

Santa Catarina coal mining: acid mine drainage characterization and neutralization

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Abstract Acid mine drainage (AMD) is an aqueous solution generally characterized by having pH below 3 and diversity dissolved metals. Due to these characteristics, AMD represents major environmental risks, in particular, water impacts as a result of solubilization and mobilization of metals. For this reason, the aim of this study is the characterization and neutralization, using NaOH up to pH 6, of three AMDs samples (CS, EDR3 and SS16). Removals above 70% occurred for Al and Fe of three samples; K, Mg and Zn for CS and EDR3; Cu for CS; and Ca for EDR3. However, Pb and Mn remained above permissible limits.

Key Words characterization, acid mine drainage (AMD), neutralization

Introduction

Brazil is the holder of one of the largest coal reserves in Latin America (Smith *et al.* 2006). The coal production is concentrated in the southern region, where 74% of active mines are in the state of Santa Catarina, 22% in Rio Grande do Sul and the rest in Paraná (Neves and Silva 2007).

One of the major impacts caused by coal mining activities is the water pollution by acid mine drainage (AMD). These environmental problems are related to the pH values typically below 3 and the diversity of dissolved metals (such as iron, aluminum, manganese and traces of lead, zinc and copper) common characteristics of AMD (Wei *et al.*, 2008).

The AMD generation occurs with the exposure of sulfide minerals present in tailing mining to the combined action of atmospheric oxygen and water. Besides the chemical reactions there is also the action of acidophilic bacteria, *Thiobacillus* spp., which convert Fe^{2+} to Fe^{3+} (Kountopoulos 1998).

The typical treatment of AMD is the neutralization and precipitation of metal hydroxides (Campaner and Silva 2009).

The active process by neutralization/precipitation has been preferred by the coal mining companies in Brazil. An alternative form of AMD treatment is being studied by Souza *et al.* (2009), the use of dry coating.

In the present study, it was used the AMD from the cell that did not receive the dry coating, from the above mentioned paper, an AMD collected in the abandoned coal bank and also an AMD from the basin coal adduction. The aim was to characterize the three samples before and after neutralization with sodium hydroxide and compare the results between samples and the law parameters.

The discharge parameters of AMD after treatment follow the guidelines of Resolution CONAMA n°357 of 17 March 2005, laying down the

conditions and discharge standards for industrial effluents.

Methods

The methodology can be described in five stages: **1st stage: Collect**

AMD samples were collected from three locations in Santa Catarina: a module for waste test in a local coal company, of the abandoned coal bank and a basin coal adduction, identified in this paper as CS, SS16 and EDR3, respectively. The first sample was collected in the last week of October 2009 and the other two in the first week of December the same year. The collection locals choice was made to obtain samples with different characteristics, able to represent different situations generating AMD:

- The AMD collected in the waste module under test has the same characteristics of drainages found in acidic lakes around abandoned tailings piles. According to Gomes (2004), there are 77 lakes and 115 areas with acidic tailings deposits in southern Santa Catarina.
- The SS16 sample from the abandoned coal bank, represents AMDs generated in the same situation and, as such, it is estimated to occur about 1,000 abandoned coal bank and, by November 2008, approximately 768 were registered in this situation in the region (Amaral *et al.* 2009).
- The AMD collected in the basin coal adduction has high concentration of dissolved metals, once it receives the waste generated throughout the coal unit.

The Figure 1 shows the AMD collection locals.

It is noteworthy that the composition of each AMD varies with productivity, climatic conditions, coal quality explored, among other factors, and therefore it cannot be said that the samples studied are representative of all situations even when derived from similar sources.



Figure 1 AMD collection locals: A) Waste module – CS; B) Abandoned coal bank – SS16; C) Basin coal ad-duction – EDR3

2nd stage: Characterization

After the collection, the samples were acidified with nitric acid to pH 1 in order to preserve samples for later analysis of atomic absorption spectrometry to identify the concentration of the following metals: Al, Cd, Cr, Cu, Fe, Mn, Mg, Ni, Pb and Zn.

The content of Fe⁺³ was determined by titration and the Fe⁺² by difference from the total Fe previously determined.

The determination of Ca, K, sulfates and chlorides was made through ion chromatography. For analysis in chromatograph the samples were previously filtered through a membrane of 0.45µm.

3rd stage: Oxidation

Whereas the aim of this study is to evaluate the metals removal efficiency in the treatment of AMD through neutralization to pH 6, it was decided to carry out the oxidation of CS sample before neutralization by addition of hydrogen peroxide, agitation and pumping air (WEI *et al.* 2005) for oxidation of Fe⁺² initially present in solution in Fe⁺³, this happened because the iron can be present at AMD in two oxidation states (II and III) and the two forms behave quite uneven: while the concentration of Fe⁺³ is equal to 10⁻⁴M for a solution pH of 3, a pH of about 8 is needed to

achieve the same concentration of the ion Fe⁺² (Johnson and Hakkberg 2005).

4th and 5th stages: Neutralization and Reanalysis

The pH of the samples was adjusted to 6, using constant agitation and sodium hydroxide (4M) (Figure 2). Sodium hydroxide (NaOH) is about 1.5 times more effective to the neutralization than lime (CaO), though at higher cost (Johnson and Hakkberg 2005). The sludge formed by the precipitation of metals was separated from the solution by filtration on filter paper for rapid filtration (Figure 3), the supernatant was characterized using the same parameters of the raw samples, according to 2nd stage. After the samples neutralizations they received new identifications: CS – CSN6, SS16 – SS16N6 and EDR3 – EDR3N6.

Results and Discussion

The results obtained by chemical analysis are compiled in Table 1, as well as the maximum allowable limits for effluent discharge, according to CONAMA Resolution 357/2005.

Observing Table 1, it was verified that the CS AMD metals with higher concentrations are: Al, Ca, Fe and K which together account for approximately 98.16% of total metals present in this sample. Mn, Mg and Zn have intermediate

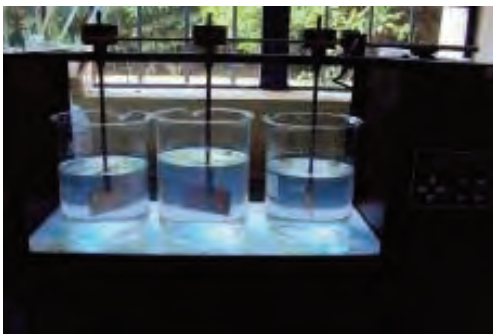


Figure 2 Neutralization: SS16 AMD.



Figure 3 Filtration: CS AMD.

Table 1 Chemical characterization of the AMD samples and limits according to CONAMA 357/2005.

Parameter	Concentration (mg.L ⁻¹)						CONAMA 357/2005
	CS	CSN6	SS16	SS16N6	EDR3	EDR3N6	
pH	1.92	6.0	3.05	6.0	1.89	6.0	5.0 - 9.0
Al	11820.00	67.50	269.00	75.00	427.00	< 0.15	--
Ca	1156.44	723.56	143.07	114.64	1609.33	314.04	--
Cd	0.39	0.12	< 0.005	< 0.005	< 0.005	< 0.005	0.20
Cr	0.27	0.08	< 0.003	< 0.003	0.02	0.02	0.50
Cu	7.77	0.11	< 0.0015	< 0.0015	0.05	0.02	1.00
Fe total	7806.00	1.62	0.65	0.07	127.80	0.02	15.00
Fe⁺²	4257.24	0	0.65	0	75.03	0	
Fe⁺³	3548.76	1.62	< 0.005	0.07	52.05	0.02	
K	1236.07	< 0.001	64.07	63.89	1738.52	58.12	--
Mn	139.30	23.50	5.45	1.15	5.45	5.44	1.00
Mg	93.66	< 0.0015	19.24	14.57	154.53	35.03	--
Ni	10.09	0.54	0.16	0.16	0.37	0.32	2.00
Pb	1.57	0.85	< 0.05	< 0.05	< 0.05	< 0.05	0.50
Zn	159.70	0.51	0.56	0.49	8.50	< 0.0015	5.00
Cl⁻	484.72	384.57	69.76	56.22	1513.42	851.71	--
SO₄⁻²	43772.28	21085.89	3671.45	466.43	3671.45	1510.27	--

concentrations, 139.30, 159.70 and 93.66 mg. L⁻¹, respectively. Since the levels of Cd, Cr, Cu, Ni and Pb are smaller than 10 mg.L⁻¹ and the sum of these metals total 0.09% of metals present in this sample. The high sulphate content of the samples EDR3 and CS, is 65% and 40% respectively, and low pH, 1.92 and 1.89 respectively are related to the concentration of sulfuric acid and free hydrogen ions (H⁺) (Gaikwad and Gupta 2008).

In the sample EDR3 the metals with the greatest concentration are Ca and K, with about 36%, followed by Al, Fe and Mg which together represent 7.66% of the total sample. And the sum of the other metals (Cr, Cu, Mn, Ni and Zn) does not exceed 14.39 mg. L⁻¹, which corresponds to less than 0.2%.

Also in Table 1, it was verified that in the SS16 sample the concentrations of Fe, Zn and Ni are smaller than 1mg/L and the content of Ca and Al correspond to 82.05% of the total metals present. The Mn concentration is less than 10 mg. L⁻¹ and K is around 60 mg. L⁻¹. The concentration of chlorides totals 1.6% of the total, and high sulfate concentration, 3671.25 mg. L⁻¹, explains the low sample pH: 3.05.

In all samples, among the five metals with the highest concentration appear K, Ca and Al.

Still in the analysis of Table 1, it was verified that some metals present in the CS AMD are not present in the EDR3 AMD or SS16 AMD, such as Cd, Cr, Cu and Pb. Another relevant observation is that even the elements that are common to the three samples have different concentrations. These differences among samples may be related

to the quality and composition of raw material extracted layer (where the coal was extracted – local geology), with the types of rocks and mineral at the site of training and AMD passage, since it has a high capacity for leaching of elements present in the ore and surrounding rocks in the mined area (Campaner and Silva 2009).

Another factor influencing the AMDs composition is the presence or absence of acidophilus bacteria in them. Since the presence of acidophilus bacteria increases the rate of oxidation of Fe²⁺ to Fe³⁺. These bacteria live and grow only in acidic pH ranging between 1.5 and 3 (Garcia Jr. 1995; Blodau 2006).

The influence of the factors above described in the samples, can be visually identified in the coloration in which they appear: EDR3 and CS with reddish coloration, justified by the presence of Fe(OH)₃ and colorless SS16 AMD. This visual analysis was confirmed by the titrimetric of the Fe³⁺ found in the CS sample (3548.76 mg. L⁻¹) and EDR3 (52.05 mg. L⁻¹), while in the SS16 sample all the iron present appears in the form of Fe⁺².

In addition, there are differences in origin of the samples, since the SS16 sample comes from abandoned coal bank while the EDR3 sample was obtained from a basin coal adduction that receives all the effluent generated in a coal unit, including AMD coming from the tailing piles. Yet the CS AMD was generated from a waste module without dry coating, in other words, the coal tailings were exposed directly to weather and, it is known, that the pyrite in contact with air (oxygen) and water oxidizes and starts hydrolysis reactions,

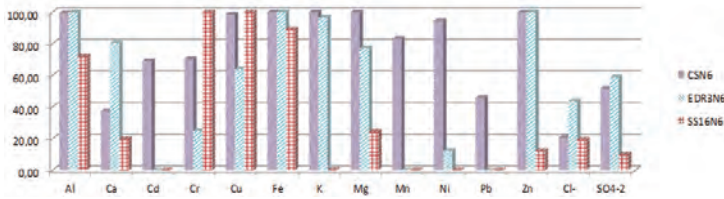


Figure 4 Removal percentages of the parameters after AMD's neutralization.

that produce sulfuric acid (H₂SO₄) and free hydrogen ions (H⁺), acidifying the medium (Kontopoulos 1998; Gaikwad and Gupta 2008).

Despite that the following metals: Cd, Cr, Cu, Pb, Ni, Mn and Zn are in smaller proportions in the samples, their presence can not be ignored, since these metals pose a risk to health and the environment, and therefore, should be removed from AMD until the maximum extent permitted by CONAMA Resolution 357/2005 for its final disposal as an industrial effluent.

The pHs 1.92, 3.05 and 1.89, of initial AMDs, as well as initial metals concentration: Fe, Cd, Ni, Pb and Zn do not meet the emission effluent limits established in Brazilian legislation (CONAMA 357/2005). Thus, the AMD physical-chemical treatment should be performed as a primary step. The sludge generated in the neutralization process must be correctly disposed or treated in order to recover the metals present in sludge.

The removal percentages after neutralization of the AMD samples in pH 6 are shown in Figure 3, for each of the parameters analyzed in each of the three samples.

It is known that the metals removal from AMD in a single step should occur in a pH range of 6 to 9. This is because the precipitation pHs of the main metals are: Fe³⁺ > 3.5, Fe²⁺ > 8.0, Al³⁺ > 4.5 and < 9.0, Mn²⁺ > 8.5 (Menezes 2009). However, the presence of other substances, such as in multi metallic systems, may interfere these pH values (Ayres *et al.* 1994).

It is observed that even after neutralization with 4M NaOH to pH 6, the Pb concentration to the sample CSN6 and Mn for all three samples extrapolated the maximum extent permitted by law.

In the sample CSN6, the Pb concentration was equal to 0.85 mgL⁻¹, of which the limit is 0.50 mgL⁻¹ and Mn appeared 23.5 times greater than the maximum allowed, while in SS16N6 exceeded only 0.15 mg. L⁻¹. In the EDR3, the Mn content is 5 times higher than allowed, as shown in Table 1.

In Figure 3 it is possible to observe that the removal percentages above 98% occurred in the CS sample for the elements: Al, Cu, Fe, K, Mg and Zn; in the EDR3 sample for Al, Fe, K and Zn, and in the SS16 for Cu and Cr.

As for the metals Cd and Cr of CS sample, the removal percentage was approximately 70% and

for sulphate about 50%. For Mn and Ni, the removal percentage was higher than 80%, in the same sample, the Ca and Pb removal concentration was around 40% and chloride in approximately 20%.

In the sample SS16, the removal percentage Fe and Al was more than 70%, while the Ca and Mg showed around 20% removal. Still in the same sample, the removal percentages of Zn and chlorides were approximately 15% and the K less than 1%.

Although the precipitation pH of most metals such as Fe²⁺, Mn, Pb, Mg, Cu, Ni, Zn, Cd, Cr and Ca are higher than the pH used in this work (6), the reduction in these metals concentration after treatment was due to co-precipitation through the action of ferric hydroxide and also of aluminum hydroxide formed during the neutralization process.

With the exception of Ni in the sample SS16N6, when the elements are shown in Figure 4 as a zero percentage because they weren't part of the composition of the raw sample.

The differences in the behavior of the samples may have been influenced due to the difference in the initial pH of the samples, the content of sulfates and chlorides. In addition to co-precipitation that can occur in other metals present in the AMD with the ferric hydroxide due to the potential difference among metals in solution (Blodau 2006).

Comparing the results obtained for SS16 sample with those presented by WEI *et al.* (2005), it is verified that both have similar characteristics and behavior. While the CS and the EDR3 samples have more than 20 times the amount of AMD sulfates characterized by the above author. This difference in concentration of sulfate can influence the solubility product of salt metal in the sample by increasing the precipitation of metals and their subsequent removal.

Conclusions

From the characterization results, it was concluded that in all samples, among the five metals with the highest concentration, K, Ca and Al appear.

The results presented for the removal percentage of metals after neutralization can conclude that this treatment was efficient (removal percentage above 70%) for Al and Fe of the three samples;

K, Mg and Zn for CSN6 and EDR3N6 samples; Cu for CSN6 sample, and Ca for EDR3N6 sample. Pb and Mn, even after treatment, still exceeded the limits allowed by CONAMA Resolution 357/2005.

It was also concluded that the overall removal percentage after treatment of AMD, was higher for the sample CS (removal percent higher than 97%), followed by the sample EDR3 (70%), while for sample SS16, the removal percentage was lower than 50%.

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