01 Apr 2011

Leaching of Potential Hazardous Elements of Coal Cleaning Rejects

Luis F.O. Silva

Maria Izquierdo

Xavier Querol

Robert B. Finkelman

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/che_bioeng_facwork/1169

Recommended Citation

L. F. Silva et al., "Leaching of Potential Hazardous Elements of Coal Cleaning Rejects," *Environmental Monitoring and Assessment*, vol. 175, no. 1 thru 4, pp. 109 - 126, Springer, Apr 2011.
The definitive version is available at https://doi.org/10.1007/s10661-010-1497-1

Environ Monit Assess (2011) 175:109–126
DOI 10.1007/s10661-010-1497-1

Leaching of potential hazardous elements of coal cleaning rejects

Luis F. O. Silva · Maria Izquierdo · Xavier Querol · Robert B. Finkelman · Marcos L. S. Oliveira · Marcus Wollenschlager · Mark Towler · Rafael Pérez-López · Felipe Macias

Received: 24 March 2010 / Accepted: 3 May 2010 / Published online: 20 May 2010

Abstract The geochemical characteristics of coal cleaning rejects (CCR) in Santa Catarina State, Brazil, were investigated. Around 3.5 million ton/year of coal waste are dumped in Santa Catarina State. Coal beneficiation by froth flotation results in large amounts of CCR composed of coaly and mineral matter, the latter characterised by the occurrence of sulphide minerals and a broad array of leachable elements. The total and leachable contents of more than 60 elements were analysed. Atmospheric exposure promotes sulphide oxidation that releases substantial sulphate loads as well as Ca^{2+}, K^{+}, Mg^{2+}, Cl^{-} and Al^{3+}. The metals with the most severe discharges were Zn, Cu, Mn, Co, Ni and Cd. Most trace pollutants in the CCR displayed a marked pH-dependent solubility, being immobile in near-neutral samples. The results highlight the complex interactions among mineral matter solubility, pH and the leaching of potentially hazardous elements.

Keywords Brazilian coal mining · Coal beneficiation · Leaching · Trace pollutants

Introduction

Coal has been used in Brazil as solid fuel for thermoelectric generation for nearly 80 years (Pires and Querol 2004; Kalkreuth et al. 2006; Silva et al. 2009a, b) and greatly supported national development. According to the local coal industry syndicate of Santa Catarina State, the average coal run per mine is 6 million ton/year, from which 3.5 million ton/year are rejected and disposed of in landfills (Marcello et al. 2008). The Santa Catarina coal mining (Fig. 1) region was already classified as an environmental national endangered area by a 1980 Federal Decree. Accordingly, this area

---

L. F. O. Silva (✉) · M. L. S. Oliveira · M. Wollenschlager
Catarinense Institut of Environmental Research and Human Development—IPADHC, Capivari de Baixo, Santa Catarina, Brazil
e-mail: felipeqma@yahoo.com.br

M. Izquierdo · X. Querol · R. Pérez-López
Institute of Environmental Assessment and Water Research (IDÆA-CSIC), C/Lluis Solé y Sabarís s/n, 08028 Barcelona, Spain

R. B. Finkelman
Department of Geosciences, University of Texas at Dallas, Richardson, TX 75080, USA

M. Towler
Inamori School of Engineering, Alfred University, Alfred, NY 14802, USA

R. Pérez-López
Department of Geology, University of Huelva, Campus “El Carmen”, 21071, Huelva, Spain

L. F. O. Silva · F. Macias
Department of Soil Science, University of Santiago de Compostela, Santiago de Compostela, Spain

Fig. 1 Location of Santa Catarina Coal basin

obtained special government assistance to address concerns on polluted soil and water quality. It also allowed the mining sector to meet Brazil's demand for steam coal while protecting the environment.

Coal cleaning is receiving great attention from process engineers given the large amounts of coal to be handled. Froth flotation is a widely accepted process for coal and coal fines beneficiation. The characteristics of high-ash-yield Brazilian coals render them difficult to wash, demanding more aggressive coal cleaning technologies. The washing technique used in Santa Catarina State consists of gravimetric separation by jigs. Coal cleaning rejects (CCR) are dumped in gob piles in mined out areas or in flat areas near coal washing plants (Fig. 2). Waste heaps are composed basically of mineral and residual coaly matter. The major environmental problems associated encompass:

1. Waste dump instability and failure (Richards et al. 1981; Stead and Singh 1989; Speck et al. 1993; Singh and Kant 2007; Steiakakis et al. 2009; Silva et al. 2010; Silva and DaBoit 2010)
2. Spontaneous combustion and subsequent deleterious emissions to the atmosphere (Querol et al. 2008; Zhao et al. 2008; Silva et al. 2010)
3. Acid leachate discharges to the environment (Cravotta 2008; Silva and Oliveria 2010)

Brazilian coal is characterised by high sulphide contents, pyrite and marcasite (Marcello et al. 2008; Lattuada et al. 2009; Galatto et al. 2009; Silva et al. 2009b). CCR contain a broad array of elements including environmentally relevant metals such as As, Cu, Co, Ge, Hg, Mn, Pb and Zn among others (Silva and Oliveria 2010). The oxygen-rich water used for coal beneficiation in conjunction with rainwater and atmospheric exposure of wastes provide an optimal scenario for pyrite oxidation to occur (Sasowsky et al. 2000; Pinetown et al. 2007). The weathering of sulphur-bearing species typically results in markedly acidic leachates enriched in sulphates, metals and metalloids, known as acid mine drainage (AMD). This is a well-known environmental issue and one of the most serious water pollution problems worldwide. Despite the natural capacity of soils to reduce solubility and bioavailability of toxic metals, environmental risks may persist at seriously polluted sites, even though mining activities ceased decades ago. This is of relevance bearing in mind that Santa Catarina State hosts over 1,000 abandoned mines (Lattuada et al. 2009).

Mining companies have valid environmental operating licenses for mine exploitation and

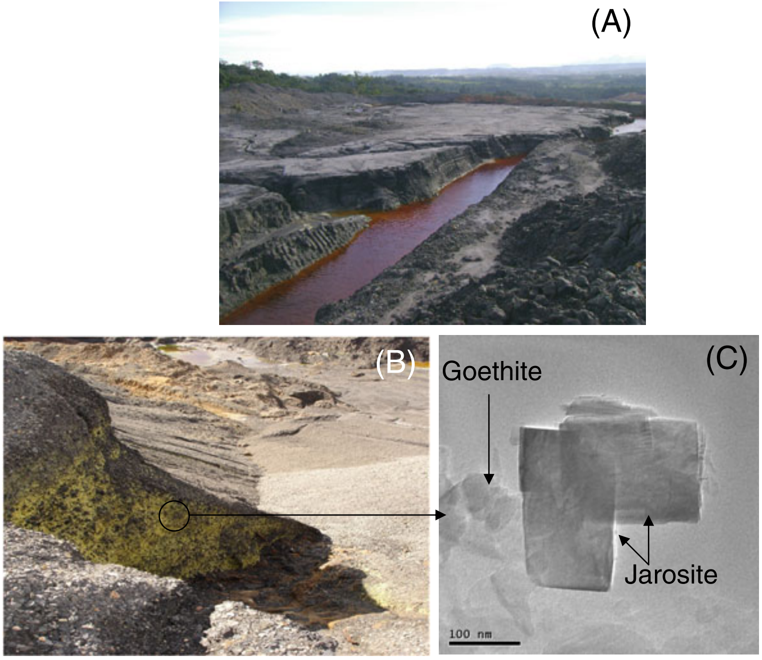


Fig. 2 Coal cleaning rejects: **a** near washing plants; **b** jarosite identification on coal residues zone (near washing plants); **c** TEM image of jarosite and goethite shown in (**b**)

preparation plants (ISO 9000 and ISO 14000), and substantial efforts are taking place on meeting environmental regulations regarding site reclamation. A number of measures to reduce the environmental impact of mining and washing activities are applied, such as restricting truck traffic at night, watering roads to reduce dust formation or covering trucks to prevent spilling. However, these measures have proven to be insufficient to prevent damage caused by mining activity at Santa Catarina coal mines over time.

Leaching of CCR dumps (percolation and runoff leachates) may severely impact the soil, surface water and groundwater resources if no prevention/remediation measures are applied. However, there are no standardised methods for reducing AMD potential (Akcil and Koldas 2006). Metal contamination associated with AMD depends on a number of factors including the amount of sulphides oxidised, the trace element content of the sulphides, the mineral assemblage in the gangue, the geology of the area and the chemistry of the water. Mitigation strategies are thus markedly site dependent and need to be based on the specific features of the impacted site.

Coal contains a number of trace pollutants in variable concentrations and modes of occurrence. The major issue in terms of environmental concern is not only the total content of a given metal but also the proportion of it transferable to an aqueous phase in ionic form. The modes of occurrence in which pollutants occur in CCR play a critical role in their mobility and subsequent release to the environment. From this, and considering that the influence of heavy metals on health and ecosystems is a growing concern, an accurate study on the occurrence and leaching of trace pollutants in CCR is of major importance. Only once these characteristics are well understood, effective strategies to reduce environmental risks could be addressed. Moreover, the USA, Japan, Colombia, South Africa, China, and Brazil, among other countries, routinely apply washing treatments for coal beneficiation (Okuyama et al. 2009; Piñeres et al. 2009; Taute et al. 2009; Silva and Oliveria 2010), which suggests that CCR are not a local issue but an ever-growing worldwide concern. Thus, the main aims of this study are (1) to determine the geochemical and mineralogical characteristics of coal cleaning residues, (2) to assess the leaching potential of these wastes for an extensive list of elements, and (2) to provide new data for technical basis of further reclamation plans for the area affected by coal mining.

Materials, methods and analytical procedures

Sampling and sample preparation

This study is intended not only to assess the current environmental situation of coal mining in Brazil but also to provide a database to assist application of mitigation measures. For this reason, fresh samples were collected immediately after the coal cleaning process. Additional samples aged for different periods of time were also collected. An Etrex® geographical positioning system unit was used to record geographical coordinates (latitude/longitude) of the sampling points. A total of 18 CCR samples from four regions in Santa Clara State (Lauro Müller, Treviso, Urusanga and Criciúma), Brazil, were selected for this study (Fig. 1) using stainless steel spatulas. Most of the samples were fresh except for three samples aged for 2 years (CR 54–56) and one aged up to 5 years (CR 20). The samples were dried in a furnace (40°C, 16 h) and subsequently homogenised and sieved through a 450-μm mesh. Subsamples were ground to pass through a 5-μm mesh for further analysis.

Mineralogical analysis

The mineralogical study was carried out by X-ray diffraction (XRD, powder method) using a Bruker diffractometer (model D8 Advanced). Working conditions were slit fixed at 12 mm, Cu Kα monochromatic radiation, 20 mA and 40 kV. Samples were run at a speed of 0.3° 2θ/min (5–65°). Fluorite as internal reference material was used to determine semiquantitative mineralogical composition. Moreover, the mineral species was investigated by means of an environmental scanning electron microscope (SEM, accelerating voltage, 20 KV; beam current, 10^{-10} A) coupled with an energy dispersive X-ray microanalysis system (EDX) and transmission electron microscopy (TEM) for chemical analyses of individual particles. Different suspensions, namely hexane, acetone, dichloromethane and methanol, were selected to prevent possible mineralogical changes in individual solvents. The suspension consisted of 10 ml of each of the solvents mixed with 0.5 g of dried and sieved coal cleaning residue. The suspension was stirred for ~1 min and then pipetted onto carbon films supported by Cu grids (Gieré et al. 2006). The suspension was left to evaporate before inserting the sample into the TEM. This method may have led to agglomeration but is a widely used standard procedure for most minerals, including metal sulphates (Kan et al. 2003).

Chemical and leaching analyses

All samples were acid digested following a two-step digestion method devised to retain volatile elements in coal dissolution (Querol et al. 1997); this consisted of a HNO_3 hot extract followed by $HF{:}HNO_3{:}HClO_4$ acid digestion of the residue. The resulting solution was then analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES) for major and selected trace elements and by inductively coupled plasma mass spectrometry (ICP-MS) for additional trace elements. The digestion of international reference materials (SARM-19) and blanks was also conducted following the same procedure to check the accuracy of the analytical and digestion methods. Analytical errors were estimated at <3% for most of the elements and around 10% for Cd, Mo and P. Mercury analyses were made directly on solid samples using a LECO AMA 254 gold amalgam atomic absorption spectrometer.

In order to study the leaching of elements, the compliance leaching test EN 12457-2 (EN 2002) was applied. This is a single batch leaching test performed at a liquid to solid ratio (L/S) of 10 L/kg with 24 h of agitation time and deionised water as leachant. In all cases, analyses were performed in duplicate. Major, minor and trace element concentrations in solid samples and leachates were determined by means of ICP-MS, ICP-AES and high-performance liquid chromatography.

Results and discussion

Mineralogy

The mineralogy of the CCR is quite diverse (see Table 1). With the noted exceptions, the minerals detected in the coal cleaning residues are those typically found in most coals and CCR (Sakurovs

Table 1 Minerals detected in CCR using combined instrumental microspectroscopic techniques and XRD

	CR 3	CR 7	CR 11	CR 13	CR 19	CR 20	CR 25	CR 27	CR 38	CR 53	CR 54	CR 55	CR 56	CR 61	CR 62	CR 63	CR 69	CR 70
Silicates																		
Quartz, SiO_2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Clay minerals																		
Chlorite, $Na_{0.5}Al_6(Si,Al)_8O_{20}(OH)_{10}.H_2O$	X					X							X					
Diopside, $CaMg(SiO_3)_2$		X			X												X	
Illite, $K_{1.5}Al_4(Si_{6.5}Al_{1.5})O_{20}(OH)_4$		X				X												
Kaolilite, $Al_2Si_2O_5(OH)_4$	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Albite, $NaAlSiO_8$		X	X	X	X		X	X	X								X	
K feldspar, $KAlSi_3O_8$	X	X	X					X	X					X				
Melilite, $CaAl_{12}MgSi_3O_{14}$		X																
Microcline, $KAlSi_3O_8$	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Mullite, $Al_6Si_2O_{13}$			X						X								X	
Muscovite, $(Ba,K)Al_2(Si_3Al)O_{10}(OH)_2$	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X
Olivine, $MgFeSiO_4$	X	X	X			X												
Talc, $Mg_3Si_4O_{14}(OH)_2$				X					X			X	X					X
Zircon, $ZrSiO_4$				X		X				X								
Suphides																		
Galena, PbS							X			X			X	X	X	X		X
Marcasite, FeS_2			X															
Pyrite, FeS_2	X	X	X	X	X		X	X	X					X	X	X	X	X
Pyrrhotite $Fe_{(1-x)}S$			X				X							X	X	X		X
Sphalerite, ZnS			X											X	X	X		X
Carbonates																		
Aragonite, $CaCO_3$	X					X												
Ankerite, $(Fe,Ca,Mg)CO_3$					X		X	X	X									
Calcite, $CaCO_3$	X	X		X	X						X							
Dolomite, $CaMg(CO_3)_2$		X			X			X	X									
Oligonite, $Fe(Mn, Zn)(CO_3)$	X										X	X	X					
Siderite, $FeCO_3$	X	X			X								X					
Phosphates																		
Brushite, $CaPO_3(OH).2H_2O$						X					X							
Monazite, (Ce, La, Th, Nd, Y)PO_4					X									X	X			

Table 1 (continued)

	CR 3	CR 7	CR 11	CR 13	CR 19	CR 20	CR 25	CR 27	CR 38	CR 53	CR 54	CR 55	CR 56	CR 61	CR 62	CR 63	CR 69	CR 70
Sulfates																		
Anhydrite, $CaSO_4$		X	X			X				X		X						
Alunogen, $Al_2(SO_4)_3.17H_2O$	X				X		X	X			X							X
Barite, $BaSO_4$																		X
Butlerite, $Fe(OH)SO_4.2H_2O$	X		X					X	X		X			X	X			X
Calcantite, $CuSO_4{\cdot}5H_2O$		X			X							X						
Epsomite, $MgSO_4 . 7H_2O$						X				X								
Ferrohexahydrite, $FeSO_4 . 6H_2O$				X			X		X	X	X					X		
Hexahydrite, $MgSO_4 . 6H_2O$		X				X												X
Gypsum, $Ca[SO_4]{\cdot}2H_2O$			X				X	X	X		X	X	X			X	X	X
Jarosite, $KFe_3^{3+}(SO_4)_2(OH)_6$						X		X	X		X	X	X	X	X	X	X	X
Melanterite, $FeSO_4 . 7H_2O$					X			X				X						
Natrojarosite, $NaFe_3(SO_4)_2(OH)_6$		X						X									X	
Schwertmannite, $Fe_{16}^{3+}O_{16}(OH)_{12}(SO_4)_2$		X			X					X								X
Rozenite, $FeSO_4 . 4H_2O$				X				X		X	X		X	X	X	X		X
Oxides and hydroxides																		
Brucite, $Mg(OH)_3$	X	X		X	X			X	X		X				X	X		
Hematite, Fe_2O_3			X						X			X	X	X		X	X	X
Goethite, $Fe(OH)_3$												X	X		X			X
Gibbsite, $Al(OH)_3$								X					X					
Rutile, TiO_2		X										X			X	X		

et al. 2007; Huang and Finkelman 2008; López and Ward 2008; Silva and Oliveria 2010). Based on XRD results, major minerals in CCR are quartz, kaolinite, gypsum, microcline, muscovite and pyrite; a similar mineral assemblage was reported by Silva and Oliveria (2010). Minor phases include albite, ankerite, barite, brucite, calcite, hematite, illite, jarosite, marcasite, mullite, oligonite, siderite, sphalerite, talc, zircon and others (see Table 1). Numerous accessory species were also observed by X-ray diffraction and by microbeam (SEM/EDX, TEM/EDX; Figs. 3 and 4).

As stated above, the use of water during coal mining in conjunction with atmospheric exposure promotes sulphide oxidation (Devasahayam 2006; Weber et al. 2006). Pyrite is known to react with water and dissolved oxygen to form sulphate and iron oxyhydroxides (Silva et al. 2010). The oxidation of pyrite may release to the environment the trace pollutants hosted, typically As, Hg, Se or Pb among others (Finkelman 1994). The following partial reactions, spectroscopically demonstrated by Raman monitoring on parallel experiments conducted with and without the presence of

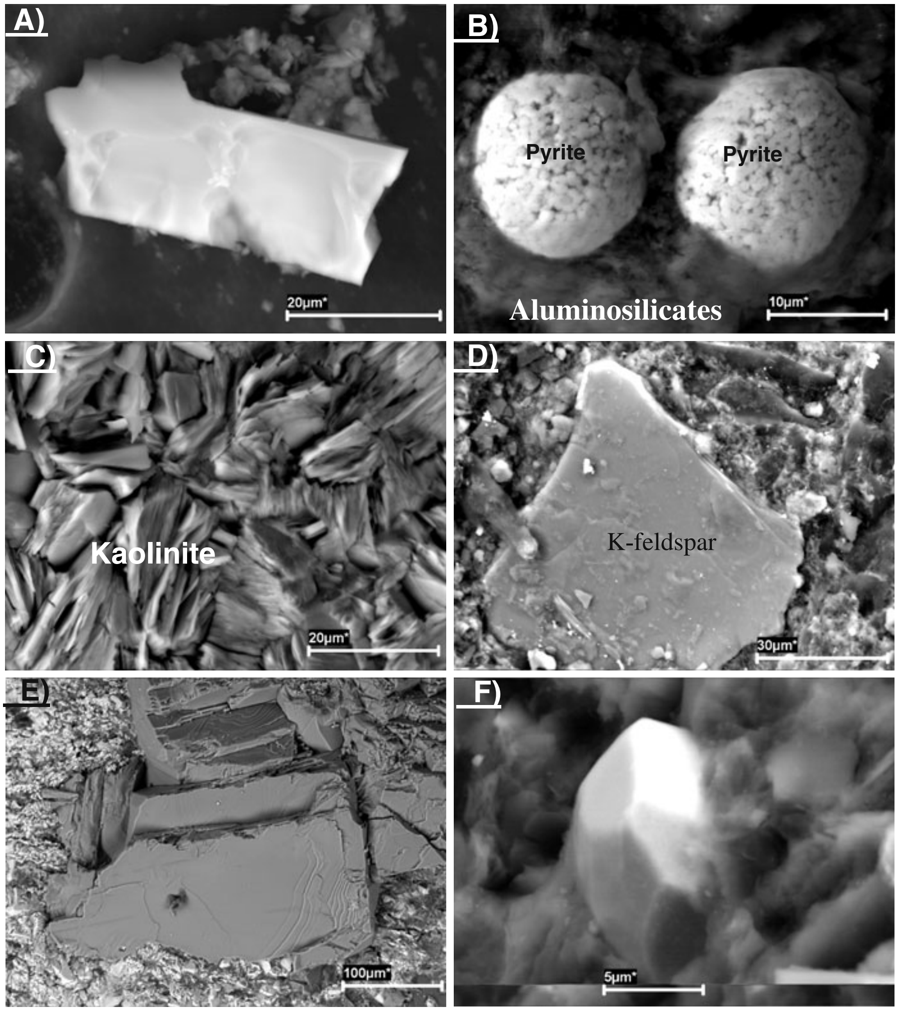


Fig. 3 Minerals in CCR (SEM images). **a** Quartz; **b** pyrite framboids, the most common form of syngenetic pyrite in coal and organic-rich shales; **c** kaolinite; **d** K-feldspar; **e** calcite; **f** zircon

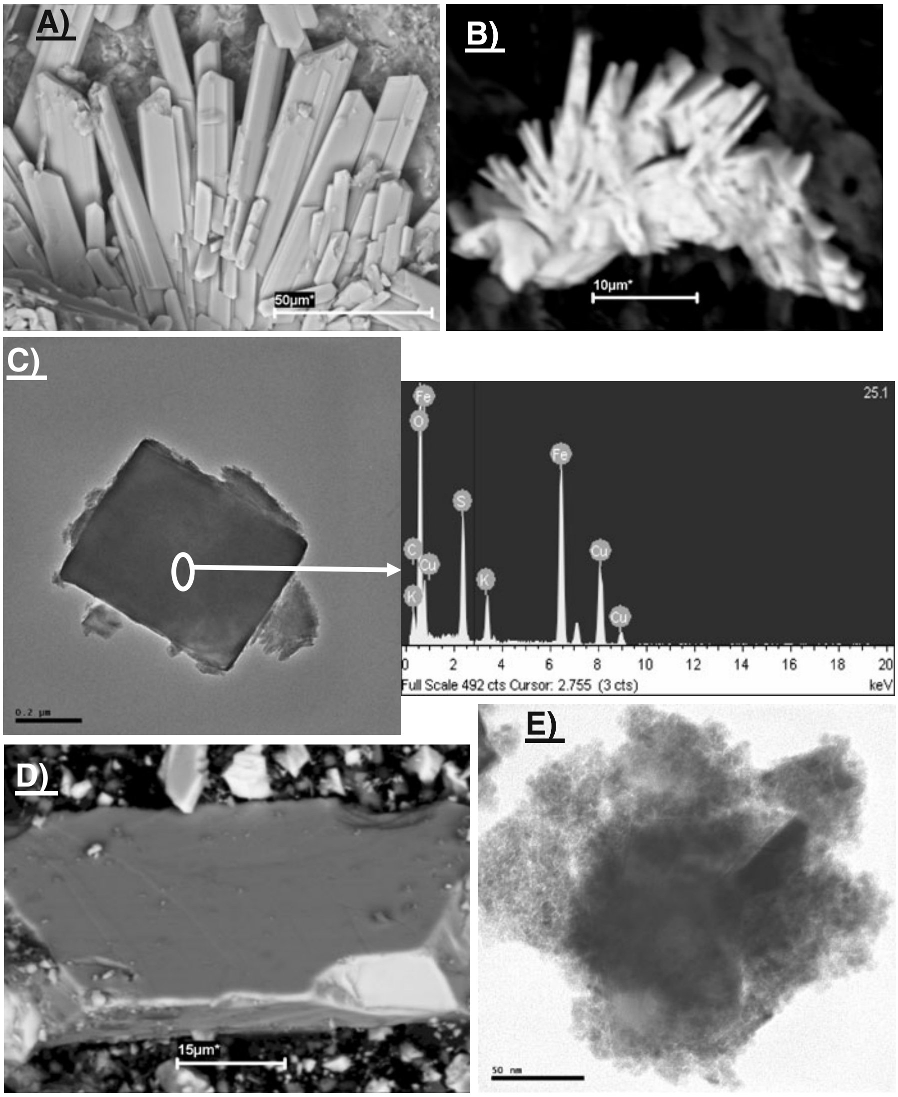


Fig. 4 **a** Gypsum (SEM image); **b** barite (SEM image); **c** jarosite TEM/EDS (copper is from Cu grids) sample CR20; **d** sphalerite (SEM image); **e** hematite (TEM image)

iron-oxidizing bacteria (Sasaki 1997), are the responsibility of the pyrite oxidation:

$$2FeS_2 + 7\,O_2 + 2H_2O \rightleftharpoons 2Fe^{2+} + 4\,SO_4^{2-} + 4\,H^+ \quad \text{(mainly chemical reaction)} \tag{1}$$

$$4\,Fe^{2+} + O_2 + 4\,H^+ \rightleftharpoons 4\,Fe^{3+} + 2\,H_2O \quad \text{(mainly bacterial reaction)} \tag{2}$$

$$FeS_2 + 2\,Fe^{3+} \rightleftharpoons 3\,Fe^{2+} + 2\,S \quad \text{(mainly chemical reaction)} \tag{3}$$

$$2\,S + 3\,O_2 + 2\,H_2O \rightleftharpoons 2\,SO_4^{2-} + 4\,H^+ \quad \text{(mainly bacterial reaction)} \tag{4}$$

giving the global oxidation of pyrite (Rimstidt and Vaughan 2003) that is kinetically enhanced by the presence of anaerobic microorganisms:

$$4\,FeS_2 + 15\,O_2 + 2\,H_2O \rightleftharpoons 4\,Fe^{3+} + 4\,SO_4^{2-} + 4\,HSO_4^{-} \quad (pH \approx 2) \tag{5}$$

Gypsum (Fig. 4a), jarosite (Fig. 4c) and schwertmannite are the most prominent sulphate phases in the cleaned coal rejects. Their formation requires wet, oxidizing and acidic conditions (Silva et al. 2010). Newly formed secondary minerals from AMD may play an important role for attenuating trace metals (Bigham et al. 1994; Webster et al. 1998; McCarty et al. 1998). Jarosite and schwertmannite are environmentally relevant because Pb, As and Cr may be assimilated within their structures (Simona et al. 2004; Stoffregen et al. 2000). Their capacity for metal/oxyanion scavenging in acid mine sites has been addressed for individual elements (Hochella et al. 2008; Cravotta 2008). However, the effect of competitive or synergistic co-sorption between oxyanionic species and metal cations remains to be resolved. This issue has been overlooked in prior studies dealing with the behaviour of contaminants in the environment (Gräfe et al. 2008).

Fine grains with variable Cr > Fe and Fe > Cr compositions were also found in the jarosite aggregates from the CCR. Different stages of pyrite alteration were observed in CCR, which provided a complete sequence of replacement by secondary jarosite (Fig. 2b). The jarosite pseudomorph after pyrite is yellow to light brown in colour (Fig. 2b). Incipient replacement primarily occurs in grain boundaries as well as along crack surfaces in pyrite crystals. As jarosite growth advances, a remnant of pyrite is eventually kept within its pseudomorphic form, as previously reported by Furbish (1963). In some cases, the boxwork has a rectilinear pattern, but mostly, it is quite irregular (Poch et al. 2009).

Leaching of potentially hazardous elements

The bulk and leachable contents of elements in the Santa Catarina CCR are shown in Figs. 5 and 6. In general, the concentrations of As, Mo and Sb in Santa Catarina coals are lower than those in other Brazilian coal regions, while Co, Hg, Pb, Mn, Li, Se, Be, Cd and Bi are within the range of Brazilian coals (Silva et al. 2009b). Values are similar to the coal from Rio Grande do Sul State. The contents of Cr, Cu, Ni, U, V and Zn exceeded those observed in other Brazilian coals (Silva et al. 2009b).

The total soluble fraction of a residue is an important consideration for evaluating potential environmental impacts. CCR are not highly soluble in water, as the estimated total soluble fraction rarely surpasses 2% wt. The major constituents solubilised from CCR are readily leachable salts, i.e. Ca^{2+} and $SO_4^2SO_4^2$, followed by K, Mg, Cl^-, Fe and Al. The remaining elements, including most trace metals, were leached in much lower levels, but few of them are still of concern given their toxicity threshold.

The pH of a solution is an important measurement for evaluating aquatic toxicity and corrosivity and the key factor in regulating sorption–desorption and leaching of trace metals in CCR. The severity of toxicity or corrosion tends to be greater under low-pH or high-pH conditions than at near-neutral pH because the solubility of many

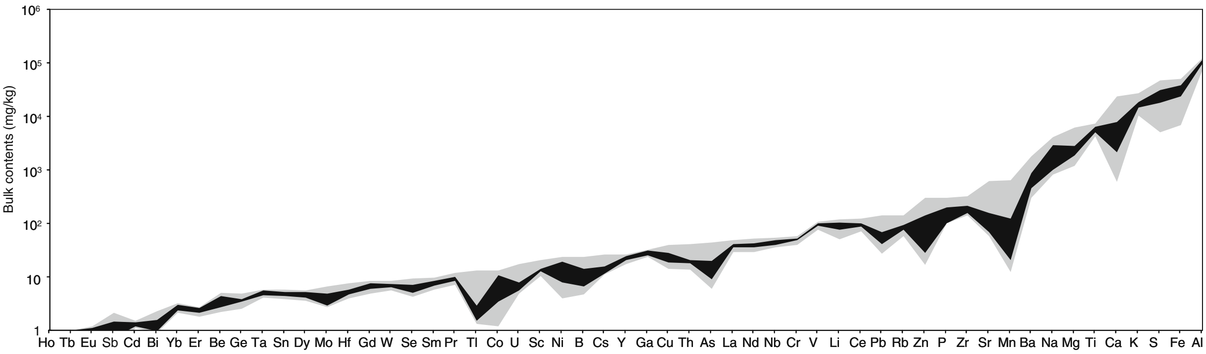


Fig. 5 Bulk content of a number of elements in the studied CCR: ranges of contents (*pale grey*) and interquartile range (percentile 25–75 range, in *dark grey*)

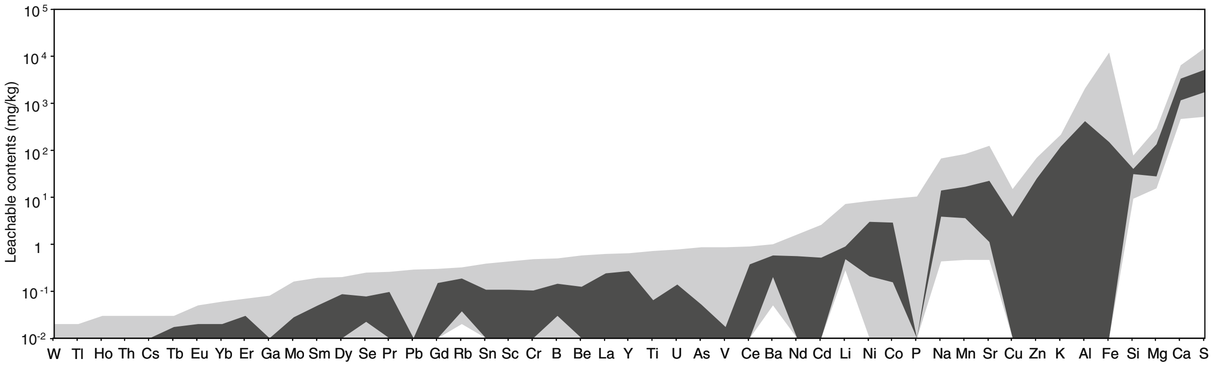


Fig. 6 Leachable contents of a number of elements in the studied CCR: ranges of contents (*pale grey*) and interquartile range (percentile 25–75 range, in *dark grey*)

metals can be described as amphoteric, with a greater tendency to be dissolved as cations at low pH or anionic species at high pH (Langmuir 1997; Gagliano et al. 2004; Mishra et al. 2008). In addition, the acidity of water molecules coordinated to a metal ion is much larger than that of uncomplexed water and generally increases with decreasing radius and increasing charge of the central metal ion. For example, the hydrolysis of Fe(III) can proceed from $Fe(OH_2)_6^{3+}$ through an entire series of ions of formulas $Fe(OH)(OH_2)_5^{2+}$, $Fe(OH)_2(OH_2)_4^+$ and $Fe(OH)_3(OH_2)_3$ (Brown et al. 1999).

According to the pH in leachates, samples can be classified in two main groups: (1) acidic samples, with pH values in the 3.8 to 4.5 range, and (2) neutral samples, with pH values ranging from 6.3 to 7.0. The low pH in group 1 is consistent with the occurrence of the slightly soluble jarosite, which was absent in group 2 samples.

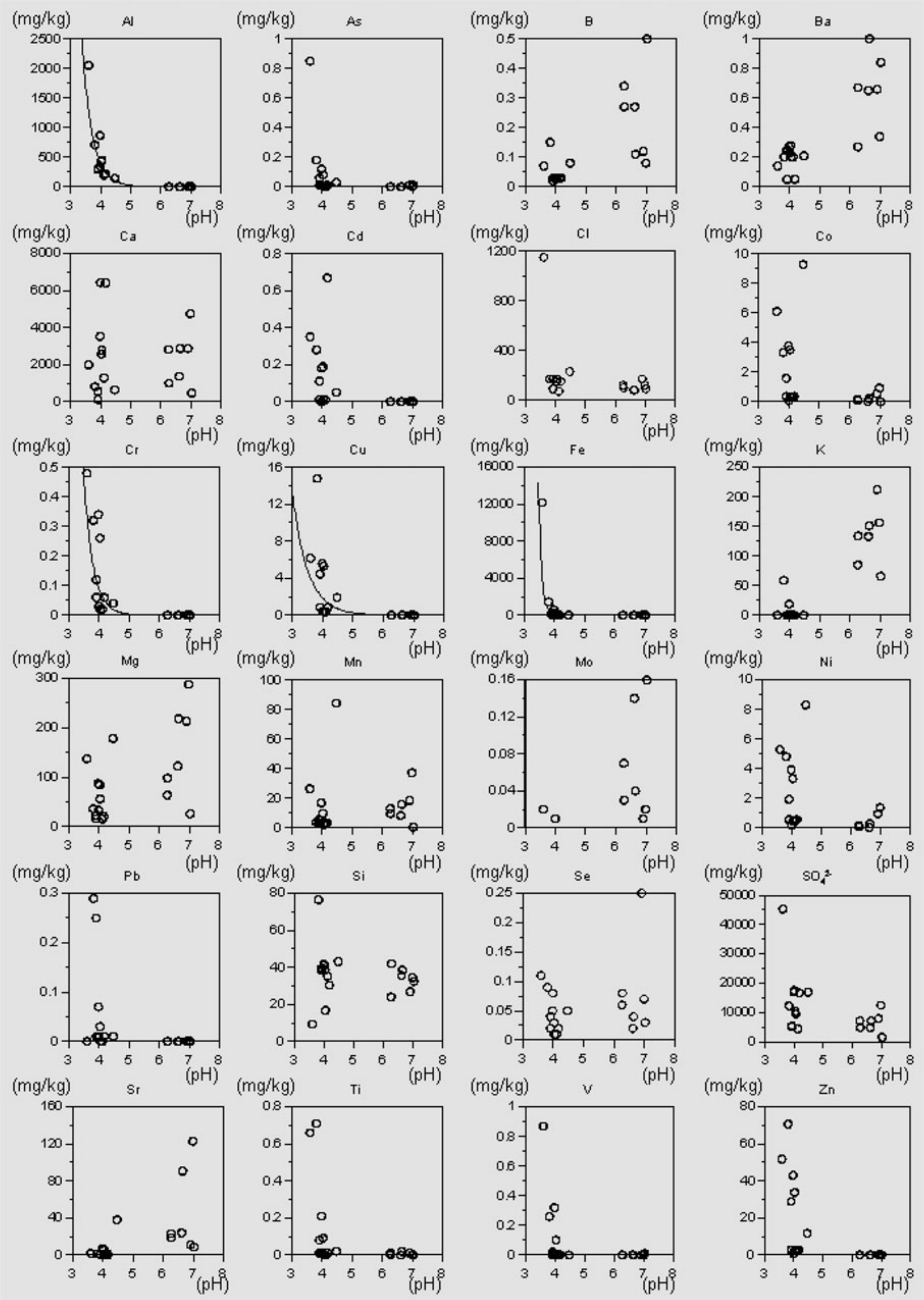
Most elements displayed a pH-dependent solubility (Fig. 7). Leachable contents were markedly high under acidic conditions, while releases decreased with the increasing pH and reached minimum values (close or below the detection limit) under near-neutral conditions. With the few exceptions mentioned below, releases of major elements tend to be scattered, and no clear correlation with pH was observed, probably due to various compounds controlling their solubility over a wide range of pH. The water extractable proportions, i.e. ratio of leachable to total element concentrations, are depicted in Fig. 8.

Nonmetals: $SO_4^{2-} > Se > NO_3^-$

Sulphur was the most abundant and mobile constituent in the leachates. Sulphate releases ranged from 0.2% to 6% (1.5% on average). This accounts for high extractable proportions reaching 92% of the total sulphur content. However, extractable fractions vary widely (Fig. 8) given that the solubility is controlled by various modes of occurrence, presumably jarosite, gypsum, schwertmannite and others sulphate minerals. Nitrate concentrations in leachable fractions were below the detection limit (0.1 mg/kg).

Selenium is present in relatively low concentrations in Santa Catarina coal (Silva et al. 2009b). In addition, Se can often substitute S in sulphides, as a partial replacement or forming seleniferous pyrite, ferroselite ($FeSe_2$) and other Se-bearing sulphides (Dai et al. 2006). Selenium concentrations in the leachable fraction were of low environmental relevance (0.01–0.3 mg/kg). Mean water soluble proportions (about 1%) are very low in comparison to those reported for coal combustion wastes (Izquierdo et al. 2008).

Fig. 7 Leachable contents of a number of elements in CCR as a function of the pH of the leachates. Values in milligrams per kilogram ▶


Al
As
B
Ba
Ca
Cd
Cl
Co
Cr
Cu
Fe
K
Mg
Mn
Mo
Ni
Pb
Si
Se
SO₄²⁻
Sr
Ti
V
Zn
(mg/kg)
(pH)
3 4 5 6 7 8
0 500 1000 1500 2000 2500
0 0.2 0.4 0.6 0.8 1
0 0.1 0.2 0.3 0.4 0.5
0 2000 4000 6000 8000
0 400 800 1200
0 2 4 6 8 10
0 4 8 12 16
0 4000 8000 12000 16000
0 50 100 150 200 250
0 100 200 300
0 20 40 60 80 100
0 0.04 0.08 0.12 0.16
0 0.1 0.2 0.3
0 20 40 60 80
0 0.05 0.1 0.15 0.2 0.25
0 10000 20000 30000 40000 50000
0 40 80 120 160

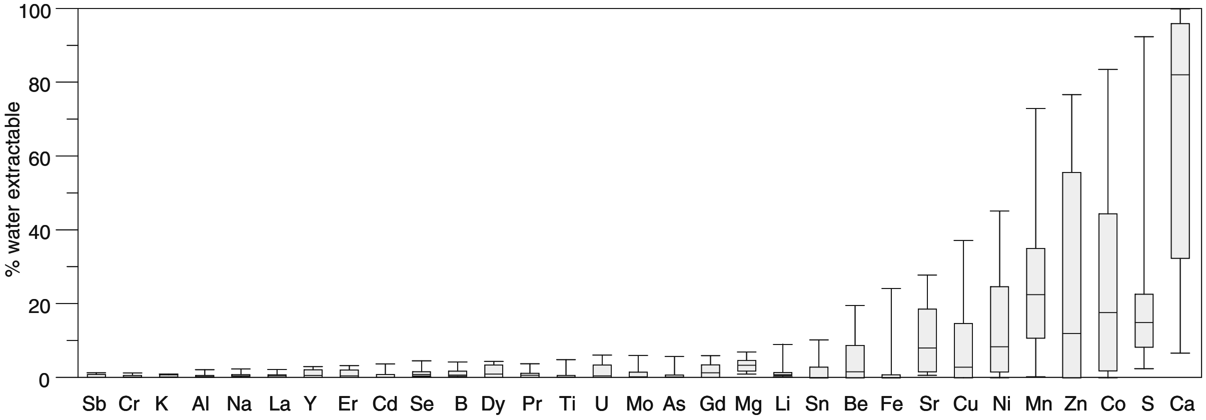


Fig. 8 Water extractable yields of a number of elements in CCR

Alkalies: Na > K > Li > Rb > Cs

The main alkali cations in the leachates were Na and K (up to 200 mg/kg), while the leachable concentrations of Li, Rb and Cs were substantially lower (up to 7 mg/kg). Water extractable fractions for those elements were in most cases close to or below 1% (Fig. 8), suggesting that their main modes of occurrence are not soluble.

Alkaline earths: Ca > Mg > Sr > Ba > Be

Calcium was the main cationic species in CCR leachates. This element was largely released (Fig. 6) and displayed a widely variable but generally high mobility. The scattered leachable contents as a function of the pH (Fig. 7) point to various species governing the solubility. Thus, Ca releases are strongly correlated with SO_4^{2-} releases in neutral leachates, suggesting gypsum as the solubility-controlling species. No correlation was found at lower pH, presumably due to the presence of other leachable sulphates (mainly jarosite). Calcium mobility at neutral pH was on the lower side, whereas releases in acidic conditions indicate that Ca availability is almost the total content. In absence of predominant carbonates in CCR, the leaching of Ca and Mg might be assumed to be controlled by the dissolution of Ca- and Mg-bearing silicates and gypsum (Rigol et al. 2009).

Leachable levels of Mg and Sr were 1 order of magnitude lower than those of Ca. Magnesium availability was kept rather constant regardless of pH, while extractable Sr (Fig. 8) showed a wider range of variation and increased with pH. The highly insoluble barite accounted for the very low Ba leaching (extractable proportions < 0.2%). Beryllium was immobile under neutral conditions. Extractable yields of this element were inversely correlated with the pH and reached 20% of the total content at low pH. It should be noted that the total contents were very close in all samples, which provides evidence of the crucial role of pH in the leaching of trace pollutants.

Metalloids: Si > B > As > Sb = Ge

The leachable contents of Si showed a narrow variation (most values around 35 mg/kg). Boron and As were leached in levels <0.8 mg/kg that in most cases, entails extractable proportions below 1% of the total content. Arsenic may not be regarded as an element of critical concern in the studied CCR given that (1) total contents are in the low range in Santa Catarina coal (Silva et al. 2009b), (2) leachable contents rarely surpass 0.05 mg/kg and (3) this element does not seem to be mobile in CCR. Co-precipitation or adsorption of As onto Fe-(oxy)hydroxides could be responsible for this retention, thus scavenging dissolved As ions (Lee et al. 2005).

The formation of schwertmannite (Yue and Zhao 2008) and jarosite (Lee et al. 2005) could be an additional sink for As. Antimony and Ge were present in very low contents in the solid samples and effectively retained, as their leachable contents were close or below the detection limit.

Transition metals: Fe > Mn > Zn > Cu > Co > Ni > V > Cd > Cr > Mo > Ti > W > Zr > Hf

The well-defined pH-dependent leaching behaviour of most of these elements should be noted. Leachable contents were generally higher under acidic conditions, with very few exceptions, which resulted in several orders of magnitude-variable releases. Iron is highly immobile in pH greater than 4.5 and releases rise with the decreasing pH. The leaching behaviour of Fe may be primarily linked to the occurrence of leachable Fe sulphates (e.g., jarosite), but in samples containing pyrite sludge, other phases are also likely to control Fe solubility (Rigol et al. 2009). Manganese in CCR showed an order-of-magnitude variation in its total and leachable contents. Extractable yields suggest a considerable mobility with respect to the other transition metals. Since Mn is still slightly soluble in near-neutral waters (Fig. 7), it can be regarded as a persistent pollutant in neutralised acid drainage (Kimball et al. 1995). An analysis of water extractable proportions as a function of the pH revealed that 12%–73% (average 34%) Mn is leachable under acidic conditions. At near-neutral pH, Mn is much more immobile as extractable yields drop to 0.3%–30% (average 10%). This could be attributed to the formation of Mn oxides and hydroxides, which are known to precipitate from oxidised waters at slightly alkaline pH values (Larsen and Mann 2005; Yue and Zhao 2008). This would account for (1) the lower extractable fractions observed in leachates around pH 7 and (2) the attenuating effects on the releases of a number of trace pollutants, as will be discussed.

Alongside Mn, Zn, Cu, Co and Ni were the main heavy metals released from the CCR (Fig. 6), with mean leachable contents of 14 mg/kg for Zn and 2 mg/kg for the remaining elements. These elements were dissolved in high concentrations at low pH, while leaching strongly decreased with pH (Fig. 7). Such a wide range of variation in the leaching behaviour as a function of the pH (above 2 orders of magnitude) is not in line with variations in the total content. Copper contents did not show a particular trend as a function of the pH, but neutral samples were enriched in Zn, Ni and Co with respect to acidic samples. Despite the higher total contents, the aforementioned elements were immobile, and leachable contents were close to the detection limit. By contrast, acidic samples revealed extractable yields up to 84% for Co, 77% for Zn, 45% for Ni and 37% for Cu (Fig. 8). It is worth mentioning the similar geochemical behaviour of few of these elements, i.e. leachable concentrations and extractable yields of Cu and Zn are linearly correlated ($R^2 = 0.93$), as well as those of Co and Ni ($R^2 = 0.96$).

Pyrite undergoes mineralogical changes leading to sulphide oxidation, with the subsequent release of hosted trace metals. The precipitation of trace-metal-bearing secondary minerals after pyrite oxidation plays a critical role in the removal of metals from AMD. Among these weathering products, Fe and Mn (oxy)hydroxides stand out for their scavenging potential. Metals such as Cd, Co, Cu, Ni and Zn are known to have a strong affinity for co-precipitating or being absorbed onto Fe/Mn-rich hydroxides (Lee et al. 2005). The high extraction rates observed for these elements at low pH are consistent with leaching models based on surface complexation with Fe and Al (hydr)oxides, since positively charged solid surfaces at low pH hinder metal sorption (Rigol et al. 2009). Consequently, these weathering products are likely to be responsible for the capture and retention of the concerned pollutants. Moreover, the high and preferential adsorptive properties of poorly ordered Fe-bearing oxyhydroxyl sulphates may account for an additional contribution to effectively reduce Pb, Cu, Zn and Cd releases under neutral conditions (Webster et al. 1998).

The total contents of V and Cr were found to be linearly correlated and showed little variation regardless of the sample. In contrast to the above metals, Cr and V are extracted to much lesser degrees (lower than 1%) revealing a low mobility whatever the pH. Zirconium and Hf, with strongly correlated contents, were highly immobile in CCR. Even though Zr contents in CCR attained 250 mg/kg, these elements were leached below the detection limit regardless of the pH, which may be attributed to the high stability of zircon under slightly acidic conditions. Wolfram was also immobile in CCR, showing leachable contents close to the detection limit with and with no particular trend as a function of the pH.

It is worth mentioning the different geochemical behaviour of Mo with respect to the remaining metals. Although immobile in an acidic environment, its leachable concentrations increased with pH (Fig. 7). The formation of MoO_4^{2-} oxyanions, which are very mobile above pH 6–7, would be responsible for the increased mobility. Nevertheless, releases were of little environmental significance and much lower than those typically observed in coal combustion wastes (Izquierdo et al. 2008)

Other metals: Al > Pb > Sn > Ga > Tl > Bi

Aluminium was leached at very low rates with respect to the high total contents. The only remarkable leachable contents were measured at acidic pH, whereas solubility sharply decreased to below the detection limit at neutral pH. This could be ascribed to higher dissolution rates of aluminosilicate and/or aluminium hydroxide minerals in acidic conditions. In general, the high solubility of Al at acidic pH can be explained by the solubility of amorphous hydroxide and hydroxysilicate phases such as gibbsite (Rigol et al. 2009). However, at basic pH, other hydroxide-silicate phases may affect the solubility of this element, thereby leading to a low but measurable amount of solubilised Al (Milne et al. 2003).

Lead is one of the most abundant toxic metals in coal (Finkelman 1994; Borges et al. 2006). Its total content in the CCR reached 100 mg/kg, but this metal was highly immobile, since leachable contents did not exceed 0.3 mg/kg regardless of pH. According to Brookins (1988), the field of stability of Pb^{2+} in a Pb–S–C–O–H system is very small, particularly when low pH values ($pH < 5$) are combined with oxidizing conditions and high sulphates concentrations in solution. Given that the lead sulphate is very insoluble, its formation and precipitation could immobilise the Pb released during oxidation of the samples. Thus, according to its immobilisation pattern and since pH tends to decrease during sulphide oxidation, it can be assumed that the CCR will not result in Pb contamination. Additional attenuation effects may be provided by the formation of schwertmannite, which is known to strongly absorb Pb (Yu et al. 1999; Gagliano et al. 2004).

Tin, Ga and Tl were leached in very low levels in the most acidic samples (up to 0.4 mg/kg), while being immobile in the remaining samples. Total and leachable contents of Bi in CCR were close to the detection limit.

Rare Earth elements and other metals: Ce > Nd > U > Th > Y > La > Sc > Gd > Sm > Dy > Pr > Er = Yb > Eu > Ho > Tb > Tm = Lu

The aforementioned elements in the CCR are mostly associated with clay and detrital phosphate minerals. The acidity of the coal-forming environment may exert an influence on their concentration. Moreover, coal beneficiation process modified the pH and Eh conditions due to sulphide oxidation. This gave rise to a particular geochemistry environment that favoured the enrichment of U, Ce, La, Th and Nd (represented, for example by monazite) and other rare earth elements (REEs). For example, humic acid and ulmic acid can complex U and other metal ions strongly, forming uranyl organic complex in the environment (Ren et al. 2004; Dai et al. 2008).

In general, the total contents of the above elements displayed a narrow variation among samples. Cerium (releases reaching 3 mg/kg but commonly around 1 mg/kg) was the REE most prominently leached, followed by Nd and La. The fact that their leachable contents are linearly correlated suggests similar crystallochemistry in the CCR. The remaining REEs were leached in concentrations <0.5 mg/kg, few of them being released close to the detection limit. Uranium, Y, Sc and Th were released in relatively low levels (<1 mg/kg).

Acidic conditions enhanced the mobility of these elements (a few examples are depicted in Fig. 9). This behaviour is in line with most metals discussed above. Significant percentages around 2–6% U, Gd, Pr, Eu, Dy, Y and La were extracted in the most acidic CCR samples, while extractable yields decreased to negligible proportions at pH over 6 (Fig. 8).

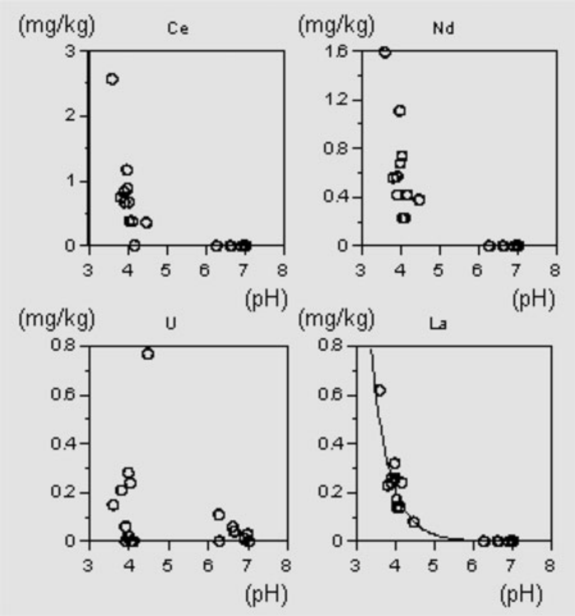


Fig. 9 Leachable contents of few elements in CCR as a function of the pH of the leachates. Values in milligrams per kilogram

Implications for waste management

Results obtained from this leaching study were compared with the waste acceptance criteria for landfilling stated in the Annex 2 of the Council decision (2002). Table 2 gives the critical values of the regulated elements and the leachable concentrations in the samples of this study. Rather than for regulatory purposes, the comparison is intended to assist in the identification of the elements of concern in the CCR. It should be pointed out that the list of elements addressed is not exhaustive and overlooks a number of elements that could be potentially hazardous in the CCR due to their low toxicity thresholds.

Table 2 brings to light that the main concerns of the CCR in terms of leaching are Zn, SO_4^{2-} and pH values, as these parameters could influence their disposal as nonhazardous waste. It is worth mentioning that it does not apply to all the studied CCR samples. The limit values for disposal as hazardous material were surpassed by only two samples for Zn and one sample for SO_4^{2}, while mean values fell in the lower range of the nonhazardous category.

However, a number of CCR samples gave rise to acidic leachates that did not meet the minimum pH of 6 required for further disposal as nonhazardous waste. The low pH in the CCR leachates may be difficult to overcome given that the origin of the CCR inevitably results in the occurrence of sulphide species susceptible to be oxidised in

Table 2 Waste acceptance criteria for landfilling according to the Annex 2 of the 2003/33/CE Council Decision (based on 1999/31/EC Directive) and comparison with leachable concentrations according to EN 12457-2 of the studied CCR (milligrams per kilogram)

	Waste acceptance criteria			Coal cleaning residues		
	Inert	Nonhazardous	Hazardous	Min	Mean	Max
As	0.5	2	25	0.01	0.1	0.9
Ba	20	100	300	0.05	0.4	1.0
Cd	0.04	1	5	0.01	0.2	0.7
Cr	0.5	10	70	0.02	0.2	0.5
Cu	2	50	100	0.01	2	15
Hg	0.01	0.2	2	0.1699	0.3686	1.132
Mo	0.5	10	30	0.01	0.06	0.2
Ni	0.4	10	40	0.03	2	8
Pb	0.5	10	50	0.01	0.09	0.3
Sb	0.06	0.7	5	0.01	0.01	0.01
Se	0.1	0.5	7	0.01	0.06	0.3
Zn	4	50	200	0.06	21	71
Cl^-	800	15,000	25,000	70	192	1,150
F^-	10	150	500	<1	<1	<1
SO_4^{2-}	1,000	20,000	50,000	1,536	11,446	45,288
pH		>6		4	5	7

atmospheric exposure. This demands the application of mitigation measures in order to prevent acidic leachate discharges to reach freshwater systems.

Conclusions

Coal cleaning rejects were primarily composed of quartz, kaolinite, gypsum and pyrite, followed by feldspars and jarosite, the main weathering product. The presence of pseudomorphic jarosite provided evidence of pyrite undergoing different oxidation rates and releasing high sulphate loads and a number of trace metals hosted. The major constituents solubilised from the CCR are Ca and SO_4^{2-}, which were largely released regardless of pH. Water leaching also removed considerable concentrations of K, Mg, Cl^- and Al.

The trace metals with the most severe discharges in leachates from CCR were Zn, Cu, Mn, Co, Ni and Cd. Metal dissolution was enhanced under acidic conditions. In acidic samples, water extractable fractions of metals increased up to 80% in a few cases, and the overall leaching was higher. Mild leaching conditions imposed by near-neutral samples substantially reduced metal leaching. Most environmentally relevant elements were highly immobile, which could be linked to coprecipitation/adsorption onto Fe and Mn oxyhydroxides. These observations underline the critical influence of the mode of occurrence and the pH on metal mobility in the CCR.

The comparison with waste acceptance criteria for landfilling pointed to Zn, sulphates and acidity of leachates as the main concern in the CCR in terms of leaching. Very few samples revealed potentially deleterious releases surpassing the limit values, which suggest that this issue could be solved if properly addressed. However, the acidity of leachates may not be easy to surmount as long as this characteristic is closely linked to CCR origin.

Further research will be conducted in order to gain insight into the geochemistry and the release dynamics of selected elements in CCR over a long time frame. An in-depth study on the leaching patterns under different conditions will assist in the design of optimal remediation strategies to prevent metal inputs in soil and water resources and the subsequent health hazards.

Acknowledgements This study was carried out with support from the IPADHC (Instituto de Pesquisas Ambientais e Desenvolvimento Humano Catarinense, in Portuguese) for coal in sustainable development, funded in part by the IPADHC and Fundo Estadual de Recursos Hídricos government of Santa Catarina State, Brazil. We acknowledge Dr. Maria Luiza for their assistance with high-resolution TEM analysis.

References

Akcil, A., & Koldas, S. (2006). Acid mine drainage (AMD): Causes, treatment and case studies. *Journal of Cleaner Production, 14*, 1139–1145.

Bigham, J. M., Carlson, L., & Murad, E. (1994). Schwertmannite, a new iron oxyhydroxysulphate from Pyhasalmi, Finland, and other localities. *Mineralogical Magazine, 58*, 641–648.

Borges, D., Gallindo, L., Furtado, A. S., Curtius, A. J., Welz, B., & Heitmann, U. (2006). Determination of lead in coal using direct solid sampling and high-resolution continuum source graphite furnace atomic absorption spectrometry. *Microchim Acta, 154*, 101–107.

Brookins, D. G. (1988). *Eh–pH diagrams for geochemistry*. New York: Springer-Verlag.

Brown, G. E., Henrich, V. E., & Casey, W. H. (1999). Metal oxide surfaces and their interactions with aqueous solutions and microbial organisms. *Chemical Reviews, 99*, 77–174.

Council (2002). Decision 2003/33/EC of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC, 16 January 2003. *Official Journal of the European Union, L 11*, 27–49.

Cravotta, C. A. III (2008). Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, U.S.A. Part 1: Constituent quantities and correlations. *Applied Geochemistry, 23*, 166–202.

Dai, S., Ren, D., Chou, C.-L., Li, S., & Jiang, Y. (2006). Mineralogy and geochemistry of the No. 6 coal (Pennsylvanian) in the Junger Coalfield, Ordos Basin, China. *International Journal of Coal Geology, 66*, 253–270.

Dai, S., Ren, D., Zhou, Y., Chou, C.-L., Wang, X., Zhao, L., et al. (2008). Mineralogy and geochemistry of a superhigh-organic-sulfur coal, Yanshan Coalfield, Yunnan, China: Evidence for a volcanic ash component and influence by submarine exhalation. *Chemical Geology, 255*, 182–194.

Devasahayam, S. (2006). Chemistry of acid production in black coal mine washery wastes. *International Journal of Mineral Processing, 79*, 1–8.

European Committee for Standardisation (2002). Characterisation of waste—leaching—compliance test for leaching of granular waste materials and sludges—Part 2: One stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 4 mm. EN 12457-2:2002.

Finkelman, R. B. (1994). Modes of occurrence of potentially hazardous elements in coal: Levels of confidence. *Fuel Processing Technology, 39*, 21.

Furbish, W. M. J. (1963). Geological implications of jarosite pseudomorphic after pyrite. *American Mineralogist, 48*, 703–706.

Gagliano, W. B., Brill, M. R., & Bigham, J. M. (2004). Chemistry and mineralogy of ochreous sediments in a constructed mine drainage wetland. *Geochimica Et Cosmochimica Acta, 68*, 2119–2128.

Galatto, S. L., Peterson, M., Alexandre, N. Z., da Costa, J. A. D., Izidoro, G., Sorato, L., et al. (2009). Incorporação de resíduo do tratamento de drenagem ácida em massa de cerâmica vermelha. *Cerâmica, 55*, 53–60.

Gieré, R., Blackford, M., & Smith, K. (2006). TEM study of PM2.5 emitted from coal and tire combustion in a thermal power station. *Environmental Science & Technology, 40*, 6235–6240.

Gräfe, M., Beattie, D. A., Smith, E., Skinner, W. M., & Singh, B. (2008). Copper and arsenate co-sorption at the mineral–water interfaces of goethite and jarosite. *Journal of Colloid and Interface Science, 322*, 399–413.

Hochella, M. F., Lower, S. K., & Maurice, P. A. (2008). Nanominerals, mineral nanoparticles, and Earth systems. *Science, 319*, 1631–1635.

Huang, X., & Finkelman, R. B. (2008). Understanding the chemical properties of macerals and minerals in coal and its potential application for occupational lung disease prevention. *Journal of Toxicology and Environmental Health. Part B, 11*, 45–67.

Izquierdo, M., Moreno, N., Font, O., Querol, X., Alvarez, E., Antenucci, D., et al. (2008). Influence of the co-firing on the leaching of trace pollutants from coal fly ash. *Fuel, 87*, 1958–1966.

Kalkreuth, W., Holz, M., Kern, M., Machado, G., Mexias, A., Silva, M. B., et al. (2006). Petrology and chemistry of Permian coals from the Paraná Basin: 1. Santa Terezinha, Leão-Butiá and Candiota Coalfields, Rio Grande do Sul, Brazil. *International Journal of Coal Geology, 68*, 79–116.

Kan, A. T., Fu, G., & Tomson, M. B. (2003). Effect of methanol and ethylene glycol on sulfates and halite scale formation. *Industrial & Engineering Chemistry Research, 42*, 2399–2408.

Kimball, B. A., Callender, E., & Axtmann, E. V. (1995). Effects of colloids on metal transport in a river receiving acid mine drainage, upper Arkansas River, Colorado, U.S.A. *Applied Geochemistry, 10*, 285–306.

Langmuir, D. (1997). *Aqueous environmental geochemistry*. New Jersey: Prentice-Hall.

Larsen, D., & Mann, R. (2005). Origin of high manganese concentrations in coal mine drainage, eastern Tennessee. *Journal of Geochemical Exploration, 86*, 143–163.

Lattuada, R. M., Menezes, C. T. B., Pavei, P. T., Peralba, M. C. R., & Dos Santos, J. H. Z. (2009). Determination of metals by total reflection X-ray fluorescence and evaluation of toxicity of a river impacted by coal mining in the south of Brazil. *Journal of Hazardous Materials, 163*, 531–537.

Lee, P., Kang, M., Choi, S., & Touray, J. (2005). Sulfide oxidation and the natural attenuation of arsenic and trace metals in the waste rocks of the abandoned Seobo tungsten mine, Korea. *Applied Geochemistry, 20*, 1687–1703.

López, I. C., & Ward, C. R. (2008). Coposition and mode of occurrence of minerals matter in some Colombian Coals. *International Journal of Coal Geology, 73*, 3–18.

Marcello, R. R., Galatob, S., Petersona, M., Riellac, H. G., & Bernardin, A. M. (2008). Inorganic pigments made from the recycling of coal mine drainage treatment sludge. *Journal of Environmental Management, 88*, 1280–1284.

McCarty, D. K., Moore, J. N., & Marcus, W. A. (1998). Mineralogy and trace element association in an acid mine drainage iron oxide precipitate; comparison of selective extractions. *Applied Geochemistry, 13*, 165–176.

Milne, C. J., Kinniburgh, D. G., van Riemsdijk, W. H., & Tipping, E. (2003). Generic NICA-Donnan model parameters for metal-ion binding by humic substances. *Environmental Science & Technology, 37*, 958–971.

Mishra, V. K., Upadhyaya, A. R., Pandey, S. K., & Tripathi, B. D. (2008). Heavy metal pollution induced pollution induced due to coal mining effluent on surrounding aquatic ecosystem and its management through naturally occurring aquatic macrophytes. *Bioresource Technology, 99*, 930–936.

Okuyama, N., Sakai, K., Komatsu, N., & Kumagai, H. (2009). Thermal extraction behavior of coal. In *Proceedings of the international conference on coal science & technology (ICCS&T), South Africa*.

Piñeres, J., Barnaza, J., & Blandon, A. (2009). Effect of pH, air velocity and frother concentration on vitrinite recovery using flotation column. In *Proceedings of the international conference on coal science & technology (ICCS&T), South Africa*.

Pinetown, K. L., Ward, C. R., & Westhuizen, W. A. (2007). Quantitative evaluation of minerals in coal deposits in the Witbank and Highveld Coalfields, and the potential impact on acid mine drainage. *International Journal of Coal Geology, 70*, 166–183.

Pires, M., & Querol, X. (2004). Characterization of Candiota (South Brazil) coal and combustion by-product. *International Journal of Coal Geology, 60*, 57–72.

Poch, R. M., Thomas, B. P., Fitzpatrick, R. W., & Merry, R. H. (2009). Micromorphological evidence for mineral weathering pathways in a coastal acid sulfate soil sequence with Mediterranean-type climate, South Australia. *Australian Journal of Soil Research, 47*, 403–422.

Querol, X., Izquierdo, M., Monfort, E., Alvarez, E., Font, O., Moreno, T., et al. (2008). Environmental characterization of burnt coal gangue banks at Yangquan, Shanxi Province, China. *International Journal of Coal Geology, 75*, 93–104.

Querol, X., Whateley, M. K. G., Fernandez-Turiel, J. L., & Tuncali, E. (1997). Geological controls on the mineralogy and geochemistry of the Beypazari lignite, central Anatolia, Turkey. *International Journal of Coal Geology, 33*, 255–271.

Ren, D., Xub, D., & Zhao, F. (2004). A preliminary study on the enrichment mechanism and occurrence of hazardous trace elements in the Tertiary lignite from the Shenbei coalfield, China. *International Journal of Coal Geology, 57*, 187–196.

Richards, B. G., Coulthard, M. A., & Toh, C. T. (1981). Analysis of slope stability at Goonyella Mine. *Canadian Geotechnical Journal, 18*, 79–194.

Rigol, A., Mateu, J., Gonzalez-Nunez, R., Rauret, G., & Vidal, M. (2009). pH Stat vs. single extraction tests to evaluate heavy metals and arsenic leachability in environmental samples. *Analytica Chimica Acta, 632*, 69–79.

Rimstidt, J. D., & Vaughan D. J. (2003). Pyrite oxidation: A state-of-the-art assessment of the reaction mechanism. *Geochimica Et Cosmochimica Acta, 67*, 873–880.

Sakurovs, R., French, D., & Grigore, M. (2007). Quantification of mineral matter in commercial cokes and their parent coals. *International Journal of Coal Geology, 72*, 81–88.

Sasaki, K. (1997). Raman study of the microbially mediated dissolution of pyrite by *Thiobacillus ferrooxidans*. *The Canadian Mineralogist, 35*, 999–1008.

Sasowsky, I. D., Foos, A., & Miller, C. M. (2000). Lithic controls on the removal or iron and remediation of acidic mine drainage. *Water Research, 34*, 2742–2746.

Silva, L. F. O., & DaBoit, K. (2010). Nanominerals and nanoparticles in feed coal and bottom ash: implications for human health effects. *Environmental Monitoring and Assessment*. doi:10.1007/s10661-010-1449-9.

Silva, L. F. O., Macias, F., Oliveira, M. L. S., da Boit, K. M., & Waanders, F. (2010). Coal cleaning residues and fe-minerals implications. *Environmental Monitoring and Assessment*. doi:10.1007/s10661-010-1340-8.

Silva , L. F. O., Moreno, T., & Querol, X. (2009a). An introductory TEM study of Fe-nanominerals within coal fly ash. *Science of the Total Environment, 407*, 4972–4974.

Silva, L. F. O., & Oliveria, M. L. S. (2010). A preliminary study of coal mining drainage and environmental health in the Santa Catarina region, Brazil. *Environmental Geochemistry and Health*. doi:10.1007/s10653-010-9322-x.

Silva, L. F. O., Oliveira, M. L. S., da Boit, K. M., & Finkelman, R. B. (2009b). Characterization of Santa Catarina (Brazil) coal with respect to human health and environmental concerns. *Environmental Geochemistry and Health, 31*, 475–485.

Simona, R., Andreas, B., & Stefan, P. (2004). Formation and stability of schwertmannite in acidic mining lakes. *Geochimica Et Cosmochimica Acta, 68*, 1185–1197.

Singh, J., & Kant, S. (2007). Impact of coal mining on leaf morphology and stomatal index of plants in Kalakote range, Rajouri (J&K), India. *Nature Environment and Pollution Technology, 6*, 715–718.

Speck, R. C., Huang, S. L., & Kroger, E. B. (1993). Large-scale slope movements and their effect on spoil-pile stability in Interior Alaska. *International Journal of Mining, Reclamation and Environment, 76*, 161–166.

Stead, D., & Singh, R. (1989). Loosewall stability in United Kingdom surface coal mines. *Canadian Geotechnical Journal, 26*, 235–245.

Steiakakis, E., Kavouridis, K., & Monopolis, D. (2009). Large scale failure of the external waste dump at the “South Field” lignite mine, Northern Greece. *Engineering Geologist, 104*, 269–79

Stoffregen, R. E., Alpers, C. N., & Jambor, J. L. (2000). Alunite–jarosite crystallography, thermodynamics, and geochronology. Sulfate minerals: Crystallography, geochemistry, and environmental significance. *Reviews in Mineralogy 40*, 453–479 (Mineralogical Society of America).

Taute, L., leRoux, M., & Campbell, Q. P. (2009). The influence of screening conditions on the generation of fires during coal processing. In *Proceedings of the international conference on coal science & technology (ICCS&T), South Africa*.

Weber, P. A., Skinner, W. M., Hughes, J. B., Lindsay, P., & Moore, T. A. (2006). Source of Ni in coal mine acid rock drainage, West Coast, New Zealand. *International Journal of Coal Geology, 67*, 214–220.

Webster, J. G., Swedlund, P. J., & Webster, K. S. (1998). Trace metal adsorption onto acid mine drainage Fe(III) oxyhydroxysulphate. *Environmental Science & Technology, 32*, 1361–1368.

Yu, J., Heo, B., Choi, I., Cho, J., & Chang, H. (1999). Apparent solubilities of schwertmannite and ferrihydrite in natural stream waters polluted by mine drainage. *Geochimica Et Cosmochimica Acta, 63*, 3407–3416.

Yue, M., & Zhao, F. (2008). Leaching experiments to study the release of trace elements from mineral separates from Chinese coals. *International Journal of Coal Geology, 73*, 43–51.

Zhao, Y., Zhang, J., Chou, C. L., Li, Y., Wang, Z., Ge, Y., et al. (2008). Trace element emissions from spontaneous combustion of gob piles in coal mines, Shanxi, China. *International Journal of Coal Geology, 73*, 52–62.