

A preliminary study of coal mining drainage and environmental health in the Santa Catarina region, Brazil

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Abstract The concentrations and loadings of major and trace elements in coal mine drainage (CMD) from 49 abandoned mines located in the coal fields of the Brazilian state of Santa Catarina were determined. The CMD sites typically displayed a wide spatial and temporal variability in physical and geochemical conditions. The results of our CMD analyses in Santa Catarina State were used to illustrate that the geochemical processes in the rock piles can be deduced from multiple data sets. The observed relationship between the pH and constituent concentrations were attributed to (1) dilution of acidic water by near-neutral or alkaline groundwater and (2) solubility control of Al, Fe, Mn, Ba and Sr by hydroxide, sulfate, and/or carbonate minerals. The preliminary results of the CMD analyses and environmental health in the Santa Catarina region, Brazil, are discussed.

Keywords Brazilian coal mining · Coal mine drainage · Drainage management · Environmental impacts

Introduction

A coal mining project can be seen to be a valuable resource in terms of its contribution to the local and national economy and its associated impact on society (Sekine et al. 2008). However, the cost associated with reclamation, mitigation, and monitoring of improperly controlled and abandoned mines can be staggering. In addition, one of the major environmental concerns related to coal mining is the contamination of surface and ground waters as a result of surface disposal of waste rock. These waste materials typically contain variable amounts of sulfide minerals. After disposal, exposure to atmospheric oxygen and water results in sulfide oxidation and the formation of mine drainage with variable pH, SO_4^{2-} , and heavy metal content.

When coal is mined, pyrite is exposed to oxygen and water, setting off a series of reactions that can result in lowered pH (unless there are sufficient carbonates to neutralize acids produced by oxidation and hydrolysis) and the release of high concentrations of metals, such as iron (Fe), aluminum (Al), and manganese (Mn). Potentially toxic trace elements, such as arsenic (As), mercury (Hg), lead (Pb), and selenium (Se), may also be released. In addition to causing poor water quality, mine drainage can affect the substrate of a stream. Ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}) to form a precipitate on the substrate (commonly referred to as “yellow boy”) in the presence of water when the pH is greater than

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about 3.5 (Rose and Cravotta 1998). In many mine-drainage streams with a relatively high pH, precipitated iron and aluminum may coat the stream substrate and cause an unstable habitat for macro-invertebrates (Schmidt et al. 2002; Simmons et al. 2005).

The pH of a solution is an important measure for evaluating aquatic toxicity and corrosiveness (Cravotta 2008). 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 metals can be described as amphoteric, with a greater tendency to dissolve as cations at low pH or anionic species at high pH (Langmuir 1997). For example, Al hydroxide and aluminosilicate minerals have their minimum solubility at pH 6–7 (Nordstrom and Ball 1986; Bigham and Nordstrom 2000), and brief exposure to relatively low concentrations of dissolved Al can be toxic to fish and other aquatic organisms (Baker and Schofield 1982).

Anions, including SO_4^{2-} , HCO_3^- and, less commonly, Cl^- , can be elevated above background concentrations in coal mine drainage (CMD) (Cravotta 2008), and polyvalent cations such as Al^{3+} and Fe^{3+} tend to associate with such ions of opposite charge (Nordstrom 2004). Ion-pair formation, or aqueous-complexation reactions, between dissolved cations and anions can increase the total concentration of metals in a solution at equilibrium with minerals and can affect the bioavailability and toxicity of metal ions in aquatic ecosystems (e.g., Sparks 2005). Eventually, the solutions can become saturated, or reach equilibrium, depending on the various sulfate, carbonate, or hydroxide minerals that establish upper limits for the dissolved metal concentrations.

In this study, we analyzed 49 samples of abandoned CMD at mine dumps in Santa Catarina State, Brazil, identifying the geochemical processes which give rise to its acidic character and evaluating the effects of the selective spoil management on its characteristics. The variation in the water chemistry is also discussed within the framework of the results.

This preliminary study of the existing CMD in Santa Catarina State relates to minerals exposed during coal mining (coal cleaning residues, CCR) and the relevant geochemical processes that explain the origin of the main elements present.

Coal zones of Santa Catarina State

The rivers of Santa Catarina State (Tubarão, Urussanga, and Araranguá) receive the effluents generated at the coal mines. Contamination of the water resources is due to coal drainage from 134 strip mine sites covering a total area of 2,964 ha, 115 waste deposit areas on a total of 2,734 hectares, 77 sites on 58 hectares with acidic pools, and hundreds of underground mines (ABMC 2008). However, the production and circulation of acidic streams in dump areas create a problem for land reclamation as it impedes the establishment of vegetation and even causes the disappearance of already well-established vegetation (SIECESC 2008).

The contact between spoils of different permeabilities allows the frequent outflow of sub-superficial water from the banks that are interconnected with the general circulation. Soil restoration work includes the use of correctors, such as lime or ashes from lignite combustion, inorganic and organic fertilizers and, on some occasions, the spreading of a layer of topsoil. The different types of spoils dumped and the procedures used have given rise to a wide variety of physicochemical conditions at the dump surfaces.

The environmental problems are the result of 120 years of mining activity and other pollution sources. In 1980, the Santa Catarina Coal Region (Fig. 1) was designated a “Critical National Area for Pollution Control and Environmental Conservation”. Due to this grave situation, the Federal Attorney General filed suit in 1993 against the federal and state governments and coal companies, seeking environmental recovery of the areas affected by coal mining in addition to termination of the environmental degradation by the active mines. In 2000, a federal judge in Criciúma, Santa Catarina, ordered the government-run companies to establish a recovery project within 6 months that would be implemented over 3 years and encompass the damage caused by coal mining activities in the entire coal region in the southern part of the state (SIECESC 2008).

Methods and analytical procedures

Water

In this study, we characterized the physico-chemical properties of waste effluent at selected acid-producing

Fig. 1 Location of the Santa Catarina coal basin



mine sites. The field work was performed during several weather seasons in 2005 (January, March, May, July, September, November) and 2006 (February, April, October, December) and included a comprehensive and detailed exploration of the study area. Forty-nine water quality control samples, the locations of which were determined by GPS, were collected from the different restoration areas, categorized as four coal mine groups (Table 2): Lauro Muller, Criciúma, Treviso and Urussanga cities. These exact locations were chosen for the study because (1) the location showed a comparatively lower resistance than surrounding areas (i.e., an indication of CMD source material); (2) nearby wetlands showed evidence of acid mine drainage (AMD); (3) the location was readily accessible and contained existing monitoring wells; (4) nearby seeps could be used to identify the hydraulic gradient for monitoring purposes. Water samples were collected in 1-L Teflon bottles that was then split into rinsed polythene bottles; preservation was done by standard methods (Clescerial et al. 1998).

The duplicate water samples that were collected were filtered through in-line 0.45- μm capsule filters into pre-rinsed, high-density polyethylene containers.

In-stream measurements of temperature, pH, redox potential (Eh), and conductivity were made using appropriate standardized field meters. The pH and Eh of the CMD waters were measured using an Orion 290A portable pH meter and an Orion Pt electrode (Thermo Scientific, Waltham, MA). A conductivity/TDS meter model 124 (Thermo Scientific) was also used. Sub-samples of the large volume samples were collected to analyze the concentration of Fe(II) and Fe(III). Fe speciation was determined colorimetrically on site using 1,10-phenanthroline with and without a reducing agent (sodium sulfite). The remaining samples were refrigerated and transported to the laboratory.

One of the sub-samples was acidified with ultrapure HNO_3 to measure the concentration of dissolved trace elements. Total concentrations of boron (B), strontium (Sr), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), Fe, Al, silicon (Si), Mn, zinc (Zn), nickel (Ni), and cobalt (Co) were determined by inductively coupled plasma–atomic emission spectroscopy (Brigs 2002). Dissolved concentrations of minor ions were determined by ICP-MS. Sulfate, Cl^- , and NO_3^- in filtered, refrigerated samples were analyzed by ion chromatography (Crock et al. 1999).

Coal cleaning residues

Coal cleaning residues rich in clays, quartz, sulfides, carbonates, sulfates, among others were sampled using stainless steel spatulas. A total of 39 samples of CCR from four CMD-impacted regions in Santa Catarina State were collected. The samples were stored in tightly sealed plastic vials or wrapped in plastic wrap and enclosed in sealed plastic bags. The air temperature and relative humidity conditions were measured in the field with a pocket hygrometer. The samples were divided into four equal portions in the field, reduced in size by hand, and finally milled in the laboratory to provide a representative sample of around 0.5 kg for subsequent laboratory analyses. Samples from each region were blended together to obtain a composite sample used for the chemical analyses.

The samples were first dried in a furnace at 40°C for 16 h and subsequently homogenized to pass through a <0.45-mm sieve. The subsamples were then ground to 50 µm for chemical analysis. Subsamples were also taken and gradually burned in a muffle furnace at 750°C for 4 h, following the procedure described in the American Society for Testing and Materials (D 3174-89, 1991; ASTM, West Conshohocken, PA) for analyses of coal. The concentrations of the elements were determined by wet chemical and X-ray fluorescence procedures.

Powder X-ray diffraction (XRD) and qualitative chemical analysis by scanning electron microscopy (SEM) and energy dispersive X-ray detection (EDX) were used to identify the minerals present (observation on whole coal natural and/or polished surfaces). The accelerating voltage was 20 kV, and the beam current was 10⁻¹⁰A. The occurrence of mineral species was also investigated by means of an environmental SEM coupled with EDX (Querol et al. 2008) and by transmission electron microscopy (TEM) for chemical analyses of individual particles (Silva et al. 2009a). Hexane, acetone, dichloromethane, and methanol were tested as suitable suspension media. The suspension consisted of 10 ml of each of the solvents mixed with 0.5 g of dried and sieved coal cleaning residue.

Results and discussion

The high quartz contents of Brazilian coals may explain the relatively low concentrations of most

trace elements, despite their higher ash yields compared to coals from the USA and other countries. The concentrations of elements in Brazilian coal that are potential environmental or health hazards are similar to those reported for U.S. coal, but these were not observed in our samples. The data obtained on trace elements in our samples are shown in Table 1. Because of the lower calorific value, combustion by-products from Brazilian coals can be expected to have larger amounts of non-volatile elements per unit of energy than U.S. coals, but the concentrations of these elements in the Brazilian combustion by-products are diluted by the high quartz contents (Silva et al. 2009b).

Water quality

Various trace elements, such as As, Co, Cu, Pb, Ni, Se, uranium (U), and Zn, are concentrated in coal (Table 1) and are harmful to the health of aquatic and

Table 1 Average values for the trace elements in the Santa Catarina CCR (ppm)

Element	Santa Catarina (CCR) ^a	Brazilian coal ^b	World coal ^c
As	6.0–43.7	24.4	0.5–80
Ba	300	N/A	0.5–150
Be	2.2–5.1	2.2	0.5–5
Co	1.2–13.1	6.0	0.5–30
Cr	39–57	15.0	0.5–60
Cu	14.3–39.7	16.0	0.1–50
Hg	0.19	0.17	0.012
Mo	2.7–6.6	3.3	0.1–10
Ni	4–23	14.0	0.1–50
Pb	26.8–139.8	11.0	2–80
Sb	0.4–2.1	1.2	0.05–10
Se	4.3–9.4	2.8	0.2–10
Sn	3.8–5.7	N/A	0.1–5
Sr	10.3–616.1	N/A	0.5–250
Th	13.8–22.8	N/A	0.1–5
U	4.9–16	2.1	0.1–5
V	76.8–105.5	22.0	2–100
Zn	16.5–297.4	53.0	5–300

CCR, Coal cleaning residue(s)

^a Silva et al. (2007)

^b Silva et al. (2009b)

^c Swaine (1990)

terrestrial organisms (US Environmental Protection Agency 2002a, b). These were also found in the CMD water samples collected in this study (Table 2). Most trace elements tend to be adsorbed or co-precipitated oxy-hydroxide compounds of Fe, Mn, and Al that form as acidic solutions, subsequently becoming neutralized or oxygenated (Kairies 2003; Silva et al. 2010a, b). Their removal from solution decreases the direct aquatic exposure of fish to these elements. However, organisms that ingest contaminated sediments, such as macro-invertebrates and bottom-feeding fish and, consequently, aquatic and terrestrial animals at higher trophic levels can accumulate toxic levels of some elements in their tissues (Smith and Huyck 1999). Regardless of the trace-element

composition, the accumulation of Fe or Al precipitates can encrust stream beds and aquatic plants, destroying the physical habitat (Earle and Callaghan 1998).

The quality of the drainage water is the final result of a combination of complex geochemical processes in which numerous ions from different sources are involved, principally those from the oxidation of sulfides and the accelerated hydrolysis of the accompanying minerals. The composition of these streams is thus determined by the type of material through which they flow as well as the time of contact with that material. The influence of these factors is reflected in the wide variation of the Eh–pH conditions and the ion concentrations found.

CMD sites typically display a wide spatial and temporal variability in physical and geochemical conditions (Carlson et al. 2002; Kairies 2003; Mugunthan et al. 2004; Lambert et al. 2004; Oliveira and Silva 2006), leading to an ensemble of solution compositions that differ greatly and which undergo changes depending on place and time. Because subsequent chemical reactions as well as some of the physical conditions in the mine wastes are linked to the specific composition of the solution in a nonlinear manner, this process is dependent not only upon the “average” chemistry of the solution, but also upon the extreme chemistry. This nonlinear feedback can produce “hot spots” in the wastes where reaction rates are very high, leading to high heat production rates and other geochemical and physical effects.

Our water samples showed a certain variability in Eh–pH conditions and ionic concentrations that illustrates the great diversity of geochemical conditions in the drainage systems (Table 2). They also showed some characteristics that are determined by sulfide oxidation, thereby markedly distinguishing them from natural waters; sulfide oxidation affected, to a greater or lesser extent, all analyzed water samples (e.g., high concentration of SO_4^{2-} ; Table 2). A high concentration of sulfate (2.1–3.2 g/L) is important in these waters for the metabolic requirement of the anion-oxidative Fe^{2+} by chemolithotrophic, acidophilic bacteria, such as *T. ferroxidans* and also for thermodynamic control of the formation kinetics of various sulfate compounds (jarosite, schwertmannite, ferrihydrite, goethite, etc.) from mine drainage systems (Kairies 2003). Severe oxidation of sulfides was found in the cuts and silt basins produced by the actions of

Table 2 Average values of the chemical-physical properties of the coal mine drainage waters

Field measurements	Group 1	Group 2	Group 3	Group 4
pH	2.71	2.87	3.85	2.44
Eh (mV)	493	470	372	459
Temperature (°C)	23.7	20.3	22.9	23.3
DO (mg/L)	7.6	8.9	9.4	9.2
EC (mS/cm)	2.79	2.68	1.69	3.96
SO_4^{2-} (g/L)	2.52	2.41	2.10	3.24
As (µg/L)	185	215	<100	208
Cr (mg/L)	0.51	0.37	0.09	0.18
Si (mg/L)	13.9	9.3	2.5	7.3
Na (mg/L)	9.6	5.4	2.8	7.8
Fe (mg/L)	1,703	1,331	1,297	1,531
Fe^{2+} (mg/L)	985	654	986	756
Fe^{3+} (mg/L)	708	731	206	875
Al (mg/L)	71	82	60	79
Sr (mg/L)	4.53	4.98	2.76	1.97
Ca (mg/L)	186.9	170.5	165.4	241.7
Mg (mg/L)	88	75	53	97
Mn (mg/L)	42	39	30	41
B (mg/L)	0.92	0.71	1.42	0.87
Zn (mg/L)	11.2	13.9	8.7	17.6
Pb (µg/L)	31	29	11	36
Cl^- (mg/L)	211.9	174.8	198.9	235.7
NO_3^- (mg/L)	86.2	37.9	ND	21.5

Eh, Redox potential; DO, dissolved oxygen; EC, electrical conductivity

Group 1, Lauro Muller—23 coal mining discharges; Group 2, Criciúma and Içara—17 coal mining discharges; Group 3, Treviso and Siderópolis—6 coal mining discharges; Group 4, Urussanga—3 coal mining discharges

O₂ and Fe(III). When the ferric iron is present in significant concentrations ($\text{Fe}^{3+} > \text{Fe}^{2+}$, $\text{Eh} > 500$ mV) and the pH is < 3.5 , oxidation kinetics and the release of protons are fast and intense. The concentrations of dissolved Fe in the samples of the CMD waters under study varied between 1,297 and 1,703 mg/L (Table 2). High concentrations of dissolved Fe^{3+} (206–875 mg/L) were found only in the most acidic streams (Table 2).

The Eh values also varied widely, although the most common range was between 372 and 493 mV (Table 2). Most of the Eh–pH conditions commonly found in the dump waters were, therefore, acidic and oxidizing (Table 2). The association between high acidity and high Eh values is mainly due to the presence of significant quantities of dissolved Fe^{3+} , which acts as a more effective oxidizing agent than O₂. An excellent correlation was found between electrical conductivity (EC) and (1) total dissolved solids ($r = 0.92$, $P = 0.009$) and (2) dissolved SO_4^{2-} ($r = 0.95$, $P = 0.001$), which confirms conductivity as a good indicator of the degree of contamination of the CMD stream waters, especially when coupled with pH/Eh measurements (Table 2). Redox conditions are of particular importance if metals occur as sparingly soluble reduced or oxidized species. Changes in the Eh are generally closely linked to a change in the pH. Under specific conditions, the oxidation of sulfide may lead to the production of acidic solutions.

High values of dissolved oxygen (DO; Table 2) were typically associated with rapidly flowing CDM from large, abandoned open drainage tunnels.

The high acidity generated during the oxidizing process gives rise to accelerated hydrolysis of the other minerals in the spoil materials (Lambert et al. 2004), causing large quantities of the constituent elements to be made soluble. The average contents of Ca, K, Mg, and Na we identified in the analyzed CMD waters suggest an effective dissolution of the abundant aluminosilicates (especially chlorite, but also sericite, K-feldspar, and albite) and rare carbonates (calcite, dolomite, ankerite) at the mine sites. The processes of sulfide oxidation and mineral hydrolysis have given rise to the mobilization of heavy metals, yielding abnormally high concentrations of these in the streams. This was especially true for Mn, for which values of up to 140 mg/L were determined. Concentrations of Mn, Zn, Ni, and Co were strongly correlated with each other and with the

SO_4^{2-} concentration (coefficients of correlation 0.73–0.87, $P = 0.001$).

The resulting drainage water has a high ionic strength. Finally, the ionic strength of the streams is determined by the extent of the influence of sulfide oxidation, as is seen by the extremely strong correlation between EC and the concentration of sulfates in the water ($r = 0.95$, $P = 0.001$).

Study of elements and minerals

For many years coal mining activities and coal production represented the largest industrial undertaking in southern Santa Catarina. However, in the past, coal mining was carried out with little regard for the environment, and it was the principal cause of water pollution in the region (SIECESC 2008).

The geology and geochemistry of the ore-bearing rocks and, to some extent, the ore processing method employed at these mines have had a considerable effect on the quality of drainage water. The change in the morphology of the land, the removal of vegetation, the random disposal of solid waste, the increased erosion and the instability of the slopes, and the opening of underground caves have all resulted in soil degradation. In addition, the seepage of waste deposits, principally due to the intense rains in the region, generates acid drainage from the abandoned mines that reaches rivers and streams of the region, aggravating the complexity of the problem.

The poorly maintained piles of CCR, which have received inadequate management in terms of compacting, impermeable coverings, and replanting, have also led to processes of spontaneous combustion, causing problems of air pollution. The tailings have also created acid run-off and led to the siltation of the rivers and streams near the piles.

The high solubilities of the various carbonate minerals compared to those of dissolved Ca, Fe, Mn, Pb, and Zn, particularly at $\text{pH} < 6$, indicate that carbonate minerals could be important sources of dissolved constituents in the mine drainage samples. However, additional qualitative and quantitative information on the composition and solubilities of impure carbonate minerals would be necessary to determine the actual sources and sinks of these elements. The oxidation of sulfides could account for the significant sulfate and As values. Carbonate dissolution is probably also responsible for the augmented levels of Ca

and Mg. Fe and Zn concentrations are probably the result of both sulfide oxidation and the dissolution of Fe-bearing carbonates and aluminosilicates. The concentrations of individual elements in the drainage waters reflect, in part, the abundance of these elements in the deposits drained by the waters.

Brazilian coal contains a considerable amount of pyrite (Pires and Querol 2004; Kalkreuth et al. 2006; Silva et al. 2009b), and pyrite has recently been shown to spontaneously generate hydrogen peroxide (H_2O_2 ; Borda et al. 2001; Cohn et al. 2005) and hydroxyl radicals ($\cdot OH$; Cohn et al. 2004) when placed in water. The formation of these reactive oxygen species (ROS) also explains the recent observation that aqueous pyrite slurries degrade yeast RNA, ribosomal RNA, and DNA (Cohn et al. 2006). Pyrite is thought to form H_2O_2 through the Fe-catalyzed Haber–Weiss reactions.

Alkalies The average contents of Na (2.8–9.6 mg/L) in the analyzed CMD waters suggest an effective dissolution of the abundant clay minerals, aluminosilicates, and carbonates at the mine sites. Water

quality criteria have not been established for the alkali earth metals.

The clay minerals also occurred as individual aggregates or in association with pyrite and calcite. Common minor elements present in illite were titanium (Ti) and Fe, while additional elements, such as Cl, Na, Mg, Ca, and S, were detected in other clay particles. The XRD analyses performed detected plagioclase, K-feldspar, subangular zircon, and traces of mullite, melilite, and talc. K-feldspar (Fig. 2a), and zircon (Fig. 2b) were also observed in the SEM analyses.

Alkaline earths Calcium and Mg were the dominant alkaline earth cations, but Sr was present at the highest concentration (4.98 mg/L) (Table 2). The concentrations of Mg, Ca, and Sr in the CMD waters were elevated in comparison to those of average river water (Silva et al. 2007) and one order of magnitude lower than those of seawater, suggesting an effective dissolution of carbonates (e.g., calcite) clay minerals, and/or aluminosilicates (especially K-feldspar).

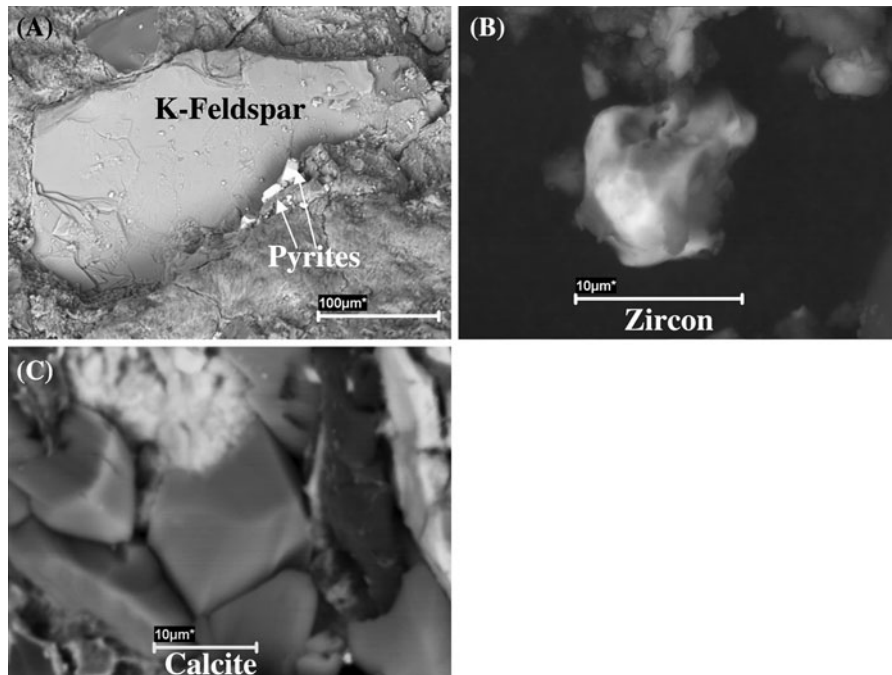


Fig. 2 Scanning electron microscopy (SEM) images that show silicates and carbonate minerals identified in the coal cleaning residue (CCR) samples. **a** K-Feldspar, **b** zircon, **c** calcite

Calcite (Fig. 2c) was found to be a common mineral in all four CCR composites. Other carbonate minerals detected by XRD analyses were aragonite, dolomite, ankerite, siderite, and oligonite. Carbonates can be beneficial by providing a buffering capacity which helps neutralize the acid formed by the oxidation of sulfides.

Transition metals The processes of sulfide oxidation and mineral hydrolysis have given rise to the mobilization of heavy metals, causing abnormally high concentrations of these metals in the streams. This was especially true for Mn, for which values of at least 30 mg/L (Table 2) were seen. Mn and Zn levels were strongly correlated with each other and with SO_4^{2-} concentration (coefficients of correlation 0.73–0.87, $P = 0.001$). The predominant transition metals, given in order of abundance, were $\text{Fe} > \text{Mn} > \text{Zn} > \text{Cr}$ (chromium) (Table 2). The median concentrations of these elements were elevated compared to those of river water (Silva et al. 2007), seawater, and various aquatic protection criteria, but they exceeded the average in exponential order.

The narrow range in the composition of the CMD compared to drainage from metal mines is due to the mineralogy of typical coal-bearing sedimentary rocks, which have limited variability and contain relatively lower levels of sulfide minerals and some metals as relatively inert organic compounds (Cravotta 2008). Although Fe-sulfide and calcareous minerals are present in coal-bearing rock at a very low level, these minerals are highly reactive and are mainly responsible for the CMD chemistry. In contrast, metal

deposits in diverse geologic settings can contain disseminated to massive concentrations of pyrite, pyrrhotite, other metal-bearing sulfides, and a wide variety of associated minerals. The wide variety of minerals in various ore deposits and host rocks influences the resultant drainage composition. The rate of weathering of minerals extracted from coal mines can be accelerated due to the ore processing methods, which greatly reduce grain size and concentrate the reactive sulfides in mine tailings.

The average contents of Fe, SO_4^{2-} , and Zn found in the analyzed CMD suggest an effective dissolution of the abundant pyrite (Fig. 3a), sphalerite (Fig. 3b), marcasite, pyrrhotite, and galena. Zn concentrations in the surface water samples were much higher in the dry season than in the wet one, but they were generally persistent in the entire drainage basin and throughout varied pH regimes. This persistence of Zn values, even in near-neutral pH regimes, is not abnormal. Herr and Gray (1995) and Foose et al. (1986) independently observed that Zn sulfides, particularly sphalerite, exhibit a high solubility in acid waters. In addition, because Zn is not readily absorbed onto particulates, once dissolved, it can persist over a wide pH range.

Metalloids X-ray diffraction patterns indicated that quartz was a major constituent in all four CCR composites. Other oxides and hydroxides detected by XRD analyses include hematite, maghemite, magnetite, goethite, gibbsite, brucite, magnesioferrite, gypsum, and calcium ferrite. Some of these phases may be products of the oxidation of pyrite and reactions with

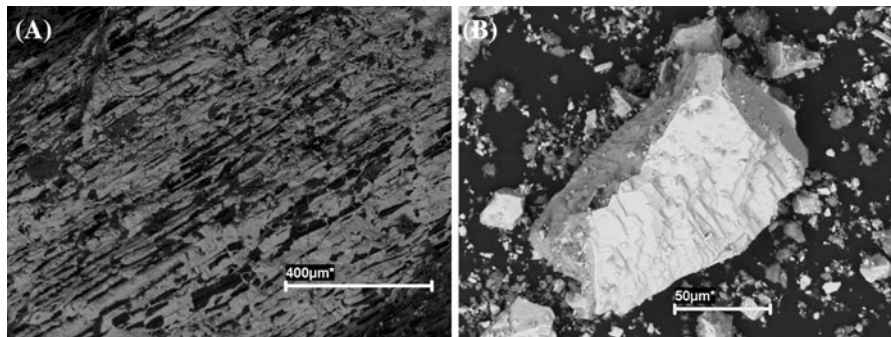


Fig. 3 Sulfides minerals identified in the CCR (SEM image). **a** Pyrite may also occur as cell- or cavity-infilling or as replacement of the maceral components in the Santa Catarina CCR, **b** powder shalerite in the Santa Catarina CCR

calcite. Quartz, bruceite, goethite, gibbsite, and hematite were detected by SEM/TEM (transmission electron microscopy) characterization.

The average contents of Si found in the analyzed CMD (Table 2) suggests an effective dissolution of the abundant silicates and rare carbonates at the mine sites. Si was the dominant metalloid element, ranging in concentration from 2.5 to 13.9 mg/L (Table 2), suggesting an effective quartz and silicate dissolution, with the median Si concentration in the CMD water being comparable.

Although the two highest concentrations of As were in low-pH and high-Eh discharges, the concentration of As generally increased with increasing pH and decreasing Eh (Cravotta 2008). Concentrations of As were positively correlated with Cl ($r = 0.81$, $P = 0.003$) and other halides, such as Fe ($r = 0.76$, $P = 0.001$) and SO_4^{2-} ($r = 0.79$, $P = 0.002$; in order of decreased significance). Attenuation of As in mine discharges results from (1) adsorption to ochre-forming “ $\text{Fe}(\text{OH})_3$ ” that precipitates under oxidizing conditions and (2) to a lesser degree, dilution. The same mechanisms apply to other mineral constituents, particularly those that are affected by the oxidation of sulfides or adsorption.

Others metals After Fe, Al was the second most abundant metal, being typically present in the milligram per liter range in acidic samples (Table 2). Most of the other metals in the various CMD samples were below the limits of detection. Pb was detected at a maximum concentration of 36 ppm, and galena was detected by XRD and SEM characterization.

Environmental health and dynamics of surfaces waters

The toxicity in the waste was mainly due to the presence of different metals, namely, Pd, cadmium (Cd), As, Cr, among others, with Al also being toxic to fish. The residue released during the process could be either recycled for further processing or sent for safe disposal without affecting human health.

At surface coal mines, where the overburden chemical processes are dominated by either calcareous or highly pyritic strata, the prediction of post-reclamation water quality is relatively straightforward.

However, at sites where neither of the two abovementioned processes clearly predominates, predicting post-reclamation water quality can be complex. Ten years ago, researchers and scientists (Silva 2006; SIECESC 2008) found that at these more difficult-to-predict sites, overburden analysis procedures generally used to predict post-reclamation water quality at surface coal mines were no more reliable than flipping a coin. Since this time, a great deal of effort has gone into improving the procedures (ABMC 2008). It should be noted that this study reports only on those components relevant to the prediction of water quality at surface mines where coal is being mined. Although the general approach is similar, the issues and interpretation of results can be quite different for hard rock operations and underground coal mining.

Statistical analysis of surface water quality data in coal mining areas from unmined, abandoned mine, and reclaimed sites in Santa Catarina showed that there were significant differences in stream flow pH, specific conductance, alkalinity, and concentrations of metals between abandoned mine, and unmined sites (SIECESC 2008). Streams at reclaimed sites had average pH values and Al concentrations similar to those in unmined sites. The average specific conductance and sulfate concentrations of stream water were about the same at reclaimed and abandoned-mine sites, but they were significantly lower at unmined sites; specific conductance and sulfate concentration actually proved to be reliable indicators of basins that had been disturbed by mining (Oliveira and Silva 2006).

In many places, the surface water was found to be contaminated before ingress to mines due to percolation through exposed solid wastes or mine waste piles or from contact with untreated sewage. Once into the mines, water with oxidated products became acidic, with the pH of the acid mine drainage increasing as a result of dilution with fresh water.

In addition to containing high levels of metals, soluble salts can temporarily sequester and subsequently release trace metals of potential environmental concern. Cd, for example, typically occurs as a minor element in sphalerite. Weathering of sphalerite leads to the precipitation of Zn salts, such as goslarite or bianchite, or to the incorporation of Zn in solid solutions of Fe^{2+} -bearing minerals, such as those of the melanterite group.

Conclusions

Regional water quality data were collected in 2005–2006 at 49 CMD sites in Santa Catarina State, Brazil. The variability in the CMD hydro-geochemistry enables different conditions of pH, Eh, DO, oxidation rate of Fe(II), and metal contents to be determined among the studied effluents. These different conditions have strong implications as they introduce additional difficulties into the design of corrective measures at the mine sites.

The redox chemistry of the CMD systems is basically controlled by the oxidation of Fe(II), which seems to be strongly catalyzed by acidophilic, Fe-oxidizing bacteria and is perfectly correlated with the electronic potential (Eh) of the acid solutions.

The acidity of CMD also depends on Fe(III) and Al content; the hydrolysis of these substances results in important increases in acidity and provokes the buffering of the AMD systems.

Our results demonstrate that selective management of spoil sites is the restoration practice that offers the best protection against contamination of surface and subsurface waters, providing a suitable procedure to apply in the future construction of dump surfaces. Improvement in the quality of drainage systems using this practice can significantly reduce the cost of treatment in the purification plant prior to effluents being discharged to the receiving catchment zone.

Future work should investigate the relationships between the stability of surface precipitates.

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