:182–191

Kotelo LO (2012) Characterizing the Acid Mine Drainage Potential of Fine Coal Wastes. MSc. in Chemical Engineering Dissertation, Department of Chemical Engineering, University of Cape Town

Broadhurst JL, Malukele WJ and Von Blottnitz H (2009) Comparison and application of sequential chemical extraction techniques for metal speciation in sulfidic copper tailings. 8th International Conference on Acid Rock Drainage (ICARD 2009), Skellefteå, Sweden, June, 2009

Miller S (2008) ACARP Project C15034: Development of ARD Assessment for Coal Process Wastes, Environmental Geochemistry International Pty Ltd. Balmain NSW, Australia

Oelofse S (2008) Emerging Issues Paper : Mine Water Pollution, Environment & tourism. doi: ISBN NO: 978-0-9814178-5-1

Opitz AKB, Broadhurst JL, Harrison STL Harrison (2015) Assessing environmental risks associated with ultrafine coal wastes using laboratory-scale tests. Advanced Materials Research 1130: 635-639

Stewart W, Miller S, Kawashima N, Li J, Smart R (2009) Development of Prediction Methods for ARD Assessment of Coal Process Wastes. 8th International Conference on Acid Rock Drainage, pp. 1–14.