

On the Contribution of Physicochemical Processes for the Retention of Heavy Metals Within Environmental Barriers

Franco M. FRANCISCA^{a,b,1} and Daniel A. GLATSTEIN^a

^a*Universidad Nacional de Córdoba, Facultad de Ciencias Exactas, Físicas y Naturales, Córdoba, Argentina.*

^b*Instituto de Estudios Avanzados en Ingeniería y Tecnología (IDIT), CONICET and Universidad Nacional de Córdoba, Córdoba, Argentina.*

Abstract. Liners are engineered layers of low hydraulic conductivity typically designed to isolate solid, semisolid or liquid waste materials from the environment. The capability of a barrier to isolate, retain or sequester pollutants is of key importance, and controls the design of landfill and surface impoundments bottom liners. The purpose of this research is to highlight the importance of considering landfill liners as non-reactive materials where chemical reactions under certain circumstances may determine the mass transport through the barrier. We show that heavy metal ions can be sequestered within a barrier by adding a small amount of steel slags in the barrier. The retention of metal ions within a compacted barrier amended with steel slag is mainly associated with the increase of the pH of the barrier material. Then, the coupled hydraulic and chemical fluxes determine the percolation time for heavy metal transport through environmental barriers.

Keywords. Remediation, industrial residues, groundwater, heavy metals, landfill.

1. Introduction

Liner design requires a broad understanding of residues and their physical, chemical and mechanical properties, but also of the environmental and hydrogeological site conditions. Most relevant waste properties include density, moisture content, field capacity, particle size distribution and hydraulic conductivity [1]. Landfill leachate is one of the most difficult contaminant fluids to study, given its temporal and spatial variation, while external factors such as rainfall or temperature modify its volume and bacterial activity, and the landfill design influences the contact time with wastes. Frequently, the main concern about leachate is the presence of heavy metals in significant concentrations.

Metals removal from water is usually accomplished by precipitation or sorption mechanisms, where several variables such as pH, metal reactivity or the cost of the material should be addressed. Precipitation is widely used for the separation of heavy metals, using solutions to form insoluble species such as hydroxides, sulfides, sulfates, carbonates or phosphates, depending on the metal to be removed [2, 3]. In particular,

¹ Corresponding Author, Franco M. Francisca, Universidad Nacional de Córdoba, FCEfyN, Velez Sarsfield 1601, X5016 CGA, Córdoba, Argentina; E-mail: franco.francisca@unc.edu.ar

Permeable Reactive Barriers (PRB) act as barriers for the contaminants but are permeable to water and, depending on the reactive material used, they allow the removal of contaminants through these mechanisms. The use of PRB has increased in the last few decades due to its low cost and high efficiency [4], while new reactive materials are continuously evaluated. Calcite is used for carbonate precipitation, hydroxyapatite as a source of phosphates, and slack lime for hydroxides precipitation or pH regulation [5]. Depending on the mineralogy and surface charges, granular materials used in PRB can also remove dissolved metals through sorption processes [6, 7].

Steel slag is among the materials being analyzed for its use on PRB. This is a byproduct of the steel industry and is mostly reused as flux, but also as aggregate in the cement and asphalt industry, or as road base and sub-base [8]. Given its physicochemical properties, new applications are continuously found, such as in the treatment of wastewater, iron recovery, CO₂ sequestration or fertilizer [9]. Due to its alkalinity, it can also be used for metal removal, since it promotes their precipitation [10, 11].

The objective of this work is to model the hydraulic and chemical behavior of a landfill bottom barrier composed by steel slag in order to analyze the incorporation of this reactive material to improve the retention of heavy metals and optimize the design of the containment system.

2. Materials and methods

2.1. Used materials

The granular materials used in this work are loessical silt, bentonite and steel slag or basic oxygen furnace (BOF).

The silt is aeolian sediment that covers over 600,000 km² of Argentine territory. This loessical sediment constitutes the most frequently used material for the construction of landfill barriers in the center and northeast of the country. Within the last three decades, several studies were carried out regarding the geotechnical, physical and chemical properties of this loessical silt [13-15]. The soil fraction used in this work consists of the clay silt fraction of the Pampean Loess, mainly composed of quartz, feldspar, gibbsite and volcanic glass, while the clay fraction is composed of illite (over 90%), montmorillonite and kaolinite.

The chemical composition of the slag used in this work is CaO (37.6 – 44.8), SiO₂ (35.0 – 37.3), Iron compounds (8.5 – 27.2), Al₂O₃ (9.3 – 14.7), MgO (5.6 – 9.6) and in less proportions K₂O, Na₂O, S and MnO.

The bentonite has more than 92% of sodium montmorillonite (data provided by supplier).

2.2. Hydraulic tests

Hydraulic conductivity tests were carried out in 55 mm diameter by 100 mm height cylindrical acrylic cells, following the ASTM D5856 [16] standard methods, with variable loading and upflow. The permeating fluid was tap water (electrical conductivity in the range of 10–15 mS/m).

Tests were carried out on the silt, the slag, a mixture of silt with 2.5% of bentonite and a mixture of silt with 20% slag. All specimens were compacted by using Proctor

standard energy (ASTM D698). Specimens were all tested at the maximum dry unit weight and two reduced energies to reach reductions in the dry unit weight that ranged approximately from 90 to 95% of the maximum dry unit weight obtained in the Proctor test.

2.3. Numerical modeling

Contaminant transport in porous media is mainly influenced by chemical and hydraulic gradients, in addition to physico-chemical conditions of the solid. Chemical gradients promote diffusive processes even in the absence of water flow and they can be represented by Fick’s first and second law. On the other hand, the amount of solute transported by a moving fluid is a function of the contaminant concentration and the water flow. In addition, mechanical dispersion induced by differences in flow path, pore size distribution and friction can be solved similarly to diffusion, but considering the effective diffusion coefficient, D^* , by the hydrodynamic diffusion coefficient, D_L . Lastly, if the porous media sorbs the solute, this effect produces retardation on mass displacement. With these considerations, the partial differential equation that governs the 1-D contaminant transport, in a homogeneous and anisotropic media, with retardation, is defined by [17]:

$$\frac{\partial C}{\partial t} = \frac{D_L}{R} \frac{\partial^2 C}{\partial x^2} - \frac{v}{R} \frac{\partial C}{\partial x} \tag{1}$$

where C is the equilibrium concentration, v is the fluid seepage velocity, and R is the retardations factor that can be directly determined by means of column test or estimated by a calibration adsorption isotherm.

Ogata y Banks [18] proposed an analytic solution for the last differential equation:

$$C(x, t) = \frac{C_0}{2} \left[\operatorname{erfc} \left(\frac{R x - v t}{2\sqrt{D_L t R}} \right) + \exp \left(\frac{v x}{D_L} \right) \operatorname{erfc} \left(\frac{R x + v t}{2\sqrt{D_L t R}} \right) \right] \tag{2}$$

C_0 is the contaminant initial concentration in a continuous injection and erfc is the complementary error function. The current work considers percolation through a compacted clay liner (CCL), and also through a composite barrier made of a CCL and a geomembrane (CCL+GM). The permeation on the CCL+GM barrier is conducted through holes (defects) on the barrier, and the flow is represented by [19]:

$$Q_h = n_d C_{q10} \left[1 + 0.1 \left(\frac{H_w}{t_s} \right)^{0.95} \right] a^{0.1} H_w^{0.9} H_b^{0.74} \tag{3}$$

n_d is the defects number on the geomembrane, C_{q10} is the contact quality factor between the CCL and GM, H_w is the leachate height, H_b is the CCL width, and a is the defect area. Typically n_d is considered as 5 defects/10.000 m², and a equals to 290 mm² [19-21]. Then, the fluid velocity is found as follows:

$$v = \frac{Q_h}{A_w * n_d} \tag{4}$$

A_w is the wet area under each imperfection. For the modeled characteristics, Glatstein et al. [22] determined that $A_w = 6.54 \text{ m}^2/\text{ha}$.

3. Results and discussion

3.1. Hydraulic conductivity

The hydraulic conductivity of tested specimens is shown in Table 1. Slag samples were highly permeable with values in the expected range for medium and coarse sand. Hydraulic conductivity of silt and silt-slag mixtures was higher than the average reference value recommended by common international standards ($k \leq 10^{-9} \text{ m/s}$). However, the addition of slag didn't significantly affect the hydraulic conductivity of the compacted silt. A similar trend is expected if the supporting material is a soil-clay mixture given that the fine fraction controls the hydraulic conductivity of the specimen.

The addition of bentonite was needed to reach hydraulic conductivities lower than 10^{-9} m/s . In all cases, the compaction effort (or maximum dry density) of specimens affected the measured conductivities; however, this effect has low relevance in comparison with the effect produced by the addition of bentonite.

Table 1. Hydraulic conductivity of tested liner materials (m/s).

Material	Dry density (kN/m^3)	k (m/s)
Slag	20.5	1.3×10^{-1}
	23.3	2.3×10^{-1}
Compacted silt	15.5	2.8×10^{-8}
	16.3	8.2×10^{-9}
Compacted silt-slag mixture	14.8	1.2×10^{-8}
	16.2	4.1×10^{-9}
Compacted silt with bentonite (2.5%)	14.8	1.0×10^{-9}
	15.6	8.0×10^{-10}

3.2. Reactive Barriers Modeling

The main focus of this work lies in the metals removal mechanisms that are characteristic of the slag, and on the reactive barrier configuration. Analyzed metal removal mechanisms include precipitation and sorption, both highly dependent on pH. In particular, the alkalinity of its chemical components confers on the slag a high acid neutralization capacity (ANC), which increases the solution pH and promotes the precipitation of metal ions.

Considering the significance of pH and the slag behavior, it is important to model the pH profile of the reactive barrier. This can be achieved by two distinct ways: the first is considering the contaminant transport equations for H^+ , assuming that the retardation factor R will be obtained by the instantaneous neutralization of this cation by the slag (Eq. 2). A second way involves the advective transport of the acid front, where the H^+ ions are neutralized until the slag ANC is saturated. Considering the above, the transport of a metal cation within a slag barrier consists of four stages:

- As the flow rate and the slag allow a pH higher than the solubilization pH of the metal, ions will precipitate and accumulate inside the barrier,
- After initial neutralization, the pH tends to decrease given that most leachates have a slightly acid nature. When the solubilization pH is reached, ions

dissolve and a highly concentrated pulse is obtained, given the sudden release of the metal,

- Once the metal ions dissolve, and as they flow through the barrier, some species can be adsorbed on the solid surface, or even precipitate as a different chemical species.
- Finally, when solubilization and sorption of ions reach equilibrium, the barrier behaves as a solid with a defined and saturated sorption capacity.

An increase in the barrier height promotes a higher pH for a longer period or distance, which turns into a greater metal accumulation due to the larger volume of leachate permeated (Figure 1). For this reason, once the pH reaches the solubilization value, the contaminant peak released at the end of the barrier is higher.

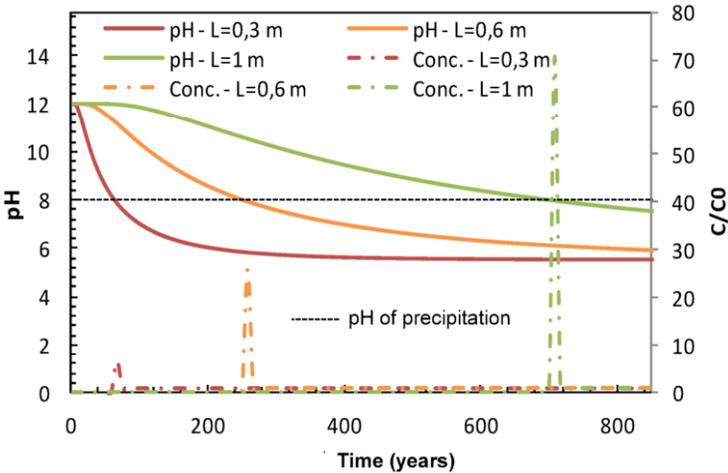


Figure 1. pH and ionic concentration change with barrier height (H_b), considering $k = 10^{-9}$ m/s, $H_w = 0,3$ m, $D_L = 2,9 \times 10^{-9}$ m²/s, $n = 0,4$, $ANC_{slag} = 100$ gH⁺/kg and $pH_p = 8$.

A second parameter that can be modified during the installation of the barrier is its hydraulic conductivity in order to consider the different experimental results as shown in Table 1. Once the liner material is defined, it is important to evaluate the influence of the barrier height and the amount of reactive material used. Numerical tests were carried out to achieve this, analyzing the following barriers a) Compacted Clay Liner (CCL), and b) Composite CCL with Geomembrane (CCL+GM).

Hydraulic conductivity, k , for the CCL was set as 10^{-8} m/s (simulating well-compacted silty liners and poorly compacted liners made of silt-bentonite mixtures) and 10^{-9} m/s (simulating well-compacted liners made of silt-bentonite mixtures). This last value reaches the hydraulic conductivity recommended by common international regulations for landfill liners. In the case of CCL+GM the hydraulic conductivity of the solid was 10^{-9} m/s. Two barrier heights (H_b) were considered: 0.6 m and 1.0 m, as in most international standards. Leachate height (H_w) was set as 0.3 m (as current regulations) and initial pH = 5 [23].

Permeation times for each condition were analyzed comparing the required time for the center of mass of the metal concentration to breakthrough of the barrier. For loess-clay barriers, this occurs when $C/C_0 = 0.5$, while in the case of slag barriers this

occurs when the pH reaches the solubilization value and the contaminant pulse is released.

When analyzing sorption, the bentonite retardation factor was considered as $R=10$, and for incorporating this mineral in 10% of the barrier mass to enhance its hydraulic behavior, as a “mix” R considered as 1.1. In the case of precipitation, the acid neutralization capacity (ANC) of the slag was considered as 100, which is analogous to retardation, for the removal mechanism considered. As 20% of the slag is used in the barrier, the “mix” factor is $R=20$.

Table 2 shows the obtained results. These results can be used to compare different barrier systems, since most regulations allow using “alternative” systems as long as they are equivalent to standard ones, as schematically presented in Figure 2. According to these results and considering the retention of heavy metals, amending a liner with slag may allow reducing the barrier height and having safer barriers against possible undesirable scenarios as increases in leachate head, or increases in hydraulic conductivity due to poor compaction conditions.

Table 2. Percolation times for different analyzed configurations for $H_w=0.3$ m.

Barrier	Properties		Breakthrough time (months)		
	k (m/s)	H_b (m)	Advection + Dispersion	Advection + Dispersion + Sorption ($R=1.1$)	Advection + Dispersion + Sorption ($R=20$)
CCL	1,0E-08	0,6	6	7	133
		1,0	12	13	251
CCL	1,0E-09	0,6	62	60	1266
		1,0	119 (a)	120	2464
CCL+GM	1,0E-09	0,6	151	167 (b)	3845 (c)
		1,0	287	316	6973

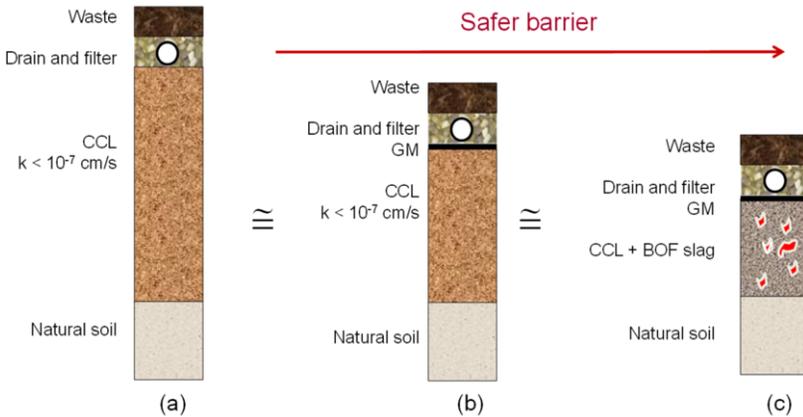


Figure 2. Increase in barrier safety with the addition of new technologies. Cases (a), (b) and (c) schematically represent the cases highlighted in Table 2.

4. Conclusions

This work analyzes the amendment of an industrial residue from the steelmaking industry on landfill liners. Main conclusions are summarized as follow:

- BOF slag increases the pH of a solution percolating through it, promoting metal precipitation and retention. For physical considerations, the addition of 20% slag does not significantly change the hydraulic behavior of a compacted soil liner.
- The addition of BOF slag increases the pH of CCL and this promotes the precipitation of most heavy metals which produces retardation of the heavy metal displacement.
- Once the ANC of the slag is saturated, a pulse of high metal concentration is generated, which should be monitored and removed by a proper drainage system.
- The addition of 20% slag increases over 20 times the breakthrough time for a conventional CCL+GM composite system, with standard operational characteristics ($k=10^{-9}$ m/s, $H_b=0.6$ m, $H_w=0.3$ m).

The results presented herein prove that the amendment of new materials and technologies for contaminant remediation and containment methods can be continuously improved, and that legislation should consistently support such changes. However, this incorporation of new technologies should not be promoted only as a possibility to reduce costs, controls on the compaction process or on the leachate extraction system, but fundamentally as an increase in the containment capacity and environment protection.

Acknowledgments

This work was supported by CONICET [grant numbers 11220150100298CO, PUE-49765], Agencia Nacional de Promoción de la Ciencia y la Técnica ANPCyT-Foncyt [grant number PICT-2014-3101], and Secretaría de Ciencia y Tecnología of Universidad Nacional de Córdoba SECyT-UNC [grant number 30720150100665CB]. Authors thank Camila Tembras for her help with the experiments involving BOF slag and Ignacio Prina for his assistance with laboratory setups in the research group.

References

- [1] R. Bonaparte, Waste Containment Systems: Construction, Regulation, and Performance. Geotechnical Special Publications N° 26, 1990.
- [2] U.S. Environmental Protection Agency (USEPA), *Wastewater Technology Fact Sheet: Chemical Precipitation* (EPA 832-F-00-018), Office of Water, Washington, 2000.
- [3] S.J. Morrison, R.R. Spangler, Chemical Barriers for Controlling Groundwater Contamination, *Environ. Prog.*, 12 (1993), 175-181.
- [4] R. Thiruvengkatachari, S. Vigneswaran, R. Naidu, Permeable reactive barrier for groundwater remediation, *J. Ind. Eng. Chem.*, 14(2) (2008), 145-156.
- [5] F.G. Simon, T. Meggyes, Removal of organic and inorganic pollutants from groundwater using permeable reactive barriers. Part 1: Treatment processes for pollutants, *Land Contam. Reclam.*, 8(2) (2000), 103-116.
- [6] S.Y. Liu, J. Gao, Y.J. Yang, Y.C. Yang, Z.X. Ye, Adsorption intrinsic kinetics and isotherms of lead ions on steel slag, *J. Hazard. Mater.*, 173(1-3) (2010), 558-562.
- [7] T.B. Musso, M.E. Parolo, G. Pettinari, F.M. Francisca, Cu(II) and Zn(II) adsorption capacity of three different clay liner materials, *J. Environ. Manag.*, 146 (2014), 50-58.
- [8] Y.L. Wei, C.Y. Lin, S.H. Cheng, H.P. Wang, Recycling steel-manufacturing slag and harbor sediment into construction materials, *J. Hazard. Mater.*, 265 (2014), 253-260.

- [9] H. Yi, G. Xu, H. Cheng, J. Wang, Y. Wan, H. Che, An overview of utilization of steel slag, *Procedia Environ. Sci.*, 16 (2012), 791-801.
- [10] D. Claveau-Mallet, S. Wallace, Y. Comeau, Removal of phosphorus, fluoride and metals from a gypsum mining leachate using steel slag filters, *Water Res.*, 47(4) (2013), 1512-1520.
- [11] F.M. Francisca, D.A. Glatstein, Influence of pH on cadmium, copper, and lead removal from wastewater by steel slag, *Desalination and Water Treatment*, Vol. 57 (45) (2016), 21610-21618.
- [12] F.M. Francisca, D.A. Glatstein, Long Term Hydraulic Conductivity of Compacted Soils Permeated With Landfill Leachate, *Applied Clay Science*, Vol. 49 (2010), 187 – 193.
- [13] R.J. Rocca, E.R. Redolfi, R.E. Terzariol, Características Geotécnicas de los Loess de Argentina. *Revista Internacional de Desastres Naturales, Accidentes e Infraestructura Civil*, Vol. 6 (2) (2006), 149-166.
- [14] F.M. Francisca, Evaluating the Constrained Modulus and Collapsibility of Loess from Standard Penetration Test, *International Journal of Geomechanics*, Vol. 7 (4) (2007), p. 307 – 310.
- [15] V.A. Rinaldi, R.J. Rocca, M.E. Zeballos, Geotechnical Characterization and Behaviour of Argentinean Collapsible Loess. *Characterization and Engineering Properties of Natural Soils* – Tan, Phoon. Hight & Leroueil (eds). Taylor and Francis Group, 2007.
- [16] American Society for Testing and Materials (ASTM), *Annual book of ASTM Standards*, Vol. 04.08, ASTM International, West Conshohocken, PA, 2007.
- [17] C.W. Fetter, *Contaminant Hydrogeology*, 2a Ed. Prentice Hall, Upper Saddle River, New Jersey, 1999.
- [18] A. Ogata, R.B. Banks, A Solution of the Differential Equation of Longitudinal Dispersion in Porous Media, *US Geological Survey Professional Papers* 411-A (1961), 1-7.
- [19] J.P. Giroud, Equation for calculating the rate of liquid migration through composite liners due to geomembrane defects, *Geosynthetics International*, 4 (3-4) (1997), 335-348.
- [20] J.P. Giroud, R. Bonaparte, Leakage through liners constructed with geomembranes. Part I. Geomembrane liners, *Geotextiles and Geomembranes*, 8(2) (1989), 27-67.
- [21] N. Touze-Foltz, M. Barroso, Empirical equations for calculating the rate of liquid flow through GCL-geomembrane composite liners. *Geosynthetic International*, 13(2) (2006), 73-82.
- [22] D.A. Glatstein, M.A. Montoro, M.E. Carro Pérez, F.M. Francisca, Hydraulic, Chemical and Biological Coupling on Heavy Metals Transport Through Landfills Liners, *The Journal of Solid Waste Technology and Management*, 43 (3) (2017), 261-269(9).
- [23] T.H Christensen, P. Kjeldsen, P.L. Bjerg, D.L. Jensen, J.B. Christensen, A. Baun, H.J. Albrechtsen, G. Heron, Biogeochemistry of landfill leachate plumes, *Applied Geochemistry*, 16 (7–8) (2001), 659-718