Analysis of Chemical Mobility of Leachate Contaminants in Gneiss Saprolite of Belo Horizonte Solid Waste Landfill (CTRS BR 040), South-Eastern Brazil

Q.C.G. Ferreira, L.A.P. Bacellar

Abstract. Municipal solid waste landfill is a potential source of contamination due to the harmful elements of the leachate, such as trace elements. In the Belo Horizonte landfill, the waste is partially disposed of directly on gneiss saprolites, with lower capacity to mitigate contaminants than upper soil horizons. Column tests were made to analyse the attenuation capacity of this saprolite. The analysis of the chemical elements concentration in soil and leached effluent after the tests and the calculation of the saturation index with PHREEQC software showed the ability of saprolite to mitigate the contamination, mainly by chemical precipitation and immobilization in the colloidal fraction.

Keywords: saprolite, landfill leachate, column tests, PHREEQC modeling.

1. Introduction

A major concern in municipal solid waste (MSW) landfills is the contamination of soil and groundwater by leachates. Major ions such as Na, K, Ca, Mg, NH$_3$, Cl, sulphide / sulphate are among the various types of components usually present in high concentrations in MSW leachates (Christensen et al., 2001), while the concentrations of trace elements are small (Kjeldsen et al., 2002), although they are the most critical elements due to their high pollution potential.

Soils are traditionally considered barriers for groundwater contamination, with high attenuation capacity, which is intensified when pH values are neutral to high (Patrick and Verloo 1998; Kjeldsen et al., 2002). In saprolites (C pedological horizon), adsorption may be small, because their levels of adsorbent constituents are usually much lower than those of surface horizons (Alloway, 1995), especially in areas of crystalline basement rocks. The elements can also be retained in complexes or in the form of insoluble precipitates in the presence of sulphides, carbonates, hydroxides and phosphates, and the two first anions are common in landfills (Pohland, 1991; Kjeldsen et al., 2002). Often, precipitation is the most important phenomenon for the retention of trace elements in soils (Young et al., 1996), although adsorption tends to increase with more alkaline pH, which is predominant in MSW landfills in methanogenic phase (Apello & Postma, 2005).

The study area is the landfill of the Center for Solid Waste Treatment at BR-040 (CTRS BR 040), which is located in Belo Horizonte city (Fig. 1), in Minas Gerais state, southeastern Brazil. The landfill area is located in the gneiss-migmatite basement (Belo Horizonte Complex), predominantly composed of fine to coarse grained gneisses, with trondhjemitic composition (Beato et al., 2003). The soil surface horizons (Oxisols and Ultisols) are of clayish texture composed of quartz and kaolinite, and secondarily of magnetite, ilmenite, hematite and goethite (Sousa, 1998). The saprolite usually has silt-sandy composition and is 10 to 20 m thick.

The local unconfined aquifer system is composed of an intergranular porosity layer in the regolith, with hydraulic communication with a fissural aquifer in the rock (Beato et al., 2003). The top of the aquifer is usually found at the base of the saprolite (C horizon), which shows estimated hydraulic conductivity of $10^{-8}$ and $10^{-9}$ cm/s. According to mathematical flow models, the hydraulic gradient reaches maximum value of 4% near the landfill (SLU, 2010).

The aquifer in the northwestern sector of the landfill is clearly contaminated, but apparently the contaminant
plume has not reached neighbouring districts (Tecisan, 2005; SLU, 2010). The concentration of some chemical elements in this plume exceeded the water potability limits established by legislation in the world and in Brazil (Brasil, 2011), especially for ammonia, chloride, total dissolved solids, iron and manganese. Some trace elements have also been detected at abnormally high levels, and the most problematic are: aluminium, barium, lead, chromium and mercury (Tecisan, 2005; Bacellar & Filho, 2008).

In this landfill, one of the largest in Brazil and located within the urban area, part of the waste was disposed of directly on the gneiss saprolite (C horizon), with no impermeable base (Sousa, 1998), which facilitated the contamination. This situation is relatively common in basement rock areas of Brazil, where the construction of impermeable bases are difficult due to the steep relief.

The objective of this study was to establish the actual chemical attenuation capacity of the saprolite found in the CTRS-BR040 landfill. This issue is relevant because hilly-rolling relief associated with gneisses is one of the most abundant landscapes in southeastern and northeastern Brazil. Since it is difficult to establish an attenuation degree in the field (Barella, 2011), column tests were carried out. Geochemical modelling softwares have evolved over the years, and today there are several tools for modelling natural and contaminated systems, such as the PHREEQCE 2.18 (Appelo & Postma, 2005). This hidrogeochemistry modelling program was used to calculate the speciation and saturation index of the leachate before and after its passage through the soil column in order to confirm the possible chemical reactions during the test.

2. Material and Methods

The compilation of previous data allowed defining representative areas for soil (gneiss saprolite) and leachate sampling to be used in the column tests. Undisturbed and disturbed saprolite samples were collected (Fig. 1), as well as 25 l of leachate samples from a 10 years old residue cell, in which temperature, Eh, pH and electrical conductivity were measured in situ with a multiparameter equipment (Myron, model 6PII). Soil was characterized with respect to: mineralogical determination by X-Ray diffratometry (Rigaku X-Ray Diffractometer / Rotaflex Ru-200Z), particle size; physical and chemical parameters (unit weight, particle specific gravity, dry unit weight, porosity, void ratio, moisture content, pH, cation exchange capacity (CEC) and organic matter content).

The concentration of major and trace elements in soil and in the leachate was characterized by ICP-OES (SPECTRO, model CYRUS CCD), the first one with sample digestion according to EPA standard method 3051A (USEPA, 2007). Sulphate, chloride and alkalinity of the leachate were determined by titration and turbidimetry, according to procedures 4500-SO₄²⁻B, 4500-Cl⁻B and 2320B, respectively (Greenberg et al., 1999). Since pH and Eh conditions varied during the column tests, the chemical and physicochemical properties of the same leachate were determined twice, the first one during the sampling (1st measure) and the second one during the column tests (2nd measure - 90th day of test). It was also made the partial digestion of particles retained in filter membranes, according to Standard Methods 3030F (Greenberg et al., 1992) to quantify elements associated with colloids, via ICP-OES.

The tests were carried out simultaneously on two glass columns of 78.54 cm² and 70 cm long, fixed on wooden support within thermal boxes to ensure thermal insulation. The soil was placed in layers in the columns and it was compacted with the same field unit weight ($\gamma = 16.0$ kN/m³). Geotextile membranes were positioned under and over the soil (Fig. 2) to equalize the flow and prevent piping erosion.

The average seepage velocity in the columns was approximately 150 times higher than that determined in the field with slug tests in order to obtain enough effluent volume for the chemical analyses (SLU, 2010). This was done by increasing the hydraulic gradient magnitude by setting a hydraulic head of 0.50 m of leachate, corresponding to a hydraulic gradient of 5 that was maintained throughout the test. The reproducibility of the two tests was considered good, since the flow, and consequently the hydraulic conductivity, of the leached effluent in both columns varied in a range consistent with that determined with slug tests in
the field ($10^6$ a $10^7$ m/s). The concentration of major and trace elements in the effluent of columns was also similar throughout the experiments (Ferreira, 2012). The duration of the column tests was 100 days, corresponding to a pore volume of 50 and 25 for columns 1 and 2, respectively, since the soil in first column was twice more permeable.

3. Results and Discussion

3.1. Soil and leachate characterization

The column test results show that while the pH values of the raw leachate were slightly alkaline (about 7.5), the first measurements of the leached effluent showed acid values (pH = 4), but from the 6th day, the pH started to rise until

<table>
<thead>
<tr>
<th>Table 1 - Chemical characterization of the soil.</th>
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<tbody>
<tr>
<td>Element</td>
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<td>Measure</td>
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<table>
<thead>
<tr>
<th>Element</th>
<th>Pb</th>
<th>S</th>
<th>Sc</th>
<th>Si</th>
<th>Sr</th>
<th>Th</th>
<th>Ti</th>
<th>V</th>
<th>Y</th>
<th>Zn</th>
<th>Zr</th>
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<tbody>
<tr>
<td>Measure</td>
<td>18.5</td>
<td>31.0</td>
<td>0.944</td>
<td>124.4</td>
<td>1.04</td>
<td>13.7</td>
<td>119</td>
<td>18.4</td>
<td>12.9</td>
<td>25.6</td>
<td>2.5</td>
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LQ = limit of quantification.
Note: As, Be, Cd, Co, Li, Mo and Ni occur below the limit of quantification (LQ).
it reached values of around 8.0 and 8.5 (Fig. 3a), as in areas under the influence of MSW landfills in methanogenic phase (Christensen et al., 2001; Kjeldsen et al., 2002). With low pH (hereinafter called acid phase), the concentration of various trace elements in the leached effluent increased, as expected.

At the collection moment, the leachate redox potential value (Eh) was very low (Eh = -225 mV), but upon contact with oxygen during the sampling operations and column assembling, it became more oxidant (Eh = 225 mV). Due to the presence of oxygen in the saprolite pores, the Eh values in the effluents collected in the first days (acid phase) are higher (around 250 mV), decreasing progressively with soil saturation and with oxygen depletion (Fig. 3b). A progressive reduction of the Eh in the columns was observed, prob-

| Elements | Conductivity | pH | Eh | Temperature | Alkalinity | Chloride | Sulphate | Al | Ba | Ca | Co | Cr | Cu | Fe | K | Mg | Mn | Na | Ni | P | S | Sr | Ti | V | Zn |
|----------|--------------|----|----|-------------|------------|-----------|----------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Unity    | µS/cm        |    |    | °C          |            |           |          |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 1st Measure | 14200         | 7.38 | -225 | 12.48       | 34.2       | 5632.5    | 8.7     | 0.229 | 0.0048 | 0.0458 | 0.0688 | 0.0014 | 0.0612 | 0.0086 | 0.0158 | 0.0541 | 0.0048 | 0.0158 | 0.0048 | 0.0158 | 0.0541 | 0.0048 | 0.0158 | 0.0541 |
| 2nd Measure | 12500         | 7.55 | 112 | 11.50       | 21.2       | 668       | 8.7     | 0.229 | 0.0048 | 0.0458 | 0.0688 | 0.0014 | 0.0612 | 0.0086 | 0.0158 | 0.0541 | 0.0048 | 0.0158 | 0.0541 | 0.0048 | 0.0158 | 0.0541 |

Note: As, Be, Cd, Li, Mo, Pb and Y occur below the limit of quantification (LQ).
ably as a consequence of the reduced porosity, which hinders the oxygen diffusion through the soil column. The Eh values in groundwater wells near the landfill are higher (around 250 mV) Bacellar & Filho (2008), probably due to the dissolved oxygen brought by water of recharge events.

The electrical conductivity values (and also the STD, with which it showed strong positive correlation) were small in the first measures, gradually increasing, while maintaining lower values than those in the raw leachate (Fig. 3c), suggesting that even after 100 days of test (40 years in the actual scale), there is still some type of chemical retention in the soil. The EC values in column 1 are larger than in column 2, probably due to the higher percolation rate in the first column, providing less contact time of soil with the leachate, with lower ion retention by the soil (Ferreira, 2012).

The PHREEQC software 2:18 was used to calculate the speciation of the raw leachate and also the leached effluent from column 2 in the initial (4th day, when the pH is acidic), intermediate (40th day) and final stages (100th day). This column was selected because it showed more regular results over time. The mineral phases that tend to precipitate were mainly carbonates, oxides, hydroxides, sulphides, sulphates and phosphates. Barite was an exception because it only tends to precipitate in the initial acidic stage, when the other mineral phases tend to solubilize. In the raw leachate, a large amount of sulphides tend to precipitate due to the very negative Eh value. The other mineral phases tend to precipitate in the raw leachate and in the last two stages.

With regard to the column effluent, the As, Be, Cd, Li, P, Pb and V concentrations were below the limit of quantification (LQ) of ICP OES. Al, As, Ba, Ca, Cu, Mn, Ni, S, Sr, Y and Zn were sensitive to low pH values, considerably increasing their concentration in the acid phase, and elements As and Pb only showed measures greater than those of LQ in this stage (Ferreira, 2012). The values of elements Al, As, Ba, Co, Cr, Mn, Ni and Pb were higher than the intervention values for contaminated groundwater adopted in Brazil (FEAM, 2010), proving the pollution potential of the leachate to soil and groundwater.

The chemical analyses of the leached effluent and the soil profile after column tests showed different behaviours for the different chemical elements. Some were leached from the soil, such as Ba, Cu, Cr, Y, V and others were retained in the soil, such as Al, Ca, S, Sr, P, Mg, Mn, K, Na, Ti, Zn, Co and Li. Ions with higher concentration in the raw leachate are Na, K, Ca (Table 2) and probably barium (high alkalinity), and of these, only calcium was retained, which explains the small reduction in electrical conductivity (Fig. 3a) during the test. However, these ions do not offer very high risks to health when compared to others commonly found in MSW landfills. In relation to Pb, one cannot tell whether there was leaching or retention, since the concentration difference in the soil before the test is very small (Ferreira, 2012).

Sulphur was retained in the soil (Fig. 4a) and its concentration in the leached effluent is lower than in the raw leachate (Fig. 4b). The modelling with PHREEQC software showed that in the raw leachate recently collected in the field, with negative Eh and slightly basic pH, there is predominance of sulphur in the form of sulphides, which can precipitate several elements, including trace elements such as Cu, Fe, Co, Ni and Zn (Ferreira, 2012). When the Eh values increases, sulphide concentration decreases and the precipitation of metals ceases. However, at low pH and high Eh values, sulphur turns into sulphate, precipitating Ba.

The geochemical modelling also indicates a tendency to precipitate barite (barium sulphate) in the initial phase, when pH is low and Eh is high, conditions which favour the occurrence of sulphur as sulphate (Ferreira, 2012) and barium in solution (Fig. 5a). There is also the possibility of barium precipitation as carbonate (BaCO$_3$ and BaCa(CO$_3$)),. Since the modelling shows that barite is unstable in the subsequent phases of the column test, it is assumed that it has been progressively leached from the soil (Fig. 5b).

Aluminium was also retained (Figs. 6a and 6b), justifying its low concentration in the groundwater in monitoring wells in the landfill area (SLU, 2010). The modelling with the PHREEQC software indicates that this element tends to precipitate as gibbsite, and perhaps in the form of carbonates.

The copper concentration in the leached effluent is smaller than in the raw leachate (Fig. 7a). However, as this element has been leached from the soil (Fig. 7b), it is assumed that it is retained in the colloidal form (Ferreira, 2012). The modelling shows the tendency of copper to pre-
Cipitate with sulphides, especially with highly reducing Eh (Eh < 0).

Iron was retained throughout the test, since its concentration in the effluent increased gradually, but always keeping lower than in the raw leachate (Fig. 8a). Since this element has been strongly leached from the soil (Fig. 8b), a considerable part of it should be associated with the colloidal phase, as evidenced by the digestion analysis of particles retained on a 0.45-μm filter (Ferreira, 2012). According to the geochemical modelling, iron tends to precipitate, as the leached effluent is supersaturated of carbonates, oxides and hydroxides. Similar behaviour was observed for titanium.

Considerable amount of phosphorus and calcium was retained at the top of the soil column (Fig. 9a and Fig. 9b), the same was observed for other elements that exhibited

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**Figure 4** - Sulphur concentration: a) in the column effluents; b) in the soil after the test.

**Figure 5** - Barium concentration: a) in the column effluents; b) in the soil after the test.

**Figure 6** - Aluminium concentration: a) in the column effluents; b) in the soil after the test.
good positive correlations with them, such as strontium, manganese and yttrium. According to the saturation index calculated for the leached effluent, phosphate may have precipitated with calcium in the form of apatite.

The manganese concentration in the raw leachate is slightly higher than the maximum allowed by legislation for drinking water (Brasil, 2001); however, concentrations found in the column effluents are much smaller, indicating strong soil retention (Ferreira, 2012). Saturation index values calculated by the PHREEQC software show a tendency to precipitate it as carbonates and phosphates.

The chromium concentration in the leached effluent is above the maximum allowed by law, constituting a potential source of groundwater contamination in the landfill area. Chromium was initially retained, but its concentration gradually increased, exceeding that in the raw leachate (Fig. 10a). The small soil leaching (Fig. 10b) may have contributed to the progressive increase of its concentration in
the column effluents and this may be a consequence of the progressive alteration of the Eh/pH conditions.

Other important trace elements such as lead, arsenic and cadmium were not detected in the leachate due to the low limit of detection of ICP-MS.

4. Conclusions

The study showed a significant reduction in the hydraulic conductivity of the saprolite during the tests, which can be explained by the progressive reduction of the porosity due to the precipitation of salts and maybe because of the growth of microorganisms. The analysis of data regarding the concentration of major and trace elements in soil and in the leached effluent after the tests, combined with the calculation of the saturation index with PHREEQC software, shows that the saprolite has some ability to mitigate the contamination from the MSW leachate, since several elements were retained in it, such as Al, Ca, Co, Li, S, Sr, P, Mg, Mn, K, Na, Ti and Zn. Chemical precipitation was certainly an important process in this mitigation process. Other elements were leached from the saprolite, such as Ba, Cu, Cr, Fe, Y and V, but some of these, such as Cu and Fe, are apparently immobilized on the colloidal fraction.

Na, K, and possibly bicarbonate constitute a significant part of the leachate solid load, and the first two tend to have conservative behaviour in the contamination plume identified in the landfill (SLU, 2010). Therefore, the slight reduction found in the electrical conductivity of the leached effluent compared to the raw leachate confirms that other ions have been retained even after 40 years of groundwater flow. As the saprolite thickness is greater and the hydraulic head exerted by the leached liquids is about 150 times smaller in the field, the actual retention power should be much more effective.

However, the retention capacity of saprolite is not complete, since the leaching of some elements such as Cr, S, Cu, Co, K, Na, Ni, V, occurred at different times during the column test. So, they can contaminate groundwater, as already shown in previous studies. Therefore, further studies should be carried out in order to elucidate the dynamics of contaminants transport in this medium.

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