Influence of Carbonation on the Microstructure and Hydraulic Properties of a Basic Oxygen Furnace Slag

Basic oxygen furnace (BOF) slag is considered as a potential alternative construction material and is used here on an experimental plot to accurately quantify the risk of pollutant release. Since pollutant release depends on flow, this initially requires characterizing BOF slag hydraulic properties. These were monitored and estimated at plot scale by carrying out water infiltration experiments and inverse numerical modeling. Monitoring the plot showed that the BOF slag studied crustated at the surface as a result of weathering processes. Numerical inversion proved that the crustated material differed from the unaltered slag in terms of water retention and hydraulic conductivity functions. Although all the data pointed to a decrease in saturated hydraulic conductivity with crusting, the trends depended on the infiltration devices used for the capillary length (tension disc vs. Beerkan). Scanning electron microscope (SEM) microanalysis of laboratory weathering cells and lysimeter measurements were monitored in parallel to study the microstructure more precisely and highlighted a reduction of porosity by clogging. On the basis of SEM observations, two conceptual models of pore reduction, based on two different pore clogging hypotheses, were applied to predict hydraulic properties. This step demonstrated that the effect on water retention and hydraulic conductivity strongly depended on the way precipitated phases form and coat grains and could explain the evolution of the transport properties observed. This study contributes to knowledge on the hydraulic properties of BOF slag and their evolution due to carbonation.

Trace element release by BOF slags results from mineral alteration processes (dissolution) that occur during weathering (contact with atmosphere and water). BOF slags contain a large number of minerals that react with water and carbon dioxide, and their dissolution leads to the precipitation of new phases (Huijgen et al., 2005; Chaurand et al., 2006; Huijgen and Comans, 2006). The evolution of BOF slag therefore specifically involves solid–liquid interactions that are strongly water content and flow-dependent (Köhne et al., 2009, for a review). Indeed, water content has a great impact on dissolution and release processes (Padilla et al., 1999). Flow homogeneity has an impact on solid–liquid interactions by governing contact between interstitial water and reactive particles (Lassabatere et al., 2004; Lassabatere et al., 2007; Lamy et al., 2009; Hanna et al., 2010). Consequently, understanding and modeling pollutant release by BOF slags first requires investigating its unsaturated hydraulic properties.

Abbreviations: BOF, basic oxygen furnace; EDS, energy dispersive system; PSD, particle size distribution; SEM, scanning electron microscope.
The hydraulic properties of BOF slag can be investigated using any field or laboratory methods (Klute and Dirksen, 1986), except those based on the use of pressure head tensiometers or water content probes. Indeed, these techniques are too sensitive to the chemical composition of interstitial water which may undergo evolution with time due to mineral weathering and related dissolution processes (Evett et al., 2012). Water infiltration experiments seem all the more appropriate as these techniques are not affected by changes in the chemical composition of water, and they are cheap, efficient, easy to use, and ensure good representativeness of soil hydraulic behavior (e.g., Perroux and White, 1988; Jacques et al., 2002). Several experimental devices, often based on the tension disc infiltrometer or in situ lysimeters, have been developed to characterize hydraulic properties. The infiltret data collected are analyzed inversely using either analytical or numerical models (Angulo-Jaramillo et al., 2000). Among the latter, the BEST algorithm (Braud et al., 2005; Lassabatere et al., 2006) was recently developed to estimate the entire set of hydraulic properties of unsaturated soil by analyzing water cumulative infiltration through a simple ring at null pressure head—Beerkan method (Braud et al., 2005). The Beerkan method and the BEST algorithm are inexpensive, robust, and efficient even at plot structure and watershed scales (Cannavo et al., 2010; Gonzalez-Sosa et al., 2010; Lassabatere et al., 2010; Yilmaz et al., 2010). Numerical modeling is also widely used to invert infiltret data (Mallants et al., 1997; Šimůnek et al., 1998; Schwartz and Evett, 2002; Ramos et al., 2006; Kodesova et al., 2010). The advantage of numerical modeling lies in the possibility of dealing with complex geometries (layered soil profiles) and inverting multiple tension disc infiltret data. However, problems of nonuniqueness have been encountered and must be solved (Šimůnek and van Genuchten, 1996).

Very few studies have been performed on the hydraulic properties of BOF slags, and most have focused on their geochemical behavior or their simplest hydraulic property, that is, porosity (Motz and Geiseler, 2001; Huijgen et al., 2005; Huijgen and Comans, 2006; De Windt et al., 2011). Yilmaz et al. (2010) performed the first complete estimation of the unsaturated hydraulic properties of a specific BOF slag as part of a broader environmental project focusing on the hydraulic and geochemical behavior of BOF slags at the scale of a road embankment (Legret et al., 2010). They also revealed the formation of a crust close to the surface due to weathering and demonstrated that this had an impact on hydraulic properties. However, some of their results require strengthening. They initially used the BEST method, which is based on the hypothesis of a uniform soil profile, whereas the formation of a crust results in a layered profile. Some questions arise concerning the representativeness of their data. Indeed the values proposed can correspond to the crust itself, the material underneath, or a mix between both layers. What is more, there is a need for additional information and more in-depth discussion about the link between the evolution of the microstructure through time (formation of the crust) and the evolution of the BOF slag’s hydraulic properties.

This article focuses on (i) the geochemical mechanisms involved in the mineral alteration and their effects on microstructure and (ii) the impact of the changes in microstructure on hydraulic properties. The BOF slag studied by Yilmaz et al. (2010) was investigated in terms of the time evolution of hydraulic properties and microstructure. Hydraulic properties were derived from the numerical modeling of water infiltration experiments using the Beerkan device and the multiple tension disc infiltrometer and on the basis of a layered soil profile. Microstructure was investigated using microanalysis, specific laboratory weathering cells, and a lysimeter.

Materials and Methods

The experimental plot composed of BOF slag was subjected to atmospheric conditions. The Beerkan device and multiple tension disc infiltrometer were used as a function of time. The data were analyzed through numerical inversion on the basis of a layered profile and compared to those obtained for a uniform soil profile. The water retention curves derived from water infiltration experiments were analyzed through the capillary bundle approach to derive the related pore size distribution of active pores in the flow. In parallel, the same material was weathered under the same atmospheric conditions using a lysimeter to monitor the chemical parameters and composition of the interstitial water in the BOF slag and the BOF slag itself. Meanwhile, weathering cells were used to (i) study mineral alteration for different weathering conditions, (ii) monitor the mass of mineral deposition, and (iii) characterize the time evolution of the microstructure using SEM micro-observation. Lastly, all the data were collected to discuss the link between changes in pore size and transfer properties.

Material and Experimental Site

The material studied was a BOF slag resulting from the production of March 2003 at the site of Fos-sur-Mer in the south of France. It resulted from mixes involving three grain size fractions—0 to 2, 2 to 4, and 4 to 6 mm—and was maturated by being stored outside under ambient weather conditions for 3 yr. It presents a narrow and coarse particle size distribution with a specific density of 2.97 g cm⁻³ (Yilmaz et al., 2010). It is mainly composed of calcium oxide phases (50%), iron oxide phases (ferrite 30% and Mg-wustite 5%), Ca-silicates phases (15%), and up to 10% slaked lime (Ca(OH)₂) (Deneele et al., 2008). The grain surface exhibits a coating in response to slag grain maturation. This external layer is composed of Ca-Carbonates and Ca-hydrates [C-S-H and Ca(OH)₂] because of the dissolution of the initial mineralogical assemblage (Deneele et al., 2008). Additional information regarding the geochemical aspects of the material characteristics can be found in Yilmaz et al. (2010) and in Deneele et al. (2008).

Seventy tons of the maturated material was embedded in a 10.9 × 6.4 × 0.52 m³ experimental road embankment, leading to an average dry bulk density of 1.93 g cm⁻³. Due to compaction and the embedment of the material by construction and earthmoving
machinery, two distinct types of surface appeared, one with coarse material (about 50%) and the other with finer material (about 50%) (Fig. 1a). The effect of machinery on soil compaction and physical properties has already been described for many cases (Keller and Arvidsson, 2004; Etana et al., 2013). Dry bulk density measurements, using annular rings 10 cm in diameter and 7 cm in height, indicated values of 1.72 g cm\(^{-3}\) and 1.93 g cm\(^{-3}\) for coarse and fine surfaces, respectively. The embankment was exposed to external weather conditions for 2 yr (Mediterranean climate, mean annual temperature of 14.9°C, mean total rainfall of 544.4 mm, data from the Marseille–Marignane meteorological station). Despite initially dry conditions, the experimental plot was humidified by rainfall events (Table 1).

**Lysimeter and laboratory weathering cells**

The BOF slag was embedded in a lysimeter, 2 m\(^3\) in volume, at the same bulk density as for the experimental site (i.e., 1.84 g cm\(^{-3}\)) and subjected to the same climate. Water was collected at the bottom and sampled for chemical characterization (major and trace metals, see the section chemical analysis and SEM microanalysis). After 2 yr, the material was sampled to determine the free lime, hydrated lime and carbonate contents of the crust (~3 cm) and the following layers: 0 to 8, 9 to 20, 21 to 33, 34 to 40, and 41 to 50 cm. Undisturbed cores were sampled and prepared for SEM microanalysis.

The BOF slag was also weathered using PVC laboratory columns 12 cm in diameter and 17 cm in height, containing a 4-cm layer of

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glass beads, between the material and the bottom of the system. The system was also equipped with an outlet and a valve to allow drainage or water entering at the bottom. First, the columns were linked to a Mariotte bottle and water saturation was ensured by capillary rise for 24 h. Afterward, the valve at the bottom was opened slightly to allow the water to drain for 30 min while water was poured on the surface to keep the top of the sample saturated. This protocol ensured the system was fully saturated with water. The systems were then subjected to several evaporation–wetting scenarios. Each setup was used once. The first setup was subjected to evaporation at room temperature leading to complete evaporation within 6 mo. The second and the third setups were subjected to watering up to saturation once and twice a month, respectively, with the assumption of complete water saturation. The weights of the systems were monitored to estimate the total solid mass \( m_s \) in the systems:

\[
m_s = \frac{V_T - m_T}{1/\rho_b - 1/\rho_w} \tag{1}
\]

where \( V_T \) is the volume of the column, \( m_T \) is the total weight of the water-saturated columns, and \( \rho_b \) and \( \rho_w \) are the mineral and water densities. Finally, sample cores were carefully extracted from the crust and below it for SEM microanalysis.

**Chemical analysis and SEM microanalysis**

BOF slag particle size analysis was determined through mechanical sieving and laser diffraction spectrometry for particles <650 \( \mu \)m. Chemical composition was obtained after alkaline fusion and sample digestion with aqua regia (mixture of concentrated HCl and HNO\(_3\)) for silica and trace elements, respectively. Concentrations were then measured using inductively coupled plasma optical emission spectrometry and inductively coupled plasma mass spectrometry.

Concerning SEM microanalysis, the samples were air dried at 60°C for several days and coated with an Au deposit, before observation with a Hitachi S570 SEM equipped with an X-ray Energy Dispersive System (EDS) and an XFlash4010 detector (Single Drift Detector). Secondary electron micrographs were taken for phase observations. Energy dispersive X-ray spectroscopy analyses were also employed to determine the atomic composition of the phases observed.

**Water infiltration experiments**

Water infiltration experiments were performed over a 2-yr calendar period from July 2007 to July 2009. The first campaign was performed just after the construction of the experimental plot and the subsequent campaigns after about 4, 12, and 24 mo. All the measurements and experiments were split into fine and coarse surfaces.

For each campaign, the particle size distribution (PSD), the bulk density, \( \rho_b \), and the initial gravimetric water content, \( w_i \), were determined using usual methods (Kutilek and Nielsen, 1994). Two kinds of water infiltration experiments were performed, that is, multiple tension disk infiltration and Beerkan experiments. Multiple tension disk infiltration experiments were used to estimate in situ hydraulic properties using a 20-cm-diameter SW80 infiltrometer (Soil Measurement, Tucson, AZ). A fine layer of Fontainebleau sand, characterized by a particle size between 0.2 and 0.3 mm and high saturated hydraulic saturated conductivity to prevent flow impedance, was used to optimize contact between the disk membrane and the material. The sand was moistened immediately before placing the disk membrane on the surface of the material to further improve contact and prevent air from entering the disk (Cameira et al., 2003). The infiltration experiments were conducted once for each infiltration stage and for each type of surface with consecutive negative pressure heads of −110, −50, −20, and 0 mm.

The Beerkan experiments were based on the use of a single ring with a radius of 48.75 mm. The cylinder was positioned on the soil surface and inserted to a depth of several mm to avoid any lateral loss of ponded water. A fixed volume of water was then poured into the cylinder at time zero: the time elapsed during infiltration of the known water volume was measured. Once the initial volume was completely infiltrated, a second known volume of water was added to the cylinder, and the time required to infiltrate was measured (in cumulative terms). This procedure was repeated for a series of between 8 and 20 known volumes to reach steady state, and the experimental cumulative infiltration was recorded. All the Beerkan experiments were performed in triplicate.

**Derivation of Hydraulic Characteristic Curves from Water Infiltration Experiments**

Water retention curves and hydraulic conductivity functions were described using the van Genuchten–Mualem model (Mualem, 1976; van Genuchten, 1980):

\[
S_c = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \left[ 1 + \left( \frac{h}{h_g} \right)^n \right]^{-m} \tag{2a}
\]

\[
m = 1 - \frac{1}{n} \tag{2b}
\]

\[
K(\theta) = K_s \left( \frac{\theta - \theta_r}{\theta_s - \theta_r} \right)^{\frac{1}{n}} \left[ 1 - \left( \frac{\theta - \theta_r}{\theta_s - \theta_r} \right)^{1/m} \right]^{2} \tag{2c}
\]

where \( \theta_r \) and \( \theta_s \) denote the residual and saturated water contents, respectively; \( K_s \) is the saturated hydraulic conductivity; \( h_g \) is the scale parameter for the water pressure head, \( n \) is a pore size distribution index, and \( l \) is a pore-connectivity parameter assumed to be 0.5 by Mualem (1976).
Hydraulic parameters were obtained by inverting water infiltration data using the HYDRUS software. The HYDRUS code is based on the numerical resolution by finite elements of Richards equation and on the inversion algorithm developed by Marquardt (1963) and is currently used to model water infiltration experiments (Šimůnek and van Genuchten, 1996; Šimůnek and van Genuchten, 1997; Ramos et al., 2006; Šimůnek et al., 2008) with the numerical option of vertical axisymmetric flow. The dimension of the numerical flow domain is 40 cm by 40 cm, which represents a cylindrical volume of 200 dm³ and is large enough to represent the moisture front below the infiltration device. Finite elements (FE) of 2 mm were used to discretize the numerical domain. The upper boundary condition corresponds to the imposed values for pressure head under the device and zero flux otherwise. The imposed pressure heads correspond to zero for the Beerkan experiments and to a series of negative values for the multiple tension disc experiments. A free drainage condition is applied to the lower boundary. A zero flux is applied to other boundaries.

Regarding estimations of hydraulic parameters, θs is derived from bulk density, and θr is considered negligible as it is for coarsest materials (Haverkamp et al., 2005) and for the studied material (Yilmaz et al., 2010). For the first campaign, the other parameters, n, b, Ks, were estimated by inverting the water infiltration experiments. First, a sensitivity analysis was run on the impact of each hydraulic parameter on water infiltration in a uniform profile. This step was aimed at determining the best methodology for identifying parameters and avoiding problems of nonuniqueness. On this basis, the tension disc infiltrometer data were first fitted to obtain the values of (n, bg, Ks). To perform this procedure, the results from the previous study of Yilmaz et al. (2010) were considered as initial values. Then, the Beerkan data were inverted with fixed values for n, by taking into account its estimation from the tension disc infiltrometer data. For the layered profiles, three options were considered: uniform profile (no crust), a crust 1.5 cm thick, and one 3 cm thick. The number of parameters to be estimated was multiplied by 2, resulting in too many degrees of freedom. Several assumptions were then required to avoid problems of nonuniqueness. In particular it was assumed that the material below the crust did not undergo any change in terms of hydraulic parameters. The material below the crust was then assigned the averaged hydraulic parameters derived from the first campaign. The comparison of the three options and the representativeness of the parameters estimated (crust, averaged profile, etc.) are discussed in the results section.

**Derivation of Pore Size Distributions**

Characteristic soil moisture curves $S_e(h)$ can be interpreted as continuous pore size distributions $S_e(r)$, assuming cylindrical capillaries with a continuous distribution of radii $r$ and the Young Laplace equation (Kutilek and Nielsen, 1994):

$$ h = -\frac{\zeta}{r} \quad [3a] $$

where $\sigma_{aw}$ is the surface tension for the air–water interface, $\beta_c$ is the contact angle, $\rho_w$ is the water density, and $g$ is the gravitational constant. $\zeta$ is a constant that lies at 14.9 mm², when $r$ and $b$ are set in mm and assuming a zero contact angle ($\beta_c \approx 0$). Lumping Eq. [2a–2b] and [3] leads to the following expression for the pore size distribution:

$$ F(r) = 1 + \left(\frac{r_g}{r}\right)^n \quad [4a] $$

$$ r_g = \frac{\zeta}{h_g} \quad [4b] $$

The drainable pore size density function $f$ is obtained by differentiating the cumulative PSD with respect to $r$ (Taylor et al., 1990):

$$ f(r) = (n-1) r^{-n-1} r_g^n \left[1 + \left(\frac{r_g}{r}\right)^n\right]^{-(2-1/n)} \quad [5] $$

The mean pore size $\bar{r}$ and the standard deviation, $\sigma_r$, can be estimated from the moments of order $k$, $\mu_k$ through (Kutilek and Nielsen, 1994):

$$ \bar{r} = \mu_1 \quad [6a] $$

$$ \sigma_r = \sqrt{\mu_2 - \mu_1^2} \quad [6b] $$

$$ \mu_k = \int_0^{+\infty} r^k f(r) dr \quad [6c] $$

Correspondingly, the characteristic microscopic pore radius $\xi_m$, that is, the mean characteristic dimension of the hydraulically functional pore, was calculated from the capillary length $\alpha_h$, as suggested by Mubarak et al. (2009). First, the capillary length was derived from the sorptivity $S$ and the saturated hydraulic conductivity $K_s$ by Haverkamp et al. (2005):

$$ \alpha_h = \frac{S^2}{c_h (\theta_s - \theta_0) (K_s - K_0)} \quad [7] $$
where $c_p$ is a function of the shape parameters for the van Genuchten water retention function (van Genuchten, 1980), and the subscript “0” refers to the initial state. Then, the characteristic microscopic pore radius can be determined by (Haverkamp et al., 2005):

\[ \xi_m = \frac{\xi}{\alpha_h} \]  

[8]

## Results

### Impact of Weathering on Water Infiltrations

Water infiltration was strongly dependent on initial water content, which is in agreement with the physics of water flow in soils. The initial water contents showed strong evolution with time (Table 1). Initially, water contents were extremely low because the first campaign was performed in summer just after the construction of the road embankment. Afterward, rainfall events humidified the experimental plot (Table 1). This humidification was favored by the drainage system that acted as a capillary barrier, retaining the water in the system. Despite this humidification, the water content remained below the range of 15%, ensuring proper hydraulic conditions for water infiltration experiments.

The measured bulk densities indicated no significant evolution with time, leading to similar values for the saturated water contents (Table 1). This measure of bulk density is not sensitive enough to highlight a decrease in porosity. The main reasons for this lack of sensitivity lie in the fact that (i) crusting affects only $\sim$3 cm whereas bulk density was measured over 10 cm depth, (ii) that the variation of porosity (in the order of a few percent) resulted in the variation of few grams for the mass of the sample (scarcely detectible using weighing scales), and (iii) that the temporal evolution was characterized by measuring bulk densities at different locations though it was apparent that the difference stemmed more from spatial variability than from temporal variability.

Beerkan experiments (Fig. 2c–2f) show that (i) cumulative infiltration is higher for the coarse zones during the two first campaigns;
Fig. 2a–2b). In addition, cumulative infiltrations exhibit distinct 
(ii) after 12 mo, the differences between coarse and fine surfaces 
vanes (Fig. 2c–2d); and (iii) cumulative infiltration decreases 
with time for all kinds of surface. The data were obtained over a 
period of 24 mo and constitute new data in comparison with those 
of Yilmaz et al. (2010), though they exhibit no clear evolution in 
comparison to the previous step (12 mo). The tension disc infil-
trometer data are in accordance with the Beerkan experiments. The 
time required for the same amount of water to infiltrate increases 
with time, exhibiting a decrease in the ability to infiltrate water 
(Fig. 2a–2b). In addition, cumulative infiltrations exhibit distinct 
shapes. For the first stage, there is a strong increase in the slope 
between −110 mm suction and the others. For the approximately 4-
and 24-mo stages, the change in the slopes is less steep. This result 
indicates a change in capillary properties (Ventrella et al., 2005).

Estimated Hydraulic Parameters
Inverse numerical modeling of tension disc infiltrometer and Beer-
kan experiments leads to accurate fits in all cases (Fig. 2, lines are 
models, points are experimental data) as confirmed by the values of 
normalized root mean square errors below 5% and determination 
coefficients ($R^2$) over 0.985 in all cases. These results clearly prove 
the quality of the fits and the adequacy of the models. In addition, 
the inversion methodology efficiently reduced the uncertainty of 
estimations and avoided the problem of nonuniqueness. All 95% 
confidence interval ranges were lower than 5% of the estimated 
values for the multiple tension disc experiments. For the Beerkan 
data, the confidence intervals were wider with ranges in the order 
of the estimated values. All the Beerkan experiments were inverted 
separately, and related estimated parameters are presented as aver-
ages and standard deviations (Table 2).

In previous studies, the representativeness of estimated parameters 
was called into question. To deal with this point, hydraulic param-
eters were estimated with three crust thickness options though 
the estimations did not change with the option. For example, $K_s$ 
and $h_g$ estimations obtained by inverting infiltrometer data with 
the uniform profile correspond to those related to the 3 cm crust 
option (Fig. 3a and 3c) and the 1.5-cm crust option (data not 
shown). For the Beerkan experiments, similar findings can be pro-
posed with the slight reservation that the discrepancies are a little 
greater (Fig. 3b and 3d). The trends are respected in comparisons 
between "coarse" and "fine" surfaces and the effect of time, that 
is, weathering. The same result was obtained with the numerical 
sensitivity analysis (data not shown). Infiltration was mainly deter-
moved by the properties of the less permeable layer, with the other 
layer having only a slight influence. In addition, the thickness of 
the more permeable layer had no clear influence. When inverting 
data, there is no means of obtaining information about these 
parameters by inverting infiltration since different configurations 
lead to similar fits. However, the estimated values corresponded 
to the parameters related to the less permeable layer in all cases. 
Consequently, in our case, we consider that the estimations are 
representative of the crust.

On this basis and on the basis of the crust thickness measurements 
in the field, we selected the values of the 3-cm crust option (Table 
2). The data are discussed successively as a function of experimental 
device. In all cases, parameter $n$ exhibits no clear variation with 
time, which strengthens the conclusions of Yilmaz et al. (2010). 
The tension disc infiltrometer estimations for $K_s$ diminish with 
time, with a total decrease of 36 and 26 in ratio for the coarse and 
fine surfaces, respectively, after 24 mo. $h_g$ decreases for all kinds of 
surfaces. The Beerkan data lead to similar conclusions for $K_s$ since 
that parameter fell by factors of 68.5 and 6.75 for coarse and fine 
surfaces, respectively. Conversely, parameter $h_g$ shows a different 
trend with a strong decrease between approximately 0 and 4 mo 
followed by a significant increase after 12 and 24 mo (Table 2).

The discrepancy in terms of the estimation of $h_g$ between tension 
disk infiltrometer and Beerkan data may result from the difference

Table 2. Estimations of hydraulic parameters $n$, $h_g$, and $K_s$ related to Eq. [2] derived from water infiltration experiments (standard deviations in parentheses for the Beerkan experiments).

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<td>$n$</td>
<td>$h_g$</td>
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<tr>
<td></td>
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<td>mm s$^{-1}$</td>
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in imposed water pressure heads. For the Beerkan data, the water pressure at the surface is null or slightly positive and the flow is mainly controlled by gravity, the saturated properties of the material being predominant. On the contrary, the water pressure at the surface is negative for the tension disc infiltrometer; the capillary effects and the related hydraulic parameters including \( h_g \) have more influence. In this case, more confidence can be given to \( h_g \) estimates when they are derived from the tension disc infiltrometer data.

**Estimated Pore Size Distributions**
The pore size frequency curves (Fig. 4a–4d) were derived from the water retention curves by Eq. [5]. Corresponding pore size means and standard deviations are shown in Fig. 4e–4f. Estimated pore size distribution changes are clearly surface independent and experimental device dependent. For the tension disc infiltrometer, there is a shift toward the left with time for both coarse (Fig. 4a) and fine (Fig. 4c) surfaces, indicating a reduction of pore size with time. This is confirmed by the decrease in mean pore size (Fig. 4e). For the Beerkan data, the trend differs with a first shift to the left between about 0 and 4 mo followed by a shift to the right (Fig. 4b and 4d). This indicates a decrease in pore size, followed by a significant increase. This is also confirmed by the mean pore size that falls by a factor of 3 after approximately 4 mo before increasing by a factor of 6 between approximately 4 and 24 mo (Fig. 4f).

The mean pore sizes correspond exactly to the characteristic microscopic pore radius \( \xi_m \) as estimated by Eq. [7–8] (Fig. 5). This shows that the mean pore size is representative of the porosity active in the flow during infiltration and that the estimated pore size distribution is representative of the porosity active in the flow instead of the whole porosity. This result is quite relevant when analyzing the effect of weathering. If the pores are completely clogged due to weathering, they become completely isolated and will not participate in the flow or in the new hydraulic water retention curve. Consequently, first, the changes in pore size frequencies and mean pore radius reveal changes in the porosity active in the flow. Second, the estimated pore size distribution corresponds to the hydraulically functional pore size distribution.

**Calcite Precipitation and Crust Formation**
Whatever the experimental conditions (experimental plot, lysimeter, weathering cells), the BOF slag formed a crust at the surface due to weathering (Fig. 1b). The crust was always between 2 and 4 cm in thickness with an average around 3 cm. At pore scale, SEM images reveal the coating of grains with precipitated phases (Fig. 1c). The analysis of the SEM EDS spectra pointed to Ca, C, and O as major elements, in concordance with the precipitation of carbonate [\( \text{CaCO}_3(s) \)]. Identical conclusions were obtained from the analysis of the profile of chemical parameters in the lysimeter (Table 3). A decrease in portlandite [\( \text{Ca(OH)}_2(s) \)] along with an increase in calcite [\( \text{CaCO}_3(s) \)] was observed in the crust close to the surface. Another point to be borne in mind is that the \( \text{CaO} \) content in the crust is in the range of the averaged content of the profile (Table 3).
Fig. 4. (a–d) Pore size densities estimated from water infiltration experiments, (e and f) mean pore radius and standard deviation from (a, c, and e) tension disc infiltrometer and (b, d, and f) Beerkan data.

Fig. 5. Characteristic microscopic pore radius pore vs. mean pore radius derived from water infiltration experiments; (a) tension disc infiltrometer and (b) Beerkan data.
The main mechanisms responsible for the weathering of BOF slags rely on the transformation of the minerals CaO(s), CaSiO₃(s), and Ca(OH)₂(s) by water (H₂O) and carbon dioxide (CO₂(g)) (Huijgen et al., 2005; Huijgen and Comans, 2006):

\[
\begin{align*}
\text{CaO(s)} + \text{H}_2\text{O} & \rightleftharpoons \text{Ca}^{2+} + 2 \text{OH}^- \quad [9a] \\
\text{CaSiO}_3(s) + \text{H}_2\text{O} & \rightleftharpoons \text{Ca}^{2+} + \text{SiO}_2 + 2 \text{OH}^- \quad [9b] \\
\text{Ca} + (\text{OH})_2(s) & \rightleftharpoons \text{Ca}^{2+} + 2 \text{OH}^- \quad [9c] \\
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_3^{2-} + 2\text{H}^+ \quad [9d] \\
\text{Ca}^{2+} + \text{CO}_3^{2-} & \rightleftharpoons \text{CaCO}_3(s) \quad [9e]
\end{align*}
\]

On the basis of the variation of mineral contents, we consider carbonation, that is, the dissolution of portlandite along with the precipitation of calcite, as one of the predominant mechanisms, as already suggested by Huijgen et al. (2005) and Huijgen and Comans (2006):

\[
\begin{align*}
\text{Ca(OH)}_2(s) + \text{CO}_2 & \rightleftharpoons \text{CaCO}_3(s) + \text{H}_2\text{O} \quad [10]
\end{align*}
\]

To quantify the effect of the replacement of portlandite by calcite on pore size distribution, we propose the following methodology. First, the changes in solid mass in the crusted layer are quantified on the basis of weathering cell data. All the cells exhibited an increase in weight with time (Table 4). Assuming that CO₂(g) and H₂O do not take part solid mass, the increase in solid mass Δms directly quantifies the mass of precipitated calcite ΔmCaCO₃(s) minus the mass of dissolved portlandite, that is, plus the change in the mass of portlandite ΔmCa(OH)₂(s). In addition, 1 mol of dissolved portlandite produces 1 mol of precipitated calcite (Eq. [10]). Then, ΔmCaCO₃(s) and ΔmCa(OH)₂(s) can be derived from Δms through mass conservation considerations, as in the following equations:

\[
\begin{align*}
\Delta m_{\text{CaCO}_3(s)} &= -\Delta m_s - \Delta m_{\text{Ca(OH)}_2(s)} \quad [11a] \\
\Delta m_{\text{Ca(OH)}_2(s)} &= \Delta m_s - \Delta m_{\text{CaCO}_3(s)} \quad [11b]
\end{align*}
\]

where \( M_{\text{CaCO}_3} \) and \( M_{\text{Ca(OH)}_2} \) stand for molecular weight. Considering the specific densities of calcite and portlandite (Table 4), the variation in mass can be transformed into variation in volume:

\[
\Delta V_s = \frac{\Delta m_{\text{CaCO}_3(s)}}{\rho_{\text{CaCO}_3(s)}} - \frac{\Delta m_{\text{Ca(OH)}_2(s)}}{\rho_{\text{Ca(OH)}_2(s)}} \quad [12]
\]

where \( \rho_{\text{CaCO}_3} \) and \( \rho_{\text{Ca(OH)}_2} \) stand for calcite and portlandite mineral densities. \( \Delta V_s \) corresponds to the void decrease in the 3-cm-thick crust, which allows determining the change in crust porosity \( P \).

The changes in porosity were calculated for all the systems and highlighted the impact of watering on mineral alteration. Although the decrease in porosity in the crust is around 1 to 2% for all the systems, the decrease is greater for the watered cells (Table 4). This demonstrates that mineral alteration is favored by contact with liquid water, as already stated by Legret et al. (2010). The BOF slag from the lysimeter and the experimental plot were exposed to meteorological conditions, that is, to water, and should have...
undergone a decrease in porosity in the same order of magnitude as the weathering cell #3 (Table 4), that is, in the range 2 to 2.5%. This range is in agreement with field measurements that do not indicate any significant change in bulk density with time, since a 2.5% variation in temporal porosity can be hidden by the precision of a bulk density measurement. It should be mentioned that a 2 to 2.5% decrease in porosity results from two antagonistic mechanisms: dissolution of portlandite and precipitation of calcite. Each phenomenon triggers a variation in porosity of \( \sim 10 \) to 15\%, an increase for portlandite dissolution and a decrease for calcite precipitation. The variation is greater for calcite precipitation, which explains why the concomitant effects lead to a decrease in porosity.

**Discussion**

**Impact of Mineral Alteration on Microstructure and Pore Size Distribution**

The results described above predicted the reduction in porosity due to mineral alteration. To derive the impact of such a decrease on pore size distribution, we considered that void volume was related to the square of the pore radius \( r^2 \), as proposed by Ghezzehei (2012) for uniform deposition in a set of identical capillary bundles:

\[
\frac{\Delta r}{r} = \left( 1 + \frac{\Delta P}{P} \right)^{1/2} - 1
\]

where \( P \) corresponds to the porosity of the crust. The decrease in porosity resulting from only dissolution or only precipitation can also be quantified in the same way. For the weathering cell 3, the calculations indicate that pore size should decrease within the range of 6 \( \mu \)m with the formation of a coating with carbonates around 50 \( \mu \)m thick (Table 5, chemical analysis line). However, these data must be considered as indicative of the likely order of magnitude of the thickness. In particular, this relies on the assumption of a unique pore size, which does not necessarily match the complex geometries of BOF slag (pore tortuosity, isolated pores, throats, etc.).

SEM microanalysis provides more direct information on the way new minerals grow and pores are reduced. The SEM observations indicated that the pore size is in the order of several hundred micrometers, and the coating thickness is from \( \sim 20 \) to 30 \( \mu \)m to more than 50 \( \mu \)m (Fig. 1c–1d). This indicates that the coating completely clogged the smallest pores leaving only the largest pores (Fig. 1d, arrow). These observations also indicate that mineral deposition is slightly pore size dependent with more deposition in larger pores. In fact, the real deposition pattern corresponds to an intermediate scenario between the homogeneous thick model from Taylor and Jaffé (1990), which assumes uniform thickness, and the linear model proposed by Wissmeier and Barry (2009), which assumes that mineral deposition is proportional to pore size.

Finally, some information on microstructure can be derived from the water retention functions estimated from water infiltration experiments. The related pore size distributions give a mean pore size in the range of 100 to 200 \( \mu \)m for the tension disc infiltrometer vs. 5 to 50 \( \mu \)m for the Beerkan data. The infiltrometer estimations agree with the SEM observations, whereas the Beerkan data lead to significant underestimations (Table 5), which might justify some distrust. Regarding the evolution of pore size with time, it is difficult to conclude definitively. On the one hand, the decrease in pore size, as predicted by tension disc infiltrometer data (Table 5), is in agreement with the reduction of larger pore size, as observed by SEM. On the other hand, the increase in mean effective pore size, as predicted by Beerkan data, is in agreement with the complete clogging of the smallest pores, forcing water to flow through the macroporosities (Table 5). The concomitancy of larger pore reduction and the clogging of smaller pores may lead to either mean pore size increase or decrease depending on which mechanism is predominant. Although the effect of clogging on the mean pore size seems difficult to predict, the concomitancy of both mechanisms may lead to a reduction in the variance of pore size, as revealed by the shape of pore size distributions (Fig. 4).

**From Microstructure to Transfer Properties**

Regarding these results, we consider the BOF slag as a porous medium with an initial mean pore size in the region of several hundred micrometers that undergoes a decrease in pore size in the region of a few dozen micrometers on average and with a complex deposition pattern. We investigated with greater precision the case of fine zones subjected to a decrease of 12% porosity for the case of (i) uniform mineral deposition (\( \sim 20 \mu \text{m decrease in pore radius} \)), and (ii) mineral deposition proportional to pore size. For these cases, we modeled the impact of pore size reduction on transfer properties, that is, water retention and hydraulic conductivity functions.

To determine the new water retention and hydraulic conductivity functions, we decided to work with volumetric pore size densities...
instead of pore size densities. These are proportional to the pore size densities as defined by Eq. [5] and are directly linked to new and initial water retention functions through (assuming negligible residual water content):

$$\theta(r) = \int_0^r f_V(x) \, dx$$ \hspace{1cm} [14a]

$$\theta^*(r) = \int_0^r f_V^*(x) \, dx$$ \hspace{1cm} [14b]

Let us consider bijective transformation function $g$ that associates the new radius $r_1$ with all the pores of original radius $r_0$. By construction, this function ensures that the number of pores of radius $r_0$ before transformation is equal to the number of pores of radius $r_1$ afterward, leading to the following equality in terms of volumetric pore size densities (Wissmeier and Barry, 2009):

$$\frac{f_V^*(\eta)}{r_1^2} = \frac{f_V(\eta)}{r_0^2}$$ \hspace{1cm} [15]

The concatenation of Eq. [14–15] provides the following general expression for the new water retention curve:

$$\theta^*(r) = \int_0^r \left( \frac{g(x)}{x} \right)^2 \frac{dg}{dx} f_V(x) \, dx$$ \hspace{1cm} [16]

where $g^{-1}$ stands for the inverse function of $g$. As suggested by Wissmeier and Barry (2009), the Mualem capillary model can be considered for the prediction of hydraulic conductivity, leading to the following expression for the new hydraulic conductivity function:

$$K^*(r) = K_s \left[ \frac{\theta^*(r)}{\theta_s} \right]^2 \int_0^\infty \left( \frac{g(x)}{x} \right)^3 \frac{dg}{dx} f_V(x) \, dx$$ \hspace{1cm} [17]

Equations [16–17] were considered to model the new water retention and hydraulic conductivity curves for the two pore size evolutions: (i) uniform coating with $r' = g(r) = r - L_f$ ($L_f = 20 \mu m$) along with the clogging of the smallest pores ($r_0 < L_f$); and (ii) linear coating with $r' = g(r) = R_{0f} r$ ($R_{0f} < 1$) with no complete clogging of any of the pores. Initial and new pore size densities and cumulative functions are illustrated in Fig. 6b–6c. The linear coating induces a decrease of all the pores, leading to an increase of volumetric density for the smaller pores, mostly between $10^{-4}$ and $10^{-2} \text{ mm}$ (Fig. 6b). The average pore size decreases from 205 to 175 $\mu m$. On the contrary, uniform coating causes the disappearance of the smallest pores, as shown in Fig. 6b, resulting in a significant increase of the average pore size to 235 $\mu m$, since clogged pores are no longer taken into account. Uniform coating increases the average pore size active in the flow by filling the smallest pores.

It seems obvious that both models predict a decrease in hydraulic conductivity functions (Fig. 6e). The drops in saturated hydraulic conductivity are 53 and 67%, for uniform and linear coatings, respectively. This is in accordance with what has been previously reported for bacterial clogging (Taylor and Jaffè, 1990; Taylor et al., 1990). Linear coating reduces saturated hydraulic conductivity more because it significantly affects larger pores. For instance, pores larger than 1 mm undergo a decrease of ~130 $\mu m$ vs. only 20 $\mu m$ for uniform coating. Assuming that saturated hydraulic conductivity results mainly from the contribution of larger pores, it seems logical that the linear coating decreases the saturated hydraulic conductivity more substantially. In both cases, the models predict a decrease of saturated hydraulic conductivity by a factor of 2, approximately. This decrease is significantly lower than the fall derived from water infiltration data (by a factor of 7 for fine surfaces). The discrepancy between the model and experimental data is discussed further.

For water retention curves, both options reduce the saturated water content in the same way, whereas their effects on capillarity are different (Fig. 6d). In comparison to the initial water retention function, the water retention curve related to linear coating exhibits far lower water contents at a water pressure head close to 0, whereas the two water retention functions merge for lower water pressure heads (Fig. 6d). Water retention by capillarity in the altered porous medium is as efficient as in the unaltered porous medium. Conversely, the uniform coating decreases water contents whatever the water pressure head value (Fig. 6d). The new water retention function exhibits a narrow shape with a considerable decrease in water content, even for low water pressure heads, indicating less capillarity in the altered porous medium. These opposing trends are directly linked to the changes in pore size distribution. For the linear coating, all the pores are reduced and capillarity is increased in all of them (Fig. 6a). For the uniform coating, capillarity is increased in the larger pores but eliminated in the smallest pores that become completely clogged (Fig. 6a). This latter effect is predominant, the mean size of the pores active in the flow increases from 205 to 235 $\mu m$, which is in agreement with the decrease in capillarity.

The changes in time of the pore size distributions derived from the water infiltration experiments (Fig. 4) can be discussed in the light of the modeled data (Fig. 6b). In some cases, the change in shapes seems to point to proportional coating. For instance, this is the case for the pore size distributions derived from the infiltrometer for coarse zones between time of approximately 0 and 4 mo (Fig. 4a vs. Fig. 6b). In other cases, the change in shape points to uniform coating with a greater decrease in the number of small pores (e.g., for fine zones as derived from the infiltrometer between approximately 4 and 24 mo). These data indicate that several kinds
of coatings may appear depending on the zone and time. In addition, some cases cannot be explained by any of the models (uniform or linear coating). All these models predict that the change mainly affects the part below the peak, that is, the smallest pores with no horizontal translation of the peak. On the contrary, the experimental pore side distributions are clearly impacted on both sides of the peak which is also subject to horizontal translation.

These discrepancies between modeled and observed data suggest that (i) the effect of mineral alteration on water retention and hydraulic conductivity functions may depend on the localization and the geometrical properties of precipitated phases, and (ii) their deposition in the material studied may not have been sufficiently well described through the assumption of linear or uniform coatings. In reality, mineral alteration leads to more complex patterns and depends on several factors. For instance, mineral deposition should also be considered as a function of water content (Wissmeier and Barry, 2009), since dissolution or precipitation mechanisms occur mainly in water-filled pores. Whereas all the pores are involved under saturated conditions, under unsaturated conditions, mineral alteration (dissolution and precipitation) occurs only in the smaller pores that remain filled with water. After several wetting or drying cycles, the effect of mineral alteration on pore size distribution is more complex than predicted considering only linear or uniform variations (Wissmeier and Barry, 2009). Indeed, the hydraulic properties involved depend on a large number of microstructural and geometrical evolutions such as pore size distribution and shape, as well as pore connectivity and tortuosity that can be affected by clogging, as demonstrated for bacterial clogging (Vandevivere et al., 1995; Baveye et al., 1998). Likewise, with mineral deposition, the way a mineral precipitate grows and occupies the void volume plays a major role (Ghezzehei, 2012). When mineral precipitation forms discrete distinct forms that grow toward the center of the pores, the friction head loss is greater and hydraulic conductivity falls by several orders (Singurindy and Berkowitz, 2005; Ghezzehei, 2012).

These assumptions point to the need for a detailed description of the effect of mineral alteration on soil structure comprising porosity, pore size distribution, pore tortuosity, and connectivity. Recently, Cai et al. (2009) proved the complexity of the mechanisms responsible for mineral deposition for the specific case of

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**Fig. 6. Conceptual model for deriving the hydraulic properties from changes in microstructure.**
secondary precipitation in the microstructure of Hanford sediments, using micro-CT. They proved that dissolution dominated in larger pores and precipitation filled small pores and clogged small throats. From their observations, they concluded the precipitation was enhanced in slow fluid flow zones in association with: (i) angular corners in pores at multigrain junctions, (ii) small pores, and (iii) throats. They also characterized the effect of such precipitation on pore connectivity and on the number of network pathways (Cai et al., 2009). Even though no information is given about the impact on hydraulic properties, they demonstrate the need to properly describe the change in microstructure by using microanalysis tools before deriving hydraulic properties.

Conclusions

This article focused on the evolution of the hydraulic properties of BOF slag due to weathering. The investigations were performed at plot scale on the basis of water infiltration experiments and at laboratory scale, using a lysimeter and weathering cells. For the latter, chemical parameters and SEM microanalysis were monitored. The lysimeter and weathering cell data were used to identify the mechanisms responsible for mineral alteration and quantify their impact on the microstructure. This impact on the microstructure was related to the time evolution of hydraulic properties. Water infiltration experiments using a multiple tension disc infiltrometer and Beerkan apparatus were conducted at field scale and numerically inverted to obtain the evolution of water retention and hydraulic functions with time.

In terms of mineral alteration, the lysimeter and the weathering cell data pointed at carbonation mainly through the dissolution of portlandite followed by the precipitation of calcite. The calcite coating of ~20 μm thick appeared to be deposited around grains, clogging throats and the smallest pores. Chemistry calculations based on monitoring the weathering of cell mass and on the hypothesis of the transformation of portlandite into calcite as the single chemical reaction, predicted a coating of ~50 μm thick, in relatively close agreement with SEM observations. Lumping the increase of pore radius resulting from portlandite dissolution and the decrease of radius resulting from calcite precipitation, led to predicting a decrease in pore radius in the region of 10 to 20 μm. At larger scales, these mechanisms were responsible for the formation of a 2- to 4-cm-thick crust whatever the experimental setup (plot, lysimeter, or weathering cells). Weathering cells indicated that mineral alteration was favored by contact with water, the latter being part of the weathering processes and serving as a carrier of CO2.

The information on the evolution of pore radius resulting from carbonation was implemented in the capillary bundle model to predict the evolution of water retention and hydraulic conductivity curves. Modeling was performed for a decrease of pore radius in the region of ~20 μm for several mineral deposition scenarios. The model indicated that the effect on hydraulic properties is clearly dependent on mineral deposition. Although both uniform and linear coating triggers a decrease in hydraulic conductivity, the effect of linear coating has a stronger effect. Regarding capillarity, the effects are the contrary since uniform deposition clogs the smallest pores and then increases the average pore radius, thereby decreasing capillarity. On the contrary, the linear coating reduces the global size of the pores without closing any, thereby favoring capillarity. Capillary bundle model predictions were compared to the evolution of water retention curves and hydraulic conductivity curves as derived from water infiltration experiments. The trends in terms of hydraulic conductivity are accurately predicted, except that the decrease is greater for the hydraulic conductivity functions derived from water infiltration experiments. Regarding the water retention curves, their evolution depends on the experimental infiltrometer and the Beerkan device. Tension disc infiltrometer-derived water retention curves indicated an increase in capillary effects whereas Beerkan derived water retention curves indicated a decrease in capillarity. We considered that more confidence could be given to the water retention functions derived from the infiltrometer since the multiple tension disk experiment involves the behavior of the material under unsaturated conditions and should be more reliable for the unsaturated hydraulic parameters. However, more information is required to reach a definitive conclusion, and in particular, it is necessary to obtain more precise data on the effect of mineral deposition in pores, which could be investigated by micro-CT (Cai et al., 2009).

Finally, these study results complement those of the study of Yilmaz et al. (2010). First, inverting water infiltration data was performed efficiently by accounting for crust formation and the layering of the profile, thereby leading to a better description of the system. However, here the main results concern the link between the chemical mechanisms responsible for weathering and microstructure evolution on the one hand, and between the latter and the evolution of hydraulic properties on the other hand. This study highlighted the need to characterize mineral deposition and its effect on pore size and connectivity before predicting and modeling the effect of weathering on water retention and hydraulic conductivity functions. Further works should be conducted on modeling pollutant transfers. Further geochemical studies are required to understand pollutant releases from BOF slag (Deneele et al., 2008; Legret et al., 2008; Legret et al., 2010), and they should be coupled with a detailed description of hydraulic properties to efficiently model and predict the fate of these pollutants. These steps are crucial before BOF slag can be considered as an alternative material for road construction and civil engineering.

References


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