Mine Water and the Environment (2020) 39:910–917
https://doi.org/10.1007/s10230-020-00690-x

TECHNICAL COMMUNICATION

A Comparison Between Predictive Tests Results and Natural Weathering in the Figueira Mine, in Southern Brazils

Mateus João Mubecane Filipe Manharage[1] · **Ernani Francisco da Rosa Filho**[1]

Received: 18 March 2020 / Accepted: 11 May 2020 / Published online: 21 May 2020

Abstract

Many studies on acid mine drainage (AMD) use predictive methods, such as humidity cells (HC), to study this problem, as it is often not possible to predict acid generation from field tests. However, some comparisons of HC testing with reality have proven to be unrealistic. In this study, we compared the results of the HC test with historical data from the Figueira mine, in the State of Paraná (southern Brazil). To carry out the work,we collected a fresh coal tailings sample from the Figueira Mine, and compared monthly measurements of pH and electrical conductivity (EC), and concentrations of Fe, Al, Mn, and Zn, over a 5 year period (from 2013 to 2017) with the predictive test results performed following protocol B of the ASTM D5744-13 (2018) standard. The elements were analyzed by ICP-OES. The pH and EC of the HC test were lower than the field data. The HC test underestimated the concentrations of Fe and Mn, while Al and Zn were overestimated. We believe that the overestimations were due to the aluminosilicate buffering capacity and cation exchange capacity of the soil.

Keywords Acid mine drainage · AMD · Coal tailings · Geochemical models

Introduction

Acid mine drainage (AMD) is one of the main problems that affect the ecosystem near mines. Many factors affect the chemistry of mine drainage, including the type and abundance of metal-bearing sulfides in ore and wall rock, kinetic rates of ore and wall rock dissolution, permeability of the ore deposit or mine tailings, and the ability of the host rock to buffer acidity (Anawar 2013). Various predictive tests (static and kinetic) have been developed; the most commonly used tests are acid base accounting (ABA) and humidity cells (HC), as it is often not possible to predict acid generation using field tests.

Geochemical models of AMD is a widely applicable and useful technique to investigate the geochemical reactions occurring in the AMD and contaminant transport in the groundwater and surface water systems. The models incorporates chemical speciation, precipitation–dissolution reactions, ion exchange, acid–base reactions, and redox reactions (Anawar 2013). Geochemical models are based on well-constrained laboratory and field observations as well as geological and geochemical assumptions. However, collection of field data can take a long time.

In Brazil, AMD studies have focused on the coal regions of the south of the country. Brazilian coal is normally classified as low rank, since it contains a high ash and sulfur content (Fallavena et al. 2013). However, the S content in Brazilian coals varies, from one bed to another and from one seam to another (ranging from 1.09 to 4.66% by weight), with the Figueira coal containing the highest concentration (Depoi et al. 2008).

In the Figueira region, Shuqair (2002) concluded that the phreatic aquifer was contaminated by mining because the tailings fields were located in the aquifer's recharge zone. Therefore, the concentrations of certain elements such as Al, As, Cd, Mo, Pb, and Zn presented anomalous values, although in the Rio das Pedras downstream from the mining area, the concentrations of these elements were within the parameters provided by Brazilian legislation. Later, Flues et al. (2008) showed that there was a slight increase in the concentrations of As, Cd, Mo, Pb, and Zn in the region's soil (for 1 km from the thermoelectric plant) and that As levels at ten sampled points were above that established by Environment Company of São Paulo State (CETESB).

✉ Mateus João Mubecane Filipe Manharage
mmanharage@gmail.com

[1] Hydrogeological Research Laboratory, Department of Geology, Federal University of Paraná, Curitiba, Brazil

Studies by Campaner and Luiz-Silva (2009) and Campaner et al. (2014) revealed that the drainage pH of the Figueira mine ranges from 3.2 to 4.6 and that it contained high concentrations of SO_4^{2-}, Al, Fe, Mn, Zn, and As in the monitoring wells and in the tailings drains. However, samples from rivers and groundwater from the municipal public water supply revealed a pH range of 7.2–7.5 and low concentrations of toxic elements, with the exception of Cd, which had a concentration slightly exceeding Brazil's groundwater limits.

Therefore, we decided to compare the drainage quality of the Figueira coal mine (operated by Cambuí Mining Co.), State of Paraná (southern Brazil) with the results obtained by a HC test carried out in the laboratory. We used the results of monitoring by the Cambuí Mining Co. over 5 years (2013–2017) on the release of metals, pH, and electrical conductivity (EC).

The mine, which is located in Figueira City, was founded in 1942. The mine is currently developed within an industrial park called Mina Amando Simões, where its coal processing facilities are located, as well as all of its supporting infrastructure. It is an underground room-and-pillar mine. The coal beneficiation process involves washing and gravimetric separation. The resulting tailings are essentially siltstone, pyrite, and some coal that does not sink in the beneficiation process. These mining tailings are deposited in tailings fields; there are currently four, numbered 1–4. Fields 1 and 2 are the oldest and have not undergone any treatment, while the tailings in 3 and 4 are placed between carbonate residue layers from a paper mill located in Telêmaco Borba, ≈ 70 km from Figueira. Field 1 has two drains, D1/1 and D2/1, with flow rates of 167.55 and 229 L/h, respectively. Field 2 has been sealed and has no flow. The effluents from the old fields are typical AMD, with a pH between 3 and 4 and large amounts of iron precipitates (Fig. 1a, b).

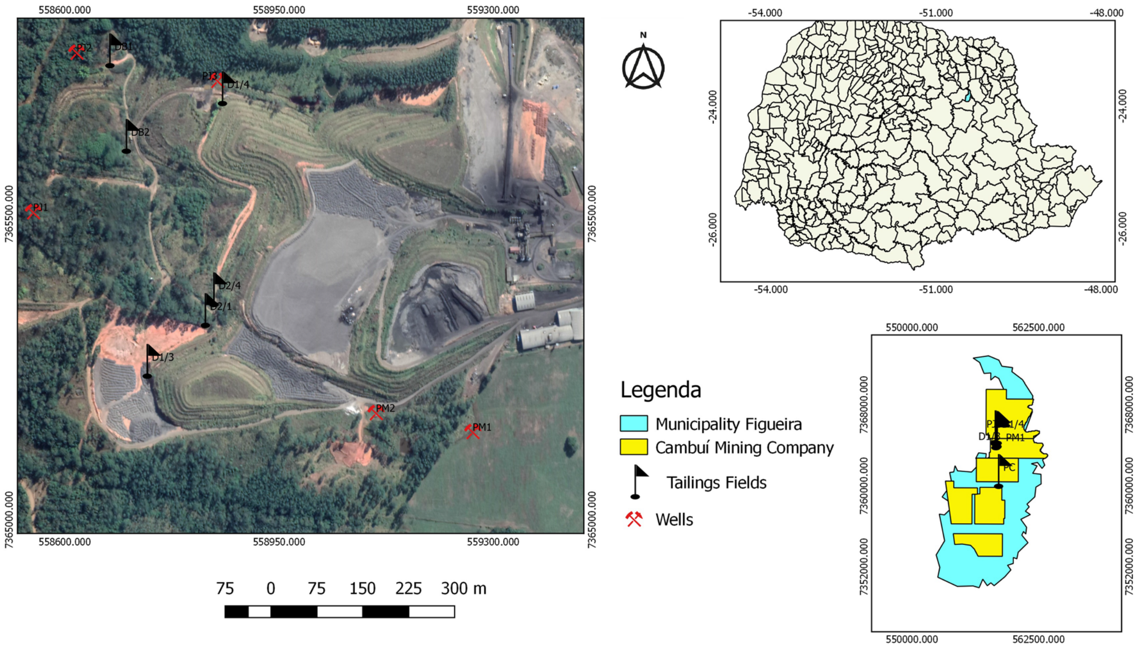
The mineralogy of the Figueira coal indicates that the major minerals are kaolinite, quartz, illite, interstratified illite/smectite, gypsum, jarosite, pyrite, rutile, calcite, and melanterite. Illite and illite/smectite are more abundant in the mineral fraction, along with similar proportions of quartz; feldspar (probably Na-rich plagioclase) also occurs. Significant proportions of pyrite and jarosite and melanterite were identified in the mineral matter. A trace amount of sphalerite and gypsum is also present, but is not a significant component (Cutruneo et al. 2014).

Localization and Geology

The economically important coal deposits on the eastern flank of the Paraná Basin (Rio Bonito Formation, of the Middle Permian) in south-southeastern Brazil have been greatly developed in the states of Rio Grande do Sul and Santa Catarina. The small Figueira deposit, located in the northeast of the State of Paraná (Fig. 2), represents only about 1% of the country's official proven and probable reserves (Borba 2001).

In the Figueira region, the outcropping stratigraphic units are of Permian age and belong to the Itararé Subgroup (Rio do Sul Formation), Guatá Subgroup (Rio Bonito and

Fig. 1 **a** Sample collection point drain-1. **b** Clots resulting from the precipitation of the iron



Coordinate system-SRIGAS 200; UTM Zona 22
EPSG 31982

Fig. 2 Location of the Cambuí Mining Company

Palermo Formations) of the Tubarão Group, and Passa Dois Group (Iratí, Serra Alta, and Teresina Formations) (Ricardi-Branco et al. 2002; Fig. 3).

The layers of pyritic coal are up to 0.5 m thick and are found in the Rio Bonito Formation (of Eo-Permian age) in the Paraná Basin (Jasper et al. 2011; Ricardi-Branco et al. 2002). The Rio Bonito Formation consists of sandstones, siltstones, shales, coals, and limestones. It is divided into a basal unit: the Triunfo Member, fluvial-deltaic deposits of whitish gray sandstones, fine to coarse conglomeratic strata, siltstones, cross-bedded carbonaceous shales, and layers where sandstones, shales, and coal predominate. An intermediate unit, the Paraguaçu, deposited on a tidal plain and platform, consists of gray, greenish, and brownish sandstones and siltstones, with intercalations of limestone, micritic and stromatolytic strata. It presents parallel and wavy flat lamination, cross micro-stratification, and bioturbation. (Figueira and Salto Aparado); at the top is the Siderópolis Member, represented by fine coastal plain sandstones (Mineropar 2001).

Methodology

Usually, kinetic tests complement static tests; therefore, they are usually performed if the static evaluation indicates an uncertain result for the potential for AMD generation (Coastech Research Inc. 1991). Static tests provide only quick information as to whether or not the rock is potentially acid generating. When the kinetics test confirm this potential, they also provide information on anticipated water quality, metal mobility, cations and anions present, as well as the influence of bacteria in the oxidation of pyrite, depending on the type of test used and the purpose of the work.

For this study, we collected coarse tailings samples, according to the NBR 10007 (ABNT 2004) Standard, and water samples from drains and monitoring wells) at the Figueira mine. The tailings samples collected were result of coal beneficiation (washing), which had been transported by truck to the tailings field 4. These samples were transported to the laboratory where they were dried for 24 h in an oven at a temperature of 50 °C. After drying, these samples were ground, from coarse (<6.3 mm) to fine (<0.074 mm), depending on the normative requirements for each test or experiment. We used <6.3 mm for the HC test, <0.250 mm for paste pH, and less than 0.074 mm for the fizz component of the ABA test. We analyzed the tailings mineralogy by x-ray diffraction and chemical leachate analysis of the HC test.

The HC test was preceded by ABA, which includes paste pH and a fizz test. The first consisted of mixing 10 g of sample with 9 mL of deionized water to a beaker and the same amount of sample to 9 mL of 0.01 M $CaCl_2$ solution (ASTM-D4972-18 2018), after which the pH of the formed

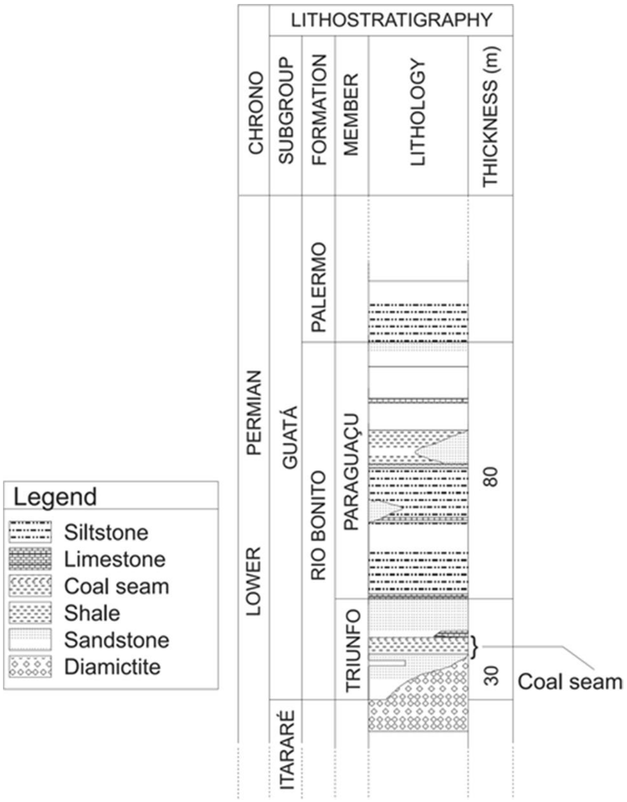


Fig. 3 Lithostratigraphic of the Rio Bonito Formation in the region (Modified from Morrone and Daemon 1985). Source: Ricardi-Branco and Ricardi (2003), authorized by Ricardi-Branco

pastes were measured. The second consisted of adding two to three drops of 25% HCl at 0.50 g previously weighed in a watch glass. Based on the reaction of the sample, it was classified based on Table 1.

The ABA test consisted of reacting 2.00 g of sample (in triplicate) with HCl (according to the fizz classification) and then titrating the solution with 0.1 N NaOH standard (exactly known concentration) to pH 7.0 using a pH meter and burette. Finally, the forms of sulfur in the tailings sample were determined based on the ASTM D2492-02 (1970) standard, validated in 2012.

The HC test was performed based on the ASTM D5744-13 (2018) standard, following protocol B, where the temperature and relative humidity were kept constant in a thermal chamber for 6 days after weekly leaching of 500 mL. The experiment was ended after 11 weeks because after that, it was not possible to collect the extract in a single day; the pores were already being filled with fine particles that hindered passage of the leachate and would have affected leachate quality. The extracts were tested for pH, EC, and metal concentrations by ICP-OES at the University's Soil Mineralogy Laboratory.

We compared the results of the HC test with historical measurements of pH, and concentrations of Fe, Al, Mn, and Zn, provided by the Cambuí Mining Co. from deposit 1, because the other tailings had been treated. We also made measurements at monitoring wells and drainage pumped from mine waters.

Table 1 Classification of samples based on fizz test (Sobek et al. 1978, authorized by the U.S. Environmental Protection Agency)

Fizz test	HCl (mL)	HCl (N)
None	20	0.1
Slight	40	0.1
Moderate	40	0.5
Strong	80	0.5

Results and Discussion

The pH and EC

Based on the results of the tests presented in Table 2 of the ABA static tests, the tailings are considered potentially acid generating. These results confirm what was also observed in the mine tailings deposits, and in the pumped mine water drainages (Table 3), and were consistent with the 5-year historical series (2013–2017) shown in Fig. 4, as well as the HC test results (11 weeks), shown in Fig. 5. The pH average in the HC test (2.95) was lower than the historical data (3.7), which appears to show that the HC test overestimated net acid production. This is believed to be due to changes over time in the tailings, likely associated with processing method changes instituted to extract more of the coal fraction, which concentrates more pyrite in the tailings (Aneel 2011).

In the HC test, the pH and conductivity variations were abrupt during the first 5 weeks; however, they settled down from the sixth week until the eleventh week (Fig. 5). This reinforces the question about the arbitrariness of HC test duration presented by Bowell et al. (2006), El Amari and Hibti (2019), and other authors, such as Pondja et al. (2017) who conducted their HC tests for less than 20 weeks and obtained satisfactory results. With regard to EC, if we analyze the mean of the HC test, we notice

Table 2 Results of static tests of tailings sample

Static test			
ABA (kgCaCO$_3$/t of tailings)			
AP	NP	NNP	RPN
299.37	−53.12	−352.49	−0.18

AP acid potential, *NP* neutralization potential, *NNP* net neutralization potential, *RPN* ratio between NP and AP

Table 3 Recent results of drainage from tailings fields and monitoring wells

Sample	pH	EC (mS/cm)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)	Zn (mg/L)
Field 1, drain 2	4.05	4.700	976.177	240.178	103.650	38.487
DB 1	3.48	8.300	1285.401	204.855	50.976	47.956
DB 2	3.50	4.200	388.534	68.979	18.317	25.393
PC1	5.37	0.031	0.282	0.481	0.011	0.005
PC2	4.33	1.220	0.954	7.659	4.582	1.308
PC3	2.80	3.200	242.844	128.398	13.424	17.505
PC4	3.27	6.700	1248.713	132.526	33.171	38.359
PC5	4.41	1.700	126.732	0.602	5.903	0.879

DB pumped drainage of water from the mines, *EC* electrical conductivity, *PC1* well 1 upstream, *PC2* well 2 upstream, *PC3* well 3 downstream, *PC4* well 4 downstream, *PC5* well 5 downstream

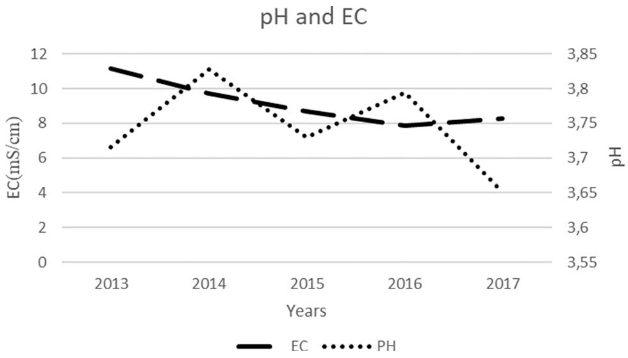


Fig. 4 Variation of pH and EC in the tailings fields

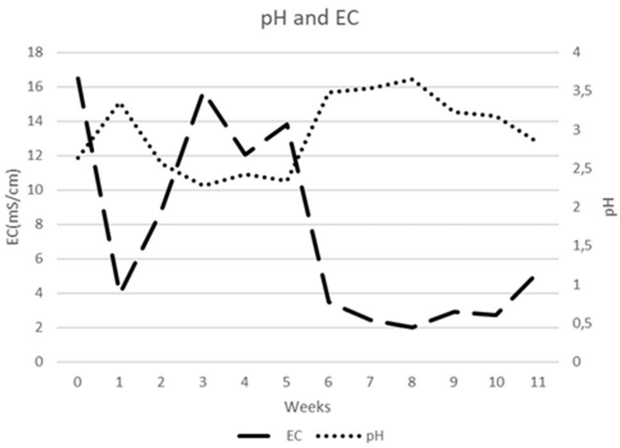


Fig. 5 Variation of pH and EC in HC test

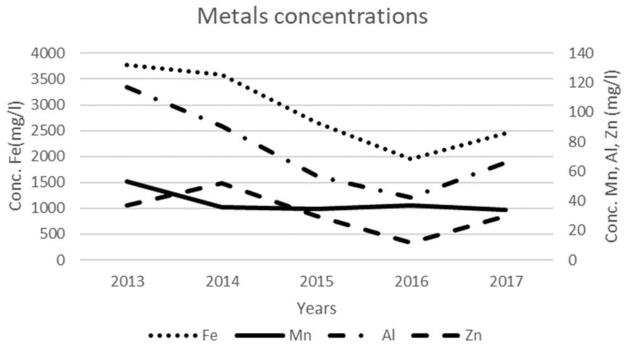


Fig. 6 Depletion of metals in the tailings fields

that the mean is low (7.5 mS/cm) relative to historical data (9.1 mS/cm). Furthermore, the standard deviation is higher (5.6) than the historical data (1.3), though when we analyze only the more or less uniform weeks, we see the average EC is even lower (3.1 mS/cm) and the standard deviation was less (1.1) than the historical data. The may be because in the HC test, we used deionized water, while rainwater contains ions and suspended particles and generally has a lower pH than deionized water.

The AMD contamination is also evident in the pH of the phreatic water and the wells downstream (2.8–4.4), which are more acidic than upstream (5.3), as shown in Table 3. This evidence of contamination is also evident in the values found for the analyzed elements, as well as the conductivity values. Well PC4 is the most influenced by contamination. Mine waters pumped into drains (DB 1 and 2) are acidic and have high concentrations of Fe, Al, Mn, and Zn.

Metals Depletion

We used the HC test to simulate natural weathering, mineral reactions, and the release of metals (Figs. 6 and 7). The field data was expected to have higher amounts of metals than the HC test because the rate of pyrite oxidation in mining waste is mainly controlled by the availability of oxygen and water on the surface of the mineral grain (Anawar 2013; Gerke et al. 1998). In the HC test, oxygen is delivered to the cells by one-dimensional diffusion that is restricted to the air phase, which differs with the tailings deposits, because of the complexity of the oxidation kinetics of pyrite and the contribution of bacteria (Gerke et al. 1998). The kinetics of pyrite oxidation and the special variability of the transport

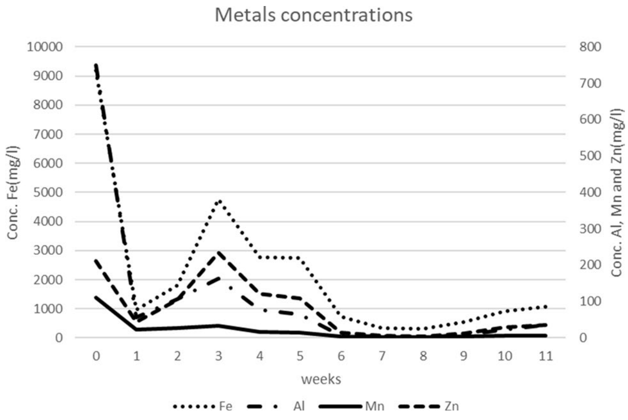


Fig. 7 Depletion of metals in the HC test

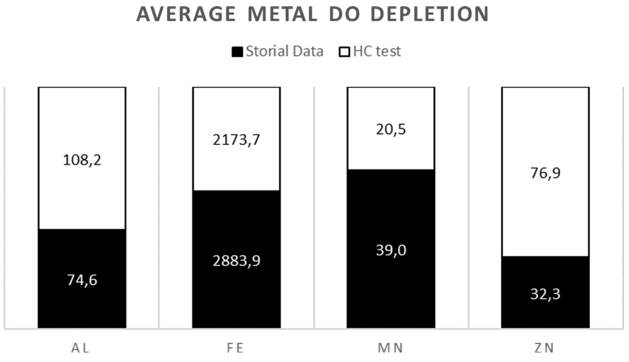


Fig. 8 Comparison of metal depletion in the HC test and in the tailings field

solute and geochemical properties can have a significant effect in the duration of oxidation, the movement of the oxidation front in space–time, and the long-term evolution of the leaching of contaminants through the acidification process in the relatively large vadose zone of rubble piles (Anawar 2013). In all cases, metal depletion was clearly affected by the pH of the solutions.

Iron (Fe)

The Fe in coal occurs in various forms, such as Fe sulfides (pyrite and marcasite), Fe carbonates, Fe-bearing clay minerals, Fe sulfates, and organically bound Fe (Sia and Abdullah 2011; Wang et al. 2008). In general, the Fe concentration tends to fall in both the HC test and the field data. In the HC test after the first wash, considered week 0, the concentration abruptly goes from ≈ 9000 to ≈ 900 mg/L in week 1, and by the end of the experiment it ends at ≈ 1000 mg/L (Fig. 7). In the historical dada, this concentration dropped from ≈ 3800 mg/L in 2013 to ≈ 2200 mg/L in 2017 (Fig. 6). The source of Fe may be pyrite or Fe(III)-(oxy)hydroxide, a product of the oxidation of pyrite (Anawar 2013). As expected, the HC test underestimates the amount of Fe produced (Fig. 8). Since high concentrations of Fe was only observed at week 0, it is likely that a small amount of Fe(III)-(oxy)hydroxide or iron sulfate salts were present in the fresh waste sample and that after washing it, the concentration dropped dramatically (Fig. 7).

Aluminum (Al)

High Al concentrations in the tailings indicate the presence of clay minerals (Sia and Abdullah 2011). Like the Fe, the Al has the same tendency to decrease, both in the field data (Fig. 6) and the HC test (Fig. 7). In the historical data, the concentration dropped from 117 mg/L in 2013 to 65 mg/L in 2017. In the HC test at week 0, the concentration was ≈ 750 mg/L, at week 1 it dropped sharply to 57 mg/L, and it ended at 35 mg/L. However, Al did not behave as expected, as the HC test had a higher average concentration of Al than the field data (Fig. 7). The likely source of Al is the dissolution of aluminosilicates. The high Al concentration at the beginning of the leaching may be masking the result or indicating the buffering capacity of aluminosilicates in this process, according to the capability sequence minerals for buffering the AMD presented by Anawar (2013), which is carbonate > aluminosilicate > (oxy)hydroxide minerals at full O_2 availability.

Manganese (Mn)

Among the other transition metals, Mn is more soluble in slightly acidic to neutral waters than many others, and therefore can persist, even in neutralized acid drainage (Larsen and Mann 2005). It usually occurs as a trace metal in coal, replacing Fe in carbonates (especially in bituminous coal, in solid solution in siderite and ankerite carbonate minerals; Finkelman 1994), however small amounts may be associated with clays in which Mn replaces Fe and Mg (Finkelman 1981; Larsen and Mann 2005), to pyrite, or be organically linked (Swaine 1994). Like Fe and Al, Mn shows the same tendency to decrease in both the field data and the HC test. The concentration dropped from 53.5 mg/L in 2013 to 8.2 mg/L in 2017. In the HC test at week 0, the concentration was ≈ 110 mg/L, at week 1 it dropped sharply to 22 mg/L then it ended at 5.83 mg/L. The Mn concentration behaved as expected, with, greater average production in the field than in the HC test (Fig. 8). In southern Brazilian coal, Mn was associated with Fe oxide/hydroxide forms; however, Mn association with the carbonate phase was principally evidenced in the Barro Branco tailings (Teixeira et al. 2008).

Zinc (Zn)

The Zn in the coal can be in the form of sphalerite (ZnS) (Finkelman 1981; Sia and Abdullah 2011; Swaine 1994), or associated with pyrite and organic matter (Swaine 1994). The principal source of Zn in the Figueira coal is sphalerite, which is present in sufficient concentration to be identified by XRD, and occurs as a minor component of the pyrite, or alternatively in some of the clay minerals (Cutruneo et al. 2014). The Zn concentration in the field data was ≈ 37 mg/L and decreased to 30 mg/L in 2017. The lowest concentration recorded in the field data was 11 mg/L in 2016. The average mobility of Zn in the HC test was higher than in the field data, which may be due to the characteristics of the soil through which the contaminants percolate (pH, grain size, mineralogy of the clay fraction, permeability, organic matter, etc.) and environmental characteristics (time of exposure of the soil to the contaminant, presence of microorganisms, hydrogeological conditions, aerobic/anaerobic conditions, and temperature) (Dyminski 2006). Shuqair (2002) demonstrated that the mobility of Zn in the Figueira tailings was directly proportional to the cation exchange capacity of the soil, which he classified as being medium to high activity and decreasing as a function of depth, inversely proportional to pH and the presence of clay minerals. Therefore, it is expected that much of the Zn could be absorbed by the soil.

The depletion of metals in general reveal the same trend as that of the Fe, considering that the experiment was conducted with fresh tailings. The underestimation of the amount of leached metals may be due to the source of the metals, because if the source is Fe(III)-(oxy)hydroxide, the tailings contained a small amount and the minerals remain in their sulfide form in the sample. This Fe(III)-(oxy)hydroxide can be formed in the natural ascent of the rainwater and groundwater table or flooding can change the pH and Eh conditions of the environment in waste emplacements. With increasing pH, jarosite becomes unstable and hydrolyzes, releasing sulfate anions and toxic elements into surface-contaminated soils. The stability of jarosite is generally limited to a relatively narrow range of acidic conditions. As pH increases, jarosite is transformed to Fe(III)-(oxy)hydroxide (Cutruneo et al. 2014).

Conclusions

Based on this comparative study between the predictive tests and the field data, we conclude that the Figueira coal tailings are potentially acid generators, as observed in the laboratory and in the field data. The physical–chemical parameters analyzed, pH, and EC behaved differently in the two situations analyzed. The pH was lower in the HC test than in the historical data, while the EC was higher in the field data.

In general, HC tests can underestimate the rate of metal release relative to what happens in reality; however, the mobility of the element or contaminant can be affected by several factors. In our study, Zn mobility was affected by the cation exchange capacity of the soil, which resulted in greater Zn mobility in the HC test than in the historical data. Al mobility have been affected by the buffering capacity of aluminosilicates. The Fe and Mn showed greater mobility in the historical data than expected.

Both in the field data, all elements presented the same sinuous behavior as the Fe, which makes us conclude that the source of the elements is Fe(III)-(oxy) hydroxide or sulfate salts and that the fresh tailings produce relatively small amounts of contaminants.

Acknowledgements We are grateful to CAPES for financing the PhD grant to the research author. We also thank the Postgraduate Program in Geology for accepting this research project and creating conditions for its progress, as well as the laboratories of hydrogeological research and mineral analysis (Geology Department), and the laboratory of soil mineralogy (Sector of Agricultural Sciences) of the Federal University of Paraná. We also thank the Cambuí Mining Company, which fully supported the research.

References

ABNT (2004) NBR 10007/2004—Amostragem de resíduos sólidos. 25

Anawar HM (2013) Impact of climate change on acid mine drainage generation and contaminant transport in water ecosystems of semi-arid and arid mining areas. Phys Chem Earth 58–60:13–21. https://doi.org/10.1016/j.pce.2013.04.002

Aneel (2011) A Situação da Produção de Carvão Mineral no Estado do Paraná em Relação a Nota Técnica n o 034 / 2011- SRG / ANEEL de 15 de junho de 2011

ASTM-D4972-18 (2018) Standard test method for soil pH. ASTM Stand Guid. https://doi.org/10.1520/D4972-18.2

ASTM D2492-02 (1970) Standard test method for forms of sulfur in coal 1. Methods 37:1–5. https://doi.org/10.1520/D2492-02R07.2

ASTM D5744-13 (2018) Standard test method for laboratory weathering of solid materials using a humidity. pp 1–23. https://doi.org/10.1520/D5744-13E01.2

Borba RF (2001) Balanço mineral Brasileiro. Fontes Energ pp 1–19

Bowell RJ, Sapsford DJ, Dey M, Williams KP (2006) Protocols affecting the reactivity of mine waste during laboratory-based kinetic tests. In: Proc, 7th international conf on acid rock drainage. american soc of mining and reclamation (ASMR), St. Louis MO, pp 247–270

Campaner VP, Luiz-Silva W (2009) Processos físico-químicos em drenagem ácida de mina em mineração de carvão no sul do Brasil. Quim Nova 32:146–152. https://doi.org/10.1590/S0100-40422009000100028

Campaner VP, Luiz-Silva W, Machado W (2014) Geochemistry of acid mine drainage from a coal mining area and processes controlling metal attenuation in stream waters, southern Brazil. An Acad Bras Cienc 86:539–554. https://doi.org/10.1590/0001-37652014113712

Coastech Reserarch Inc (1991) Acid rock drainage prediction manual. North Vancouver

Cutruneo CMNL, Oliveira MLS, Ward CR, Hower JC, deBrum IAS, Sampaio CH, Kautzmann RM, Taffarel SR, Teixeira EC, Silva

LFO (2014) A mineralogical and geochemical study of three Brazilian coal cleaning rejects: demonstration of electron beam applications. Int J Coal Geol 130:33–52. https://doi.org/10.1016/j.coal.2014.05.009

Depoi FS, Pozebon D, Kalkreuth WD (2008) Chemical characterization of feed coals and combustion-by-products from Brazilian power plants. Int J Coal Geol 76:227–236. https://doi.org/10.1016/j.coal.2008.07.013

Dyminski AS (2006) Contaminação de solos e águas subterrâneas. pp 1–19

El Amari K, Hibti M (2019) A comparison between kinetic test results and natural weathering: the abandoned Kettara Mine tailings pond. Mine Water Environ. https://doi.org/10.1007/s10230-019-00642-0

Fallavena VLV, De Abreu CS, Inácio TD, Pires MJR, Azevedo CMN, Fernandes ID, Ferret LS, Martínez-Tarazona MR (2013) Detailed characterization of certified reference material of Brazilian coal. Quim Nova 36:859–864

Finkelman RB (1981) Modes of occurrence of trace elements in coal. US Geol Surv Circ. https://doi.org/10.1016/s0166-5162(00)00043-4

Finkelman RB (1994) Modes of occurrence of potentially hazardous elements in coal: levels of confidence. Fuel Process Technol 39:21–34. https://doi.org/10.1016/0378-3820(94)90169-4

Flues M, Sato IM, Cotrim MB, Filho PMF, Camargo IMC (2008) Avaliação da influência da operação da termoelétrica a carvão na concentração dos metais e As no solo de Figueira, PR - Brasil. Quim Nova 31:25–30. https://doi.org/10.1590/S0100-40422008000100005

Gerke HH, Molson JW, Frind EO (1998) Modelling the effect of chemical heterogeneity on acidification and solute leaching in overburden mine spoils. J Hydrol 209:166–185. https://doi.org/10.1016/S0022-1694(98)00106-1

Jasper A, Uhl D, Guerra-Sommer M, Hadad AA, Machado N (2011) Charcoal remains from a tonstein layer in the faxinal coalfield, lower Permian, southern Paraná Basin, Brazil. An Acad Bras Cienc 83:471–481. https://doi.org/10.1590/S0001-37652011000200009

Larsen D, Mann R (2005) Origin of high manganese concentrations in coal mine drainage, eastern Tennessee. J Geochem Explor 86:143–163. https://doi.org/10.1016/j.gexplo.2005.06.001

Mineropar (2001) Atlas Geológico do Estado do Paraná. Secretaria de Estado da Indústria, do Comércio e do Turismo, Curitiba

Morrone N, Daemon RF (1985) Jazida de Urânio de Figueira, Paraná. In: Guimarães AD (ed) Principais depósitos minerais do Brasil, 1a Edição. DNPM e CVRD, Brasília, pp 133–142

Pondja EA, Persson KM, Matsinhe NP (2017) Assessment of coal mine water in Moatize by static and leaching tests. Sustain Water Resour Manag 3:403–412. https://doi.org/10.1007/s40899-017-0106-7

Ricardi-Branco F, Arai M, Rösler O (2002) Megaspores from coals of the Triunfo Member, Rio Bonito Formation (Lower Permian), northeastern Paraná State, Brazil. An Acad Bras Cienc 74:491–503. https://doi.org/10.1590/S0001-37652002000300011

Ricardi-Branco F, de Ricardi M (2003) Licófitas da Formacão Rio Bonito (Permiano Inferior, Bacia do Paraná), nordeste do Estado do Paraná, Brasil. Rev Bras Paleontol 6:19–28

Shuqair SMS (2002) Estudo da contaminação do solo e água subterrânea por elementos tóxicos originados dos rejeitos das minas de carvão de Figueira no estado do Paraná. Univ of São Paulo

Sia SG, Abdullah WH (2011) Concentration and association of minor and trace elements in Mukah coal from Sarawak, Malaysia, with emphasis on the potentially hazardous trace elements. Int J Coal Geol 88:179–193. https://doi.org/10.1016/j.coal.2011.09.011

Sobek AA, Schuller WA, Freeman JR, Smith RM (1978) Field and laboratory methods applicable to overburdens and minesoils. US Environmental Protetion Agency, Cincinnati

Swaine DJ (1994) Galena and sphalerite associated with coal seams. In: Fontboté L, Boni M (eds) Sediment-hosted Zn-Pb ores, vol 9. Springer, Berlin, Heidelberg, pp 349–350

Teixeira EC, Pestana MHD, Sanchez J, Fernandes I (2008) Geochemical distribution of metallic elements in the mineral matter of Brazilian coals. Environ Technol. https://doi.org/10.1080/09593339409385506

Wang J, Yamada O, Nakazato T, Zhang Z-G, Suzuki Y, Sakanishi K (2008) Statistical analysis of the concentrations of trace elements in a wide diversity of coals and its implications for understanding elemental modes of occurrence. Fuel 87:2211–2222. https://doi.org/10.1016/j.fuel.2007.10.012