# Fenton's Reaction by Sulphide Oxidation on Coal Mining Rejects

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**Abstract**

Fenton's reaction is used in acceleration weathering test for sulphides associated with Brazilian Coal Mining Residues (CMR), that are vulnerable to oxygen and water during the mining of coal. TEM and SEM/EDX were used to determinate the origin, occurrence and ordering of minerals in remaining coals and other lithological units, before and after applying the test. Oxidation of CMRs was analysed by determination soluble sulphur (sulphate) and dissolved metals by ICP-MS or ICP OES. As dissolved sulphate increases, dissolved Zn, Cd, Cu and Co concentrations increase, conducting to undetectable amounts in the remaining solid phases; dissolved Ni and Mn also increase with the mobilized sulphur, but the remainder in the solids is the most relevant fraction; Fe and Pb are not mobilized due to precipitation as jarosite or hematite in the case of Fe or as sulphate in the case of Pb. Agreement between the observed results and the predictions by geochemical modelling is discussed. The accelerated weathering procedure based on Fenton's Reaction has shown the release of toxic metals from the sulphide fractions associated with coal residues. The use of SEM/EDX, TEM, XRD, ICP-MS and ICP OES analyses were conducted on various samples from the Santa Catarina coal region with the aim of improving the understanding of the mineralogy and geochemistry of CMRs. The measurements were conducted on the original materials as well as on the materials left after applying the accelerated oxidation by hydrogen peroxide. Accordingly with the theoretical predictions by geochemical modelling, the experimental results demonstrate the effective oxidation of pyrite, as well as the other metal sulphides, by hydrogen peroxide within a short time period complete after 72 h. In terms of relative mobility (% of total metal released during the test), Cu, Co, Cd and Zn appear as metals of high mobility, liberating practically all total content. The released concentration of Ni and Mn increases as sulphate increases but a considerable concentration of both metals remains immobile in the solid phases. The Fe presentes a relatively lower release, because it suffers processes of further immobilization after pyrite oxidation, even at lower pH values, due to secondary mineral precipitation, such as jarosite; this fact considerably limits its mobility. Finally, Pb presents a practically null mobility and it does not represent a risk of potential contamination even in samples with high sulphide concentrations due to the possible formation of insoluble lead sulphate.

***Keywords:*** *Fenton's Reaction, accelerated weathering, coal mining residues, environmental impact*

## 1. Introduction

Petroleum crises during the last few years have increased the significance of researching coal. Although abundant, existing coal reservoirs throughout the world could supply energy requirements for a long time, efficient use is limited by the coal's high sulphur content, as found in Brazilian coal, for example. The abundant presence of sulphide minerals associated with coal causes great concern as to the environmental impact of oxidation (Bortoluzzi, 2003; Giere et al., 2006; Silva et al., 2009a; Silva et

al., 2009b), together with the know CO2 production after coal firing.

This study investigated the nature of the coal mining residues (CMRs) and attempts to quantify the extent to which interaction has taken place or could take place between the coal or coal bearing strata and the surrounding environment, by using an accelerated weathering procedure based on the Fenton's reaction, i.e. using $H_2O_2$ as the oxidant to examine experimentally the oxidation of metal sulphide mineral phases associated with Brazilian coals.

The purpose is to evaluate the process of oxidation of the sulphides material in order to deduce the environmental fate of Fe, Ni, Cu, Pb, Mn, Zn, Co, Cd, $H^+$ and $SO_4^{2-}$ in the Santa Catarina coal mining region. The results of such research are of great use in the design of prevention and remediation strategies for mine-affected regions.

## 2. Methods

*2.1 Study area*

The South of Brazil, comprising the states of Santa Catarina and Rio Grande do Sul, has been known for its abundant and economically important coal beds since the beginning of the 20th century.

While most of the coal reserves are found in the southernmost state of Rio Grande do Sul, the state of Santa Catarina boasts the greatest production (DNPM, 1996; SIECESC, ABCM).

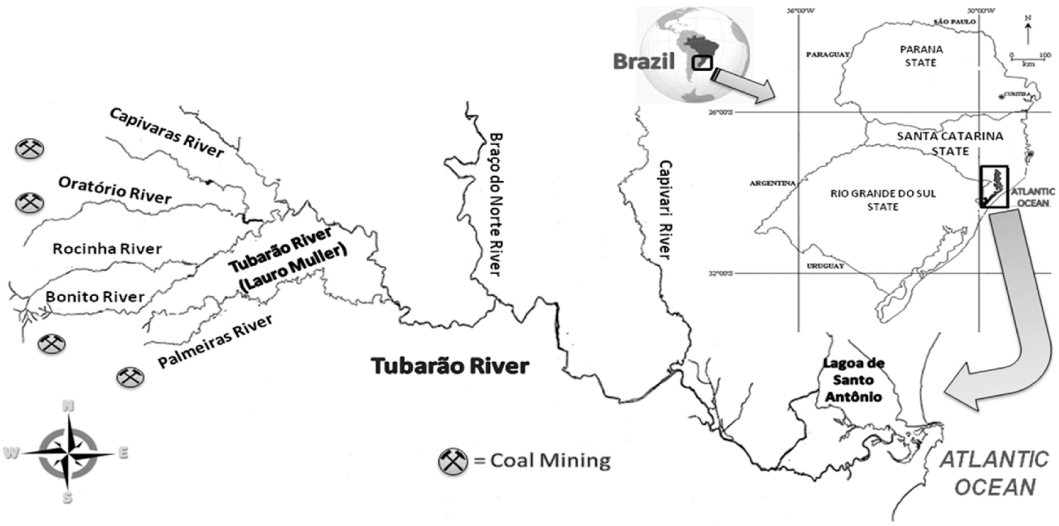


Fig. 1. Location of Santa Catarina state coal basin (Southern Brazil).

*2.2 Coal mining residues samples*

The 17 samples used for this study were obtained from Santa Catarina (Fig. 1). The samples were collected directly at source from open air hollows in the region of Lauro Muller city, which impacts in the hydrographic basin of the Tubarão River. The samples, gathered from different spots on the most recent stack in the same week, were stored in sample bags weighing between 20 and 25 kg. The samples, collected following either (ABNT, 1983) and/or (ASTM, 1996) procedures, were homogenized according to (ASTM, 1991) norm D2797 and split into batches for the various analyses. Samples belong to two groups of materials: a) CMR-S: Sediments originating from areas in contact with layers of coal, rich in carbonaceous substance (%C = 2.9–5.9) with variable levels of sulphur (%S = 0.2–3.2) and acid reaction. b) CMR-O: Distinct sediments collected in the influence areas of the mines, but with low levels of carbonaceous matter and sulphur (%S < 0.1) and low acid reaction.

*2.3 Mineralogical analysis procedures*

The occurrence of mineral species was investigated by means of Powder X-ray diffraction (XRD), environmental Scanning Electron Microscope (SEM) coupled with an energy dispersive X-ray microanalysis system (EDX) (Querol et al., 2008) and Transmission electron microscopy (TEM) for chemical analyses of individual particles. Prior to TEM analysis different suspensions were selected, namely hexane, acetone, dichloromethane and methanol, as a function of the mineral considered in order to prevent possible mineralogical changes when a proper suspension is not used. The suspension consisted of 10mL of each of the solvents mixed with 0.5 g of dried and sieved coal mining residue. The mixture was placed in an ultrasonic bath for 30 min. The suspension was stirred for~1min, pipetted onto lacycarbon films supported by Cu grids (Giere et al. 2006) and finally left to evaporate before the TEM analysis was performed (Kwan and Voelker, 2003).

Analytical electron microscopy using a Scanning Electron Microscopy (SEM) and transmission electron microscope (TEM) offers great advantages in both spatial resolution and reduced sample volume to perform the analysis. Studies by Hochella et al., 1999 and Genovese and Mellini, 2007 have demonstrated the benefits of utilizing TEM in acid-mine drainage systems as it allows the analyst to see particles, even down to the nano-scale, as well as their associated chemistry and crystallography (Silva et al., 2009a).

*2.4 Oxidation by $H_2O_2$*

Hydrogen peroxide is an eco-friendly, strong oxidant and effluents treated with it are more susceptible to biodegradation. Consequently, hydrogen peroxide in the presence of a catalyst is gaining importance for secondary or even primary treatment of industrial effluents, including sulphide-bearing wastewaters, to meet the desired discharge limit. In this work, a forced oxidation of the coal cleaning residues with hydrogen peroxide was performed as an accelerated weathering test to evaluate the mobilizable metallic fraction associated with sulphides and the release potential during oxidation.

All experiments were carried out batchwise in a mechanically agitated glass reactor. Previously, pretreated samples (powdered, sieved through 2-mm mesh and homogenized) were oven-dried at 45 ◦C for 24 h and then transferred to a desiccator. Powdered samples of 1 g were treated with 100mL aqueous solution of 15% $H_2O_2$ (Merck, Germany, diluted with Milli-Q ultrapure water), previously adjusted to pH= 5.5, and kept in an isothermal shaker bath at 30 ◦C for 72 h. An aliquot of 10mL was withdrawn at preset intervals (of 1, 2, 6, 24, 48 and 72 h) and immediately filtered.

Leachates were collected, weighed and separated into two aliquots. Sulphate, nitrate, conductivity, Eh and pH were determined immediately after the collection in the first aliquot. The second aliquot was acidified with concentrated HCl to prevent precipitation reactions and the total contents of elements and S were determined by ICP OES.

The optimum time of oxidation was set at 72 h in line with the results by Urrutia et al., 1987 that had observed the segment of the kinetic and of oxidation of the sulphides with $H_2O_2$ for 27 days, showing little or no variation after the first 72 h.

## 3. Results and discussions

*3.1 Elemental content*

Table 1 shows the average range of variation (confidence level at 95%) of the total elemental composition of each metal in the unchanged coal washing residues grouped according to the type of material and the sulphur content, CMR-S and CMR-O respectively.

Table 1. Range of the elemental composition (mean value and confidence interval at 95% of significance), for trace element contents, of the CMRs distributed as CMR-S and CMR-O.

| mg/kg[1] | CCR-S | CCR-0 | mg/kg[1] | CCR-S | CCR-0 | % | CCR-S | CCR-0 |
|---|---|---|---|---|---|---|---|---|
| As | 19.5(1.0) | 8.3(0.5) | Mo | 32.8(1.3) | 3.4(0.1) | Al | 10.23(0.52) | 10.22(0.42) |
| B | 9.8(0.6) | 15.0(1.7) | Ni | 66(1) | 19.2(0.8) | Ca | 0.53(0.21) | 0.76(0.03) |
| Ba | 538(24) | 952(33) | Pb | 71(2) | 45(4) | Fe | 3.13(0.42) | 2.94(0.17) |
| Be | 3.1(0.2) | 4.6(0.1) | Sb | 1.23(0.05) | 1.03(0.17) | K | 1.54(0.15) | 1.57(0.04) |
| Bi | 1.5(0.4) | 0.91(0.04) | Se | 5.4(0.5) | 5.3(0.2) | Mg | 0.27(0.01) | 0.40(0.02) |
| Cd | 4.5(0.2) | 1.3(0.2) | Sn | 57(4) | 5.0(0.1) | Na | 0.12(0.01) | 0.28(0.01) |
| Co | 5.4(0.2) | 11.1(0.5) | Sr | 91(7) | 242(66) | P | 0.29(0.01) | 0.020(0.003) |
| Cr | 48(1) | 53(1) | Ta | 5.1(0.2) | 4.9(0.2) | Ti | 0.55(0.03) | 0.46(0.09) |
| Cu | 24(1) | 25(2) | Th | 31(1) | 22.6(0.1) | | | |
| Ga | 28(1) | 27(1) | U | 6.5(0.7) | 9.4(0.5) | | | |
| Ge | 3.8(0.2) | 3.7(0.2) | V | 92(2) | 98(2) | | | |
| Hf | 5.0(0.3) | 5.4(0.4) | W | 6.9(0.2) | 7.0(0.3) | | | |
| La | 37.0(0.2) | 38(1) | Y | 22(1) | 24.4(0.7) | | | |
| Li | 89(4) | 81(3) | Zn | 246(2) | 191(11) | | | |
| Mn | 51(3) | 235(11) | Zr | 183(9) | 200(11) | | | |

The pyrite difference in the samples seems to directly influence the concentrations of all the toxic elements, with a clear tendency to increase parallel to the sulphur content, except for Mn. These results are supported by other studies that investigated the origin and correlations of metals with different sulphides (Bostick and Fendorf, 2003; Dellwig et al., 2002; Schoonen, 2004) and the geochemical mobility of metals (Alastuey et al., 1999; Ernstberger et al., 2002).

A suggested explanation for the high concentrations of Pb and Zn is both elements' association with pyrite (galena and sphalerite respectively) in the coal from the Santa Catarina Basin, whereas Cd may occur primarily as a replacement for Zn in the mineral sphalerite.

*3.2 Mineralogical characterization*

The principal oxide detected in the CMRs analysed was hematite, closely mixed with quartz, feldspar and rutile. The hematite probably reflects the oxidation of pyrite in the coal, as indicated by studies on American coals (Pinetown et al., 2007). The formation of iron oxides and hydroxides is considered the driving force behind the geochemical cycling of metals and the dissolution of redoxsensitive metal oxides (Ha et al., 2008) or biomineralization products (Banfield et al., 2000).

Carbonate minerals are common in the CMRs samples studied. They are represented by calcite and, to lesser extents, by dolomite and ankerite. Calcite is mostly associated with coal macerals and occurs in association with vitrinite and also in cell-filling form in inertinite in Genesee feed-coal (. Goodarzi , 2002). Sulphide minerals consist of pyrite (Figs. 2D and 3A), marcasite, pyrrhotite, sphalerite and galena. The composition of pyrite surface and the tendency of metal ions from aqueous solution to be adsorbed on them can, to a considerable extent, also influence the rate of oxidation. This is consistent with the fact that metals like Na, K, Ca, Mg, Al, Ni, Cu, Ag, Pb, Zn, Cd and As, are known to occur on the natural pyrite surface (Al et al., 1997).

Pyrite is the main species promoting the sulphur oxidation in the coal mining residues samples studied. Pyrite weathering, the main process leading to acid mine drainage (Singer and Stumm, 1970), results from a combination of oxidation and dissolution processes involving ferric ion and oxygen and from microbial activity (Rimstidt and Vaughan, 2003). Additionally, pyrite is an ubiquitous component in the environment and should thus be considered as a reservoir of reductants for oxidized species with environmental relevance, such as heavy metals.

*3.3 Oxidation of the sulphides and mobilization of elements*

For a long-term assessment of the mobility of heavy metals from CMRs, it is particularly important to obtain information about potential acid immission and internal acid formation in relation to the buffer capacity of the contaminated site and their environment (Schuwirth et al., 2007). Thus, the oxidation of CMRs by hydrogen peroxide can give such information especially if we consider the presence of other metals together with the pyrite phases. In a forced oxidation experiment with $H_2O_2$ almost all total sulphur occurred in the form of sulphide and the sulphur of the $SO_4^{2-}$ does not represent a significant percentage in the original samples. Experimental results show that the dominant sulphur products during oxidation of pyrite by $H_2O_2$ are aqueous sulphate, hydrated iron sulphates and elemental sulphur.

The maximum acidification produced by the complete oxidation of sulphide minerals in CRMs was evaluated. In all the analysed samples (Fig. 2A), the pH of the system reaches values between 2 and 3 when the sulphur content varies between 0.5 and 1.0%, and reaches values lower than 2 when sulphur content is greater than 1%. The release of soluble Fe follows a parallel trend to the percentage of S− oxidised to $SO_4^{2-}$, but in many samples a lower concentration of dissolved total Fe was detected, as a function of the S content; this effect can be an indication of a fast precipitation of mineral phases of Fe, such as the detected freshly formed jarosite.

Fig. 2B shows the molar fraction diagram obtained when pyrite, in amount equivalent amount to 145mM (in a carbonate–hydrogensulphide environment), is subjected to a continuous hydrogen peroxide attack, like in the experimental setup conditions used for samples 2–6. As seen the pyrite oxidation first promotes the appearance of sulphate in solution, to form the soluble Fe (II)–sulphate complex, as well as the precipitation of siderite. As the oxidation proceeds, the siderite fraction decreases while the soluble Fe(II)–sulphate complex increases until it reaches a state in which all the oxidised pyrite becomes the soluble Fe(II)–sulphate. In this step of the oxidation process, gypsum is formed by reaction of the freshly oxidised sulphate species and the calcium ions released by the acid attack in the calcite phase.

When all the pyrite has been oxidised, the added hydrogen peroxide starts oxidising Fe(II) to Fe(III). If sulphate ions are available in sufficient quantities, hydrogen–jarosite can be saturated but only if specific conditions are fulfilled.

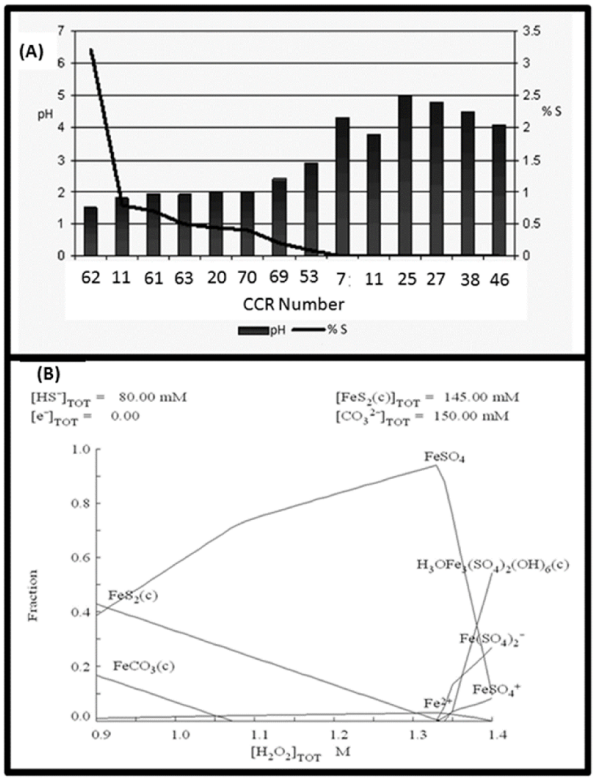


Fig. 2. (A) Variability of pH versus S concentration content in CMRs for some of the analysed samples; (B) theoretical modelling of pyrite oxidation as a function of the hydrogen peroxide addition in a carbonate beadrock.

The chemical modelling shows that carbonate is required in the near environment to neutralise the excess of hydrogen ions produced during the oxidation reaction. If that carbonate is not available, jarosite is not formed and the prediction gives hematite as the stable Fe(III) solid phase (we have experimentally detected several hematite crystals in all the analysed CMRs).

The second chemical condition required for hydrogen–jarosite to saturate is that sulphate must reach a given concentration in the solution around the CMR solid materials. The sulphate ions enter the system by two routes. In one, sulphate is released by the Fe(II)–sulphate complexwhenthe Fe(II) is oxidised to Fe(III), breaking the stable sulphate complex. Few of the other metal sulphides produce so many hydrogen ions as the oxidation of pyrite. In our samples, the increase in %S is accompanied by a systematic increase in the total acidity (Fig. 2B). High sulphide oxidation rates were found in samples with low pH (<3), increasing the elements' mobilization into the medium. Our current results indicate that the efficiency of $H_2O_2$ treatment in partially oxidized CMRs depends on the proportions of Fe-oxides and sulphides present in the sample.

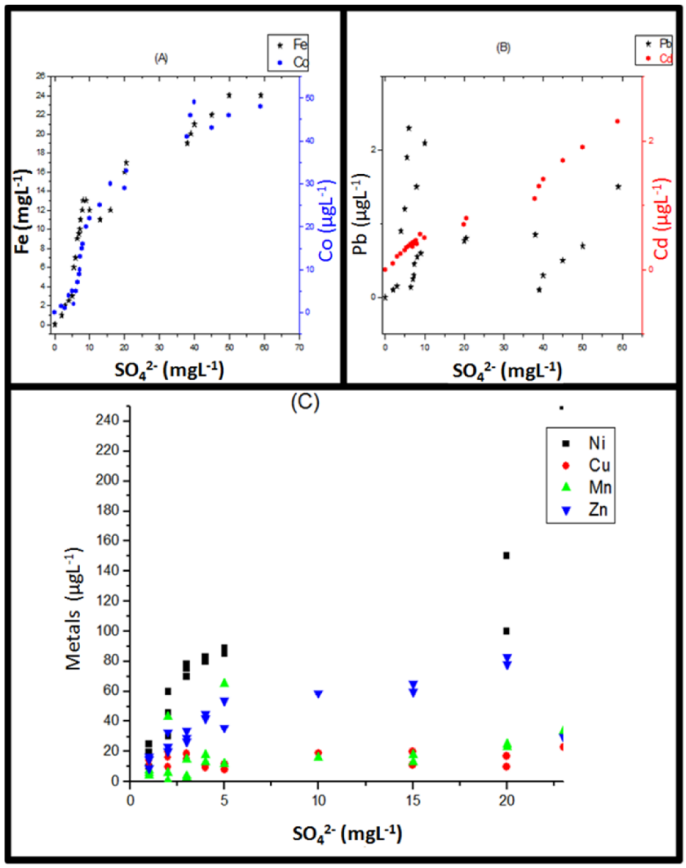


Fig. 3. Concentration of metals as a function of $SO_4^{2-}$ concentrations during the oxidation of the CMRs with $H_2O_2$.

During the oxidation of the CMRs with hydrogen peroxide, the mobilized fraction of metals is mainly attributed to the association of metal sulphides with coals, like it is shown in Fig. 3.

The low Fe mobilization during the oxidation (see Fig. 3A) corresponds to a group of samples that liberated into the solution less than 8mg $L^{-1}$ of $SO_4^{2-}$, which corresponds to the total oxidation of 0.2% of pyritic sulphur; this group of samples presents a dissolution pH slightly acidic (>4.0), thus the Fe is quickly immobilized and must be present in low concentration in solution (most part of the total Fe is as trivalent iron that precipitates as oxy-hydroxides at such pH values).

## 4. Conclusions

The accelerated weathering procedure based on Fenton's Reaction has shown the release of toxic metals from the sulphide fractions associated with coal residues. The use of SEM/EDX, TEM, XRD, ICP-MS and ICP OES analyses were conducted on various samples from the Santa Catarina coal region with the aim of improving the understanding of the mineralogy and geochemistry of CMRs. The measurements were conducted on the original materials as well as on the materials left after applying the accelerated oxidation by hydrogen peroxide.

Accordingly with the theoretical predictions by geochemical modelling, the experimental results demonstrate the effective oxidation of pyrite, as well as the other metal sulphides, by hydrogen peroxide within a short time period complete after 72 h. In terms of relative mobility (% of total metal released during the test), Cu, Co, Cd and Zn appear as metals of high mobility, liberating practically all total content. The released concentration of Ni and Mn increases as sulphate increases but a considerable concentration of both metals remains immobile in the solid phases. The Fe presents a relatively lower release, because it suffers processes of further immobilization after pyrite oxidation, even at lower pH values, due to secondary mineral precipitation, such as jarosite; this fact

considerably limits its mobility. Finally, Pb presents a practically null mobility and it does not represent a risk of potential contamination even in samples with high sulphide concentrations due to the possible formation of insoluble lead sulphate.

These results demonstrate that in restoration practice the selective management of spoils can be considered to offer the best protection against contamination of surface and subsurface waters and is the method which should be applied in the future construction of dump facilities.

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