

## ACID ROCK DRAINAGE I - LABORATORY STUDIES ON ACID GENERATION FROM A COAL MINE OVERBURDEN

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### ABSTRACT

The paper reports experiments on acid generation from sulfide - bearing overburden of Candiota Coal mine which is located in the state of Rio Grande do Sul, southern Brazil. This is the first of a two part laboratory study to develop an abatement strategy for acid rock drainage in Candiota. In this part of the study the aim was to characterize the overburden and test an experimental apparatus which enabled easy follow up of the ARD and also was adequate to simulate the actual field conditions. Lysimeters were used for this purpose. Results proved satisfactory and the same apparatus will be used in further lab tests to design geochemical barriers to abate ARD in a subsequent phase of the program designed by the research team.

### INTRODUCTION

Several evidences of acid rock drainage (ARD) from overburden in Candiota Mine have been reported in recent years. In order to address systematically this issue, the Brazilian Centre for Mineral Technology - CETEM has proposed a test program to develop engineering solutions to abate ARD in the mine, based on consistent laboratory data. It was conceived in two phases. Phase I was aimed at the characterization of the acid generating material and at the definition of an experimental set up which enabled the simulation of ARD in lab scale. This experimental apparatus should also allow a careful follow up of the acid generating process that takes place when the overburden of Candiota is exposed to the atmosphere and the continuous action of rain. Phase II will address the abatement of acid generation by studying the formation of a lime/silicate geochemical barrier to prevent acid drainage. Results of this second phase of the study will be published elsewhere.

### DESCRIPTION OF THE STUDY AREA

The Candiota Coal Mine is operated by Companhia Riograndense de Mineração - CRM, a State owned company and it is located in a subtropical region in southern Brazil close to the border of Republic of Uruguay as shown in Figure 1. The operation is headquartered in the village of Candiota which is about 2000 kilometres away from Brasilia and 410 kilometers from Porto Alegre, the State's capital city. The local population is 12,000 people and the main economic activities in the region are coal mining, power generation, cattle breeding and rice cropping. The local landscape is mainly dominated by small and smooth elevations locally called *coxilhas* which are usually not higher than 100 ft and covered by pastures.



Figure 1. Location of Candiota Mine (Mina Candiota)

Temperatures vary over a wide range in Candiota during the year. From a mild and rainy winter ( $-4^{\circ}\text{C}$  in July) to a hot summer ( $+40^{\circ}\text{C}$  in January). The average temperature is about  $17^{\circ}\text{C}$  though. Even in severe winters, snow is rare and when temperature drops below zero degrees Celsius, heavy frosts occur. The cumulative annual rainfall is 1,400 mm. Rains are more intense from July to October. The relative air humidity is slightly higher in winter (83%) than in summer (73%) and the region has about 2,440 hours of sun/year (SOARES et al. 2000).

Coal reserves represent a significant fraction of the non-renewable energy resources in Brazil and the largest deposits are located in Rio Grande do Sul. They account for 28 billion tons or 89.3% of Country's total reserves. Candiota, the State's larger deposit, is equivalent to 44 % of its reserves or 38% of the Country's total reserve (DNPM, 1995).

Candiota Mine produces about 100,000t of coal per month and the company has 15 claims in the region, which are called *malhas* numbered 1 to 15. The whole area is approximately 65km by 25km encompassing a coal reserve of almost 12 billion tons (MME 1985). The operation started back in 1961 and since then, different areas have been mined. The present target is a 1.9 million ha area called Malha 4 which is strip mined with a 38 cubic yard walking dragline.

The ash content of Candiota coal is particularly high, averaging 50.3 % (dry basis) in the run of mine (ROM) and its sulphur content is 2.4%. Heavy metals are present in the ore body and a sulphide - rich overburden generates acid drainage when exposed to oxidising conditions. The ROM is crushed and conveyed to a thermo - power station 4 km away from the mine site. The ash which results from coal burning, is partially consumed by the local cement industry but most of it goes back to mine and fills some of the empty spaces created in mined areas.

As a result of both mining process and ore characteristics, large amounts of wastes are generated on site. Weathering of these wastes propitiates bacteria development (*Thiobacillus ferrooxidans* *Thiobacillus thiooxidans* species), which accelerate pyrite oxidation producing ARD.

SOLARI and FIELDER (1988), discuss the environmental impact of the coal mining in Candiota, on some of the main water courses of the region. Water samples analysed (mg/L): Fe [10.0 - 237.0]; Zn [0.35 - 1.72]; Co [0.28 - 0.63]; Ni [0.26 - 1.17]; Mn [2.80 - 12.3]; Cd [0.004 - 0.01] and Cu [0.01 - 0.10]; pH (2.3 - 3.0) which is beyond the limits imposed by State's legislation. Results show that ARD was a fact in the area at that point in time and authors called the attention to the fact that due to the expected increase of the coal production situation could get worse and ARD prevention and/or effluent treatment in the Mine was imperative.

Recent analytical results from main streams showed pH varying from 1.88 to 5.51, Eh from 490 to 740 mV, conductivity from 4.07 to 10.10 mScm<sup>-1</sup> and sulfate concentrations up to 800 mg/l.

Other works such as, ANDRADE (1985), FIEDLER (1987), ZANELLA (1988) and, SOARES (1995); also

brought about the environmental problems caused by ARD in Candiota as well as the problems caused by the ashes produced at the local thermo power station. These ashes are usually encapsulated by reactive overburden in the mine which is also pointed out as a possible source of environmental contamination.

## ARD: A GENERAL OVERVIEW

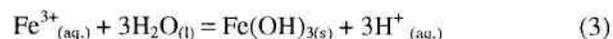
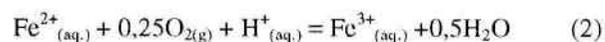
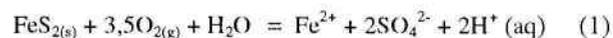
Acid rock drainage is fundamentally a geochemical process and its primary requirements are as follows:

- Presence of sulfide minerals;
- water or humid atmosphere;
- oxidant (usually oxygen)

The main factors which determine the rate of acid generation are:

- pH of the water;
- temperature;
- oxygen content of the gas phase, if saturation is less than 100%;
- oxygen concentration in the water phase;
- degree of saturation with water;
- chemical activity of Fe<sup>3+</sup>;
- surface area of metal sulfides exposed to atmosphere;
- chemical activation energy required to initiate acid generation;
- biological activity (such as iron oxidizing bacteria)

The major reactions associated to this geochemical process are:



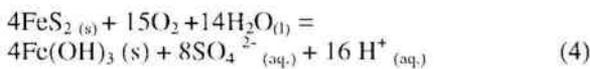
Iron II (Fe (II)) and acidic hydrogen ions (H<sup>+</sup>) are released into water which drains from mine galleries, tailings and overburden piles (equation 1). Iron II ions oxidize to Iron III (Fe(III)) as shown in equation 2. Then Fe (III) hydrolyses (equation 3) to produce a yellowish-orange amorphous Fe(OH)<sub>3</sub> precipitate called "yellow boy". This process releases even more (H<sup>+</sup>) into aquatic environment and pH continues to decrease.

The net effect of reactions represented by equations 1-3, is therefore the release of  $H^+$  into water due to pyrite oxidation and the lining of the water stream bed with amorphous Fe(III) hydroxide.

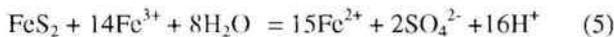
Precipitation of other Fe (III) - bearing phases, such as goethite ( $\alpha$  -  $FeOOH$ ) or schwertmannite [ $Fe_8O_8(OH)_6SO_4$ ] (BINGHAM et al., 1990; BIGHAM, 1994, apud BLOWES et al. 1995) may occur, thereby releasing different amounts of  $H^+$ .

Alternatively, Fe(III) may be consumed by oxidation of other sulfide minerals occasionally present.

Equation 4 which is the addition of equations 1-3, represents the overall reaction.



Below water table, oxidation is sustained by ferric ions formed during oxidation occurring above water table. The sub-water table reaction can be expressed by:



The practical implication of the reaction represented by equation 5 is that rehabilitation should be implemented sooner after tailings discharge to prevent the build up of ferric iron in pore water solutions (van HUYSTEEEN 1998).

## EXPERIMENTAL METHODS

The experiments were carried out with a test sample of freshly excavated overburden characterized at the beginning and at the end of the experiment. Mineralogical characterization was carried out by X-ray diffraction and scanning electron microscope - SEM and the mineral chemistry and phases were analyzed by electron microprobe connected to an image analyzer. The sample was also screened and analyzed for total sulfur in each size fraction.

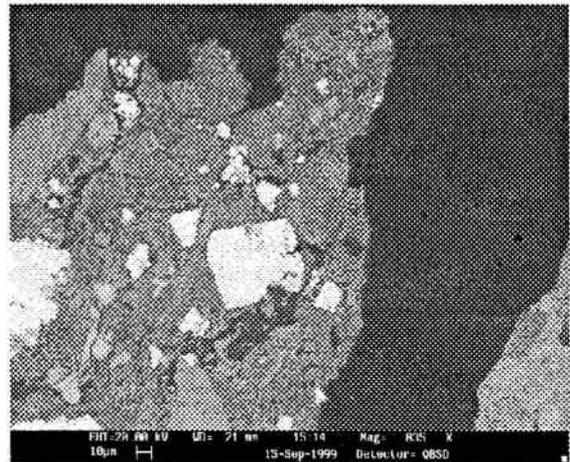
The net acid generating potential ratio (NPR) was determined by the Sobek method (SOBEK et al 1978).

The ARD was simulated in a lysimeter loaded with about 25kg of overburden. This test sample was submitted to wet and dry cycles and the leachate collected on each cycle was analyzed throughout the experiment for Eh, pH, conductivity, total dissolved solids (TDS) and dissolved chemical species (Fe (II), Fe(III), zinc, manganese, sulfur and aluminum).

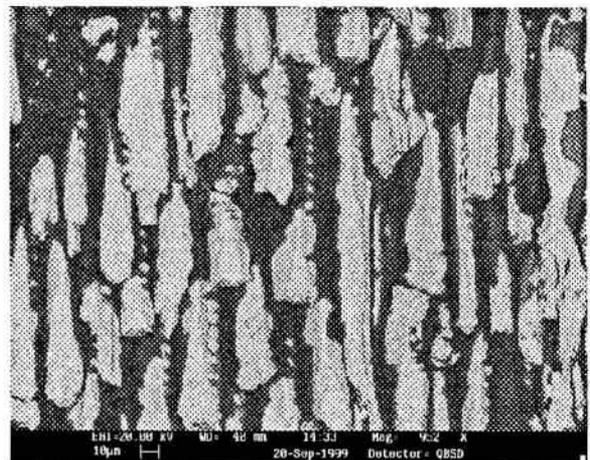
## RESULTS AND DISCUSSION

The test sample analysed 0.36% total sulfur, mostly as pyrite and its NPR was  $-0.07$  t  $CaCO_3,eq$  / 1000 t of overburden.

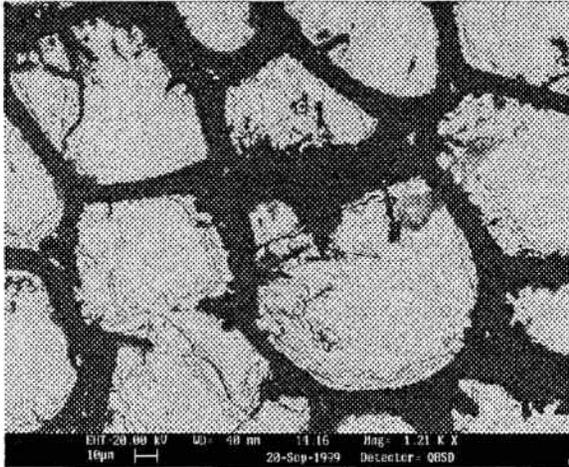
Kaolinite, muscovite, coal, zircon quartz and pyrite were identified as major minerals. SEM analysis revealed that higher total sulfur contents are associated with coarser fractions as shown in Table I. Pyrite occurs as inclusions in clay mineral particles and/or as individual crystals in the coal. (Photomicrographs 1,2 and 3).



Photomicrograph 1: Pyrite disseminated in clay minerals associated with coal.



Photomicrograph 2: Pyrite coatings on vertical fracture surfaces of coal.

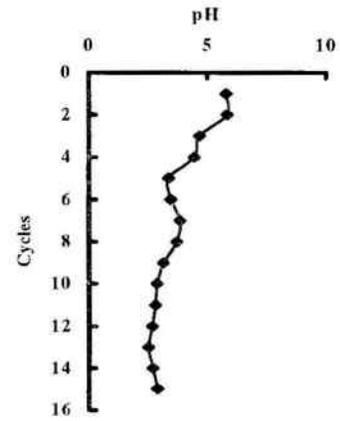


Photomicrograph 3: Pyrite disseminated in coal.

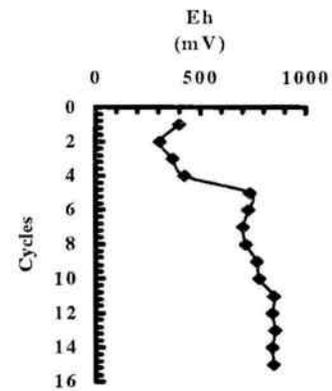
Table I. Sulfur percentages in various size fractions of the test sample.

Size	WT	S <sub>T</sub>
(mm)	%	%
>1.680	44.0	0.74
>0.420	22.0	0.38
>0.074	25.0	0.24
>0.044	3.2	0.38
>0.037	1.1	0.34
<0.037	4.8	0.076

Figure 2a and 2b show results of the lysimeter test. It is evident that up to the fourth cycle the pH of the leachate is still above 4.5 and the Eh never rises above 500mV denoting mild ARD and possibly predominant abiotic conditions.



(a)



(b)

Figure 2(a) and 2(b). pH and Eh vs number of wet and dry cycles.

Under abiotic conditions, the rate of pyrite oxidation by O<sub>2</sub> decreases as the pH decreases, and pyrite oxidation by Fe<sup>3+</sup> (equation 5), becomes the dominant oxidation mechanism (BLOWES et al. 1995). As shown in Figure 2a, by the sixth cycle the pH reached 2.0 to 2.5, speeding up the acid production, due to the chemical and biological pyrite oxidation.

Simultaneously, by the sixth cycle the Eh presented an abrupt increment to about 800mV (Figure 2b) propitiating very favorable conditions to the performance of the *T. ferrooxidans*. It is well known that for a pH smaller than 3.0 the solubility of iron increases and the rate of Fe(OH)<sub>3</sub> precipitation decreases resulting an increasing on Fe<sup>3+</sup> activity (STUMM and MORGAN, 1996). The ratio Fe(III)/Fe(II) increases. As a result of the pyrite oxidation and bacterial oxidation of Fe(II), there is a simultaneous increment in conductivity and TDS (total dissolved solids), as well as an increase in the concentration of sulfate, and metals in solution such as aluminum, zinc and manganese (Figure 5).

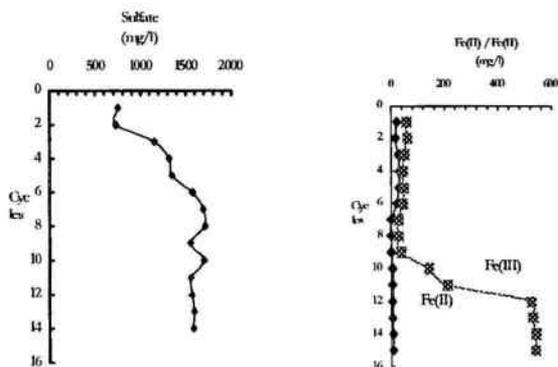


Figure 3. Sulfate and iron concentrations in leachate vs. number of wet and dry cycles.

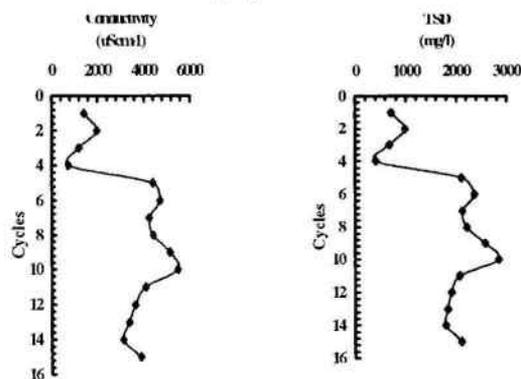


Figure 4. Conductivity and TDS in leachate vs. number of wet and dry cycles.

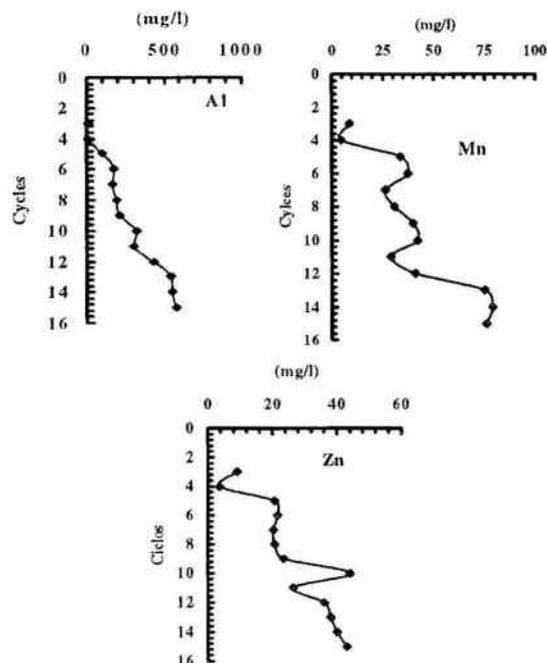
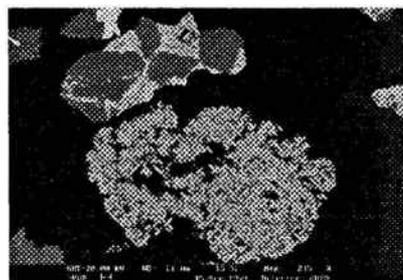


Figure 5. Dissolved chemical species vs. number of cycles.

The mineralogical characterization of the weathered overburden at the end of the experiment showed jarosite (Photomicrograph 4)  $[KFe_3(SO_4)_2(OH)_6]$ , goethite ( $\alpha$  -  $FeOOH$ ) and hematite  $Fe_2O_3$ , which are formed from pyrite oxidation, as well as anatase.



Photomicrograph 4. Jarosite precipitated in the chemically weathered overburden.

### CONCLUSIONS

The chemical and mineralogical analysis performed were crucial for future experiments on ARD generation and abatement. They showed that in the overburden of Candiota pyrite is mainly associated with coarse size fractions (>1.68mm) and it is easily available to be oxidized.

The experimental set up was adequate to simulate field conditions in the laboratory and enabled easy sampling and close follow up of the acid generation.

Lysimeter test results confirmed that the overburden of Candiota coal mine presents a NPR (net acid generating potential ratio) value of  $-0.07441$  t  $CaCO_3$  eq/1000t and it is an acid producing material.

Phase II of the test program will be focused on designing geochemical barriers to abate ARD in situ. The investigations will be carried out using local raw materials and aiming at elucidating the mechanisms involved in the production of these barriers.

### REFERENCES

- ANDRADE, A. *Characterisation of Flying Ashes from Candiota Coal. Porto Alegre, RS. M.Sc. Thesis. Rio Grande do Sul Federal University, Brazil, 1985 (in Portuguese).*
- BLOWES, W. D. et al. *Microbial, chemical and mineralogical characterization of the Kidd Creek Mine tailings impoundment, Timmins*

Area – Ontario, Geomicrobiology Journal, v. 13, p. 13 -31, Feb. 1995.

- FIEDLER H.D.; Solari, A.J. *Environmental Impact of Candiota Mine on Regional Surface Waters*. In: Proceedings of the III National Meeting on Mineral Treatment and Hydrometallurgy, pp. 483-498, Brazil - 1988 (in Portuguese).
- FIEDLER, H.D.. *Characterization of Candiota Coal and Environmental Consequences of its reprocessing*. M.Sc. Thesis. Rio Grande do Sul Federal University – Brazil, 1987 (in Portuguese).
- MINISTRY OF MINES AND ENERGY (MME) 1985. *Coal Industry Annual Report*, Brasília (in Portuguese).
- NATIONAL DEPARTMENT FOR MINERAL PRODUCTION (DNPM) *Coal Industry Annual Report 1995*, Brasília - Brazil 1995 (in Portuguese).
- SOARES E.R.. *Heavy Metal Mobility in Materials from Candiota*. M.Sc. Thesis 58p., Viçosa Federal University - Brazil, 1995 (in Portuguese).
- SOARES, P. S.; BORMA, L.S.; SOUZA, V.P., van HUSSTEEN, E. *Alternatives for Mitigation of Acid Mine Drainage in a Coal Mine*, In Proceedings of the 6<sup>th</sup> International Conference on Environmental Issues and Management of Waste in Energy and Mineral Production, May 30 - June 2, 2000, Calgary, Canada.
- STUMM, W.; MORGAN, J. J. *Aquatic Chemistry - Chemical Equilibria and Rates in Natural Waters*. John Wiley & Sons, Inc, (eds.) 1022 pp , 3rd. Ed. 1996.
- van HUYSSSTEEN, E. CANMET INTEMIN Overview of Environmental Baselineing. Published by CANMET/MMSL ISBN 0-660-17565-7. (1998). Issued on CD-Rom entitled Baselineing - A reference manual obtainable from CANMET/MMSL or INTEMIN
- ZANELLA R.. *Investigation on Environmental Issues Related to Coal Burn up and Exploration in Candiota*. M.Sc. Thesis. Santa Maria University - Brazil, 1988 (in Portuguese).