Analysis of the potential impact of capillarity on long-term geochemical processes in sulphidic waste-rock dumps

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Abstract

Assessing long-term production of acid rock drainage (ARD) from waste-rock dumps (WRDs) requires a careful analysis of the processes controlling acid-generating geochemical reactions under unsaturated conditions. In this work, we focus on the potential control of capillarity on these reactions, as previous studies showed that capillarity affects the activity of water and solutes in the unsaturated zone through the pore water pressure. We used capillarity-corrected thermodynamic databases and compared calculated speciation and solubility results with those from databases that do not account for capillarity. We developed a simple dynamic model with reduced geochemical components to analyze in detail the effect of capillarity. Results indicate that under low pH conditions simulations with capillarity-controlled reactions generate relatively larger dissolved sulfate concentrations from the WRDs over longer time scales, when compared against simulations without capillarity control. This occurs because capillarity strongly controls the formation of secondary sulfate-bearing minerals such as gypsum. When sufficient oxygen and carbon dioxide partial pressures are maintained within WRDs (such as in well-ventilated systems) and calcite content is insufficient to buffer acidity, the amount of secondary gypsum was calculated to be much larger in capillarity-corrected models. No appreciable effects of capillarity were observed under conditions where gypsum was not generated. Model results are also insensitive to temperature changes in typical climatic ranges. These results indicate some of the conditions by which capillarity should be accounted for as a key component to make accurate long-term predictions concerning with ARD from WRDs, and for the correct interpretation of potential processes such as calcite passivation.

1   Introduction

The processes that dominate acid rock drainage (ARD) from sulphidic waste-rock dumps or piles (WRDs) on long temporal scales are poorly understood, yet predictions are required to make informed decisions for operation and management of mining waste. WRDs are usually composed of blasted rocks that do not have an economical value, but often contain ore and reactive gangue minerals in sufficient quantities to generate hazardous drainage. WRDs are unsaturated porous media typically characterized by heterogeneous distributions of physical and chemical properties (Smith and Beckie, 2003). The most important process is the interaction of sulfide and metal-bearing minerals with oxygen, water and microbes. Extensive reviews of the main processes characterizing ARD are provided by Lottermoser (2010) and Nordstrom (2011). Fig. 1A depicts a typical WRD and the basic processes generating ARD from these facilities.

Capillarity may have an important impact of ARD dynamics on WRD. Large capillary forces are typically associated with fine-grained materials, which are ubiquitous in WRDs due to geological heterogeneity and rock blasting or milling of waste rocks. From a hydraulic perspective, capillarity can affect the hydraulic behavior of WRDs, such as the infiltration patterns, as discussed by Smith and Beckie (2003). Under extreme arid conditions it can even be the only physical transport mechanism affecting aqueous speciation in the vadose zone (e.g. Acero et al., 2009; Smuda et al., 2014). From a geochemical perspective, theoretical works showed that capillary forces can have a strong impact on water chemical potential and water-soil geochemistry (e.g. Lassin et al., 2005; Mercury and Tardy, 2001; Tardy and Nahon, 1985; Zilberbrand, 1997). Moreover, previous studies showed that fine-grained materials are much more reactive than coarse-grained particles, especially when oxidation takes place on freshly crushed rocks. Strömberg and Banwart (1999) concluded that particles smaller than 0.25 mm contribute to more than 80% of the sulphide and silicate dissolution and oxidation.

It is therefore important to assess the potential impact of capillarity on ARD reactions in WRDs. This task is challenging to do through experiments or models. The common modeling approach is to simulate aqueous reactions using thermodynamic properties of the saturated zone in the presence of a gas phase. However, this approach does not properly account for the effect of capillarity on the chemical potential of water (e.g. Lassin et al., 2005).

Mercury and Tardy (1997a, 1997b, 2001) proposed a theory in which the thermodynamic and electrostatic properties of water at positive pressure head can be "rescaled" to obtain equivalent properties under capillary tension conditions. The theory relies upon the concept of relative humidity of the air entrapped in the unsaturated zone, and is the basis for the numerical code THERMO-ZNS (Lassin et al., 2005). This code generates pressure-dependent and temperature-dependent thermodynamic standard properties of
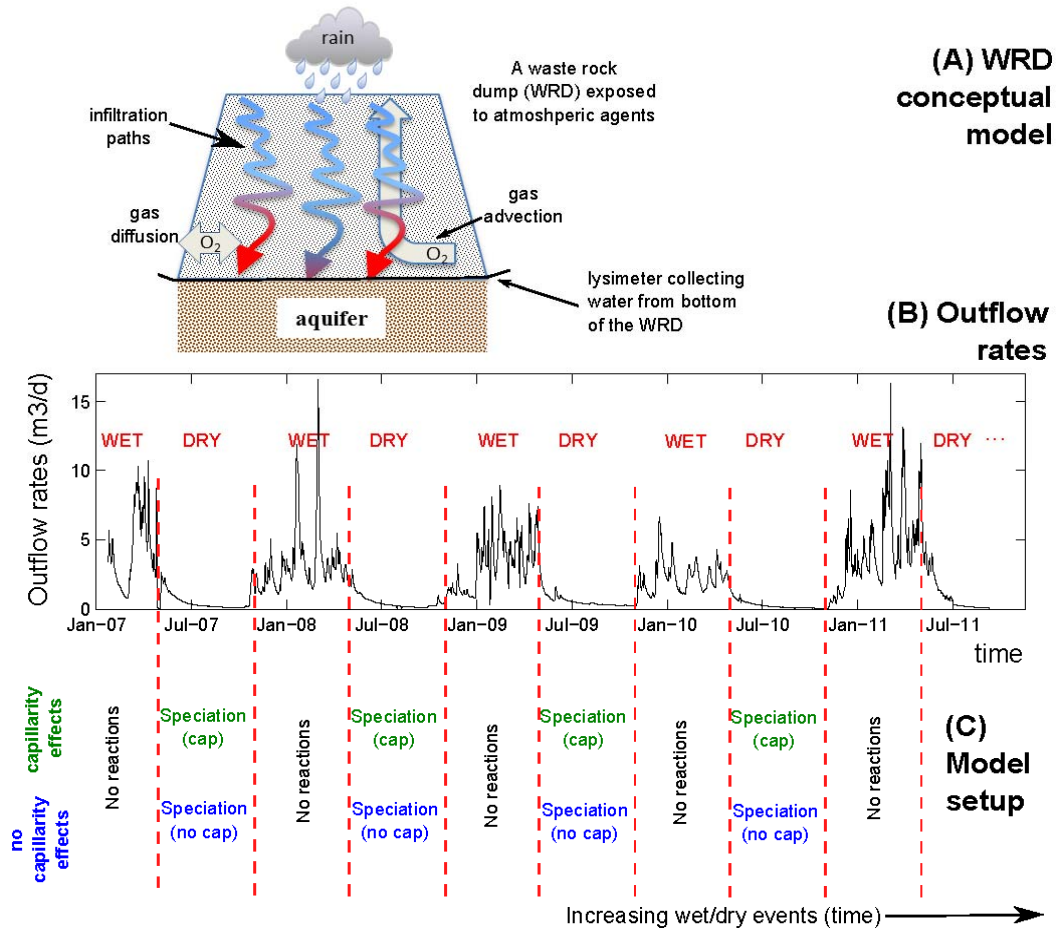
Fig. 1: (A) Conceptual model describing the basic processes characterizing a WRD. (B) The assumption of wet/dry seasonality based on observation from flow field from a representative experiment. (C) The sequential steps for each model. "cap" indicates simulations performed using THERMO-ZNS thermodynamic database, while "no cap" indicates simulations with the Thermoddem database.

water, aqueous species, minerals and gases in capillary systems. The capillary-corrected thermodynamic database can be used for speciation calculations in codes such as PHREEQC (Parkhurst and Appelo, 1999). Capillary-corrected databases have been successfully used to explain aqueous reactions occurring in unsaturated conditions (e.g. Bouzid et al., 2011a, 2011b; Lassin et al., 2013, 2005; Mercury et al., 2004; Pettenati et al., 2008). Lassin et al. (2005) suggest that capillarity strongly affects the relative stabilization of pyrite and iron sulfate as well as solubility and consumption of oxygen. Their analysis is based on the interpretation of the results by Borek (1993), Hollings et al. (2001) and Jerz and Rimstidt (2004), who performed analyses on pyrite oxidation at different humidity conditions and showed a clear dependence between relative humidity and oxidation rates

The goal of this paper is to assess the importance of accounting for capillarity for informed long-term management of WRD. Specifically, we focus on the following questions:

(a) What is the potential influence of capillarity on the long-term geochemistry and production of ARD from WRD (e.g. effect on pH, sulfate production, calcite consumption and gypsum generation, etc.)?

(b) What impact do other parameters such as oxygen concentration and temperature have on capillarity-controlled reactions?

We developed and analyzed a relatively simple model system that, while idealized, contains the important constituents of typical real-world systems and allowed us to obtain useful and understandable insights about the role of capillarity on long-term ARD dynamics from WRD. In our model simulations, we fixed the initial mineral content, total recharge and used a limited number of minerals and components. Then, we performed sensitivity analyses on the impact of a few selected variables of most significance.

The paper is structured as follows. Section 2 outlines the key concepts behind the theoretical and mathematical conceptualization of the impact of capillarity on geochemical reactions. Section 3 illustrates the adopted conceptual model we used to analyze the impact of capillarity on ARD reactions, how the conceptual model is translated into a numerical framework, based on THERMO-ZNS and PHREEQC simulations, and introduces the reference and sensitivity scenarios. Results are shown in Section 4. In the following Section 5, a discussion is focused on some of the most relevant results from the analysis. The paper ends with the main conclusions drawn from this work.

2 Theoretical background

In the following, we briefly outline the mathematical model that relates capillarity and thermodynamic properties of water. A more exhaustive development of these concepts is described in Lassin et al. (2005) and Mercury and Tardy (2001).

The main factor used to rescale thermodynamic and electrostatic properties of water in the unsaturated zone is the relative humidity of the air (R_H). At equilibrium with liquid water and for a fixed temperature (T), R_H is related to the activity of liquid water a_w by

$$a_w = \frac{R_H}{100} = \frac{p}{p_0} \tag{1}$$

where p is partial pressure of the water vapor in the ambient air and p_0 is the partial pressure of saturated vapor. From Eq. (1), one can observe that the water activity is directly related to the water partial pressure in the atmosphere. A definition of activity

similar to the one adopted in Eq. (1) was first used by Scott (1957), who studied deterioration of food by microorganisms, and provides the basis of so-called isopiestic measurements of water activity (e.g. Sablani et al., 2001). It accounts for the osmotic effects due to the presence of solutes in the aqueous solutions and which decrease the activity of water as concentrations increase.

Eq. (1) may not hold for water under capillary tension (i.e. in the unsaturated zone). This occurs since in the HKF convention (Helgeson et al., 1981) water is in its standard state when it is pure and liquid, whatever the temperature and pressure. At its standard state, for pure water $a_w = 1$. Thus, according to Eq. (1), equilibrium could never be reached between pure capillary water and vapor pressures lower than p_0 (i.e. $p/p_0 < 1$). According to the Young-Laplace equation, however, pure water can equilibrate with unsaturated vapor if a curved meniscus can develop at the interface, which is representative of a pressure difference between the gas and the liquid phase. In order to reconcile these approaches and to be able to describe the whole range of situations between pure capillary water and free aqueous solution at equilibrium with the same relative humidity, Lassin et al. (2005) proposed to transform Eq. (1) into

$$RTln\left(\frac{p}{p_0}\right) = RT\ln(a_w) + \int_{p_r}^{p_w} V_w dP \qquad (2)$$

where dP is the unit change of internal pressure associated with capillarity water, V_w is the molar volume of pure water, p_w is the water pressure and p_r is the reference pressure (at 1 bar); R is the universal gas constant and T is the absolute temperature. Eq. (2) traduces the equality of the chemical potential of vapor in the humid air (left-hand side of the equation) with that of liquid water in the capillary aqueous solution (right-hand side). It thus represents thermodynamic equilibrium between the two phases. If water is pure, $\ln(a_w) = 0$ and only pressure effects act to achieve equilibrium with vapor. On the other hand, if the aqueous solution is free (i.e., water is not confined between pore walls or inside a capillary tube, then the liquid-gas interface is flat and $p_w = p_r$), the pressure term is zero and only osmotic effects act to achieve equilibrium with vapor. In porous media, real life is intermediate.

The molar volume of liquid water, V_w in Eq. (2), is calculated according to the equation of state of Wagner and Pruss (2002) as recommended by the International Association for the Properties of Water and Steam (IAPWS). Knowing the dielectric constant of water (Johnson and Norton 1991; Fernández et al. 1997), and the HKF equation of state for aqueous species (Helgeson et al., 1981), one can calculate a number of thermodynamic and electrostatic properties of water, aqueous species, minerals, gases and chemical reactions in the (p_w, T) or (R_H, T) or (ρ, T) conditions fixed by Eq. (2). $\rho = 1/V_w$ is the density of water.

These calculations are implemented in the numerical code THERMO-ZNS (Lassin et al., 2005), which was used to carry out this analysis. THERMO-ZNS generates compatible

thermodynamic properties of water, aqueous species, minerals and gases for selected chemical elements and specified P and T, which are used as capillarity-corrected PHREEQC database. Using this database coupled to PHREEQC, one can estimate saturation indices in the unsaturated zone by including the correction of the Debye-Hückel parameters in the calculation of the activity coefficients. As a reference thermodynamic database, THERMO-ZNS uses the Thermoddem database (Blanc et al., 2012) (available at http://thermoddem.brgm.fr).

3 Conceptual and numerical model setting
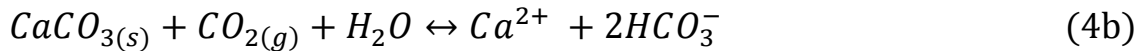
3.1 Basic geochemical reactions

WRD are characterized by very complex structures and several short-term processes (e.g. Al et al., 2000; Lefebvre et al., 2001; Smith and Beckie, 2003; Smith et al., 1995). To understand the potential role of capillarity on long-term generation of ARD, we focus only on a few of the most important processes occurring within WRD. The first basic process considered here is the oxidation reaction for pyrite, typically written as

$$FeS_{2(s)} + 3.5O_{2(g)} + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+. \tag{3}$$
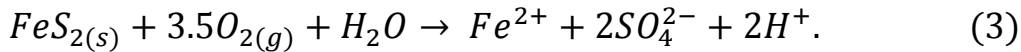
The most important external factors controlling this reaction over the long-term are oxygen concentration, carbon dioxide concentration, water availability and temperature (Lefebvre et al., 2001). Controlling intrinsic factors are abundance and reactivity of acid-producing and consuming minerals. For example, if calcite is present and available for reactions (e.g. not 'passivated'), it can buffer pH and affect ARD dynamics. Calcite dissociates or precipitates according to two general equations (e.g. Sherlock et al., 1995):

$$CaCO_{3(s)} + H^+ \leftrightarrow Ca^{2+} + HCO_3^- \tag{4a}$$

or

$$CaCO_{3(s)} + CO_{2(g)} + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{4b}$$

The first occurs in 'closed' systems, where $CO_{2(g)}$ is initially present to equilibrate carbonic acid but no $CO_{2(g)}$ is restored within the domain once consumed by reactions. The second occurs in 'open' systems, when $CO_{2(g)}$ is supplied externally and available for reactions. In closed systems, less calcite is consumed and less acidity is buffered than in open systems.

Two secondary minerals typically form as a consequence of these reactions. Gypsum can be produced in sulphate-rich waters during acid neutralization,

$$CaCO_{3(s)} + 2H^+ + SO_4^{2-} + H_2O \leftrightarrow CaSO_4 \cdot 2H_2O_{(s)} + CO_{2(g)}. \tag{5}$$
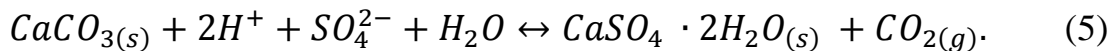
Gypsum precipitation has the double role of storing sulphate and potentially 'passivating' calcite surfaces. Passivation is described for instance in Booth et al., (1997), and is referred to as a general mechanisms that reduces carbonates reactivity (by rimming or coating minerals' reactive spots), hindering their long-term ability to buffer pH. While passivation is not directly simulated within this work, a discussion regarding a possible quantification of the role of capillarity on passivation is addressed in Section 5.

Ferrihydrite, $Fe(OH)_{3(s)}$, can be produced if ferrous iron, Fe(II), released by pyrite oxidation, oxidizes into ferric iron, Fe(III). This may occur if enough oxygen is present in the pores. The formula is typically written as :

$$Fe_{2+} + 0.25\ O_{2(g)} + 2.5\ H_2O = Fe(OH)_{3(s)} + 2H^+ \qquad (6)$$
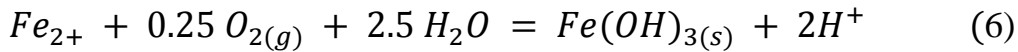
which suggests that, in addition to a role of Fe(III) storage, ferrihydrite precipitation would contribute to increase the acidity.

3.2 Simplified conceptual model

We considered a WRD located in a region characterized by distinct wet and dry seasons. As a representative example, Fig. 1B displays observed outflow rates from the lysimeter at the base of an experimental waste-rock pile, clearly indicating distinct hydrological patterns between summers and winters. In this context, during wet seasons water content may be relatively high within the WRD, permeability and advective transport of gas relatively low, and transport of $CO_{2(g)}$ and $O_{2(g)}$ reduced. On the other hand, during dry seasons water saturations may be low in coarse-grained material, but still high in fine-grained zones of WRD, due to the presence of capillary forces. In heterogeneous WRD with well-mixed proportions of coarse and fine materials, oxygen-rich air can reach low-permeable zones in the dry seasons and locally fuel gas-dependent pyrite and calcite reactions. Their aqueous-phase products cannot substantially migrate from these regions however, due to the low hydraulic conductivity (K) of fine-grained material and in absence of drainage. They are more mobile during the wet season as evidenced by the "first flush" (Nordstrom 2011).

In light of these considerations, we designed a simplified conceptual model where the WRD is viewed a batch reactor (Fig 1C), pyrite oxidation is the leading ARD-generating process and calcite is the main pH-buffering agent. The model was set up on the following steps.

- Step 1: We considered a WRD with a heterogeneous distribution of coarse and fine materials; we assumed a constant rainfall that maintains completely water-filled pores throughout the winter and prevents ARD reactions from occurring by

the inhibition of gaseous oxygen; the pores are considered completely water filled initially.

- Step 2: We imposed a sharp transition between wet and dry season and assumed that at the transition the coarse-grained pores drain instantaneously, while the fine-grained regions retain water. At the same time, $O_{2(g)}$ and $CO_{2(g)}$ levels immediately return to atmospheric values in the large pores adjacent to the fine pores where ARD reactions occur.

- Step 3: Pyrite oxidation takes place in the dry season and it is limited by the availability of oxygen. No evaporation occurs. Capillary water becomes enriched by ARD, but it is confined in fine grained regions.

From the beginning of the second wet-dry cycle, the WRD is flushed by (clean) rain water, which mixes with capillary water and generates ARD discharge. We assume that during each wet season, one half of the dry-season capillary water is displaced from the fine-grained regions by clean rain water resulting in a 50% dilution of the capillary water each wet season. The model looped from Step 1 to 3 for 100 wet-dry cycles. At the end of each cycle, the model provided a measure of the average annual aqueous concentration of the seasonal discharge from the entire pile.

Because of these assumptions, the numerical modeling burden is greatly simplified compared to a full reactive transport model. A more sophisticated model would allow for pyrite oxidation reactions to be represented by the shrinking-core or similar models where the reactivity of pyrite decreases over time (e.g. Acero et al., 2009; Amos et al., 2004) and allow reactions to occur also in wet seasons. We stress that we used an idealized model to isolate the potential role of capillarity on ARD without the confounding factors of other complex processes.

3.3 Scenarios descriptions

We considered a reference initial scenario, and alternative secondary scenarios to test the sensitivity of different parameters on capillarity and ARD.

All simulations consist of a representative volume of reactive porous medium, composed of a solid matrix and a pore space containing 1 kg of water (at saturation). The solid matrix consists of reactive and inert minerals. The instantaneous reactive solid/water ratio is not constrained by porosity. The reactive mineralogy, per kg of water when the pores are completely filled, is assumed to be composed of 0.1 moles of calcite, 0.1 moles of pyrite, and 0.01 moles of sphalerite, galena and chalcopyrite. These minerals and concentrations were arbitrarily selected to represent a simple geochemical system with common elements found in ore deposits and WRDs, such as Zn, Pb, Cu, Fe and S. We set calcite, gypsum, malachite, smithsonite, cerrusite as secondary phases allowed to precipitate or dissolve during the simulations. Their initial content is set to zero (except for calcite, which is also a primary minerals). This selection of secondary minerals is also

arbitrary but based on the commonly observed WRDs (e.g. Peterson, 2014). We set a constant water temperature at 10°C throughout the year and initial atmospheric concentration of $O_{2(g)}$ and $CO_{2(g)}$. Because natural environments never fully equilibrate with $O_{2(g)}$ (Garrels and Christ, 1965), however, we arbitrarily limited the concentration of $O_{2(g)}$ available for dissolution to 10^{-2} moles For simplicity, we assume isothermal conditions, although many WRDs heat up from the exothermic oxidation reactions (e.g. Lefebvre et al., 2001).

Three alternative scenarios are used for a sensitivity analysis:

- a model with reduced concentration of $O_{2(g)}$ and $CO_{2(g)}$. It simulates a system where generic factors such as exothermic pyrite reactions, size of the tailings or initial bulk gas permeability, etc. hinder the efficiency of gas transport within the WRD (e.g. Binning et al., 2007; Harries and Ritchie, 1981; Lefebvre et al., 2001; Ning and Zhang, 1997; Ritchie, 2003). In this scenario, termed "low-O_2", to distinguish from the reference "high-O_2" scenario, we limited the amount of $O_{2(g)}$ available for dissolution to $1/100^{th}$ of its value in the high- O_2 scenario.

- a model with different T. It provides insights to both understand whether the design of WRD can be based on a temperature criterion, and assess how this parameter influences capillarity-controlled speciation (Eq. 2). We studied a scenario with T=0.1°C (mimicking the average annual T in WRD in arctic and subarctic regions, e.g. Smith et al., 2013) and a scenario with T=20°C (similar to those in temperate climates, e.g. Peterson, 2014)

- a model with 10 moles of calcite per kg of pore water (when the pores are fully saturated), to gain insights into the behavior of circumneutral systems (e.g. Peterson, 2014; Sherlock et al., 1995; Smith et al., 1995) where capillarity effects on pyrite oxidation reaction may be inhibited.

3.4 Numerical implementation

Taking advantage of THERMO-ZNS, we built a set of PHREEQC simulations characterized by the same initial conditions and general model parameters described above, but different thermodynamic databases. Specifically, we developed a new database with capillary-corrected equilibrium constants and activity-coefficient model and compared the results with simulations using a traditional, non-corrected database.

For the simulations without capillarity correction (referred to as 'no cap') we used the standard Thermoddem database. For the simulations with capillarity correction (referred to as 'cap'), we assumed that p_w (Eq. 3) drops from 0 MPa during wet conditions to -100 MPa during the dry seasons. The latter is a representative value among those reported by Lassin et al. (2005), based on the work by Borek (1993), Hollings et al. (2001) and Jerz and Rimstidt (2004), and which corresponds to a local relative humidity of about 45-50%, depending on the temperature.

These databases were in turn used in PHREEQC to compute capillarity-controlled speciation and mineral-solution equilibria during dry seasons (no reaction takes place in the wet season, according to our conceptual model explained above).

4   Model results

4.1   Reference scenario

The results for reference high-O_2 scenario are plotted as black lines in Fig. 2a to Fig. 2f, which depict respectively pH, dissolved sulphate, pyrite, calcite (primary minerals), gypsum and ferrihydrite (secondary minerals). In each graph, the vertical axis represents variable-specific quantities (notice that the scale for sulphate is logarithmic), while horizontal axis shows the number of wet-dry cycles. Data referring to the case where capillarity affects equilibrium reactions (simulations using THERMO-ZNS-based thermodynamic database) are depicted with blue full lines, while simulations using the default Thermoddem database are shown in blue-dashed lines.

The effect of capillarity is striking. While pH (Fig. 2a) seems not to be affected by capillarity forces, sulphate release in water (Fig. 2b) is much larger, or at least maintained over more wet-dry cycles (i.e. longer times), when capillarity controls speciation. Specifically, after approximately 50 wet-dry cycles it seems that capillarity maintains sulphate at a constant value (about 1×10^{-2} mol/kg of water), while in the simulations without capillarity sulphate decreases by several orders of magnitude in 10-15 cycles. This important result indicates that calculations considering capillarity could be more conservative than those that do not account for capillarity.

Primary minerals are not affected by capillarity. Fig. 2a and Fig. 2b respectively indicate that the modeled rate of pyrite and calcite consumption does not strongly vary between the two thermodynamic databases. This explains why pH is not affected by the impact of capillarity.

Secondary minerals, on the other hand, are more sensitive to capillarity. Fig. 2c and Fig. 2d illustrate respectively that the content of gypsum and ferrihydrite strongly depend on capillarity. For high-O_2 conditions, gypsum and ferrihydrite are much larger when capillarity is accounted for than when it is not. This is a very relevant result from our analysis, especially for gypsum, which acts as a long-term reservoir of sulphate, maintaining sulphate concentrations over longer time scales in presence of capillarity-controlled reactions than without capillarity control. In the long run, gypsum can also passivate calcite, reducing the acid buffering capacity of calcite and other minerals. Further discussion on passivation is presented in Section 5.
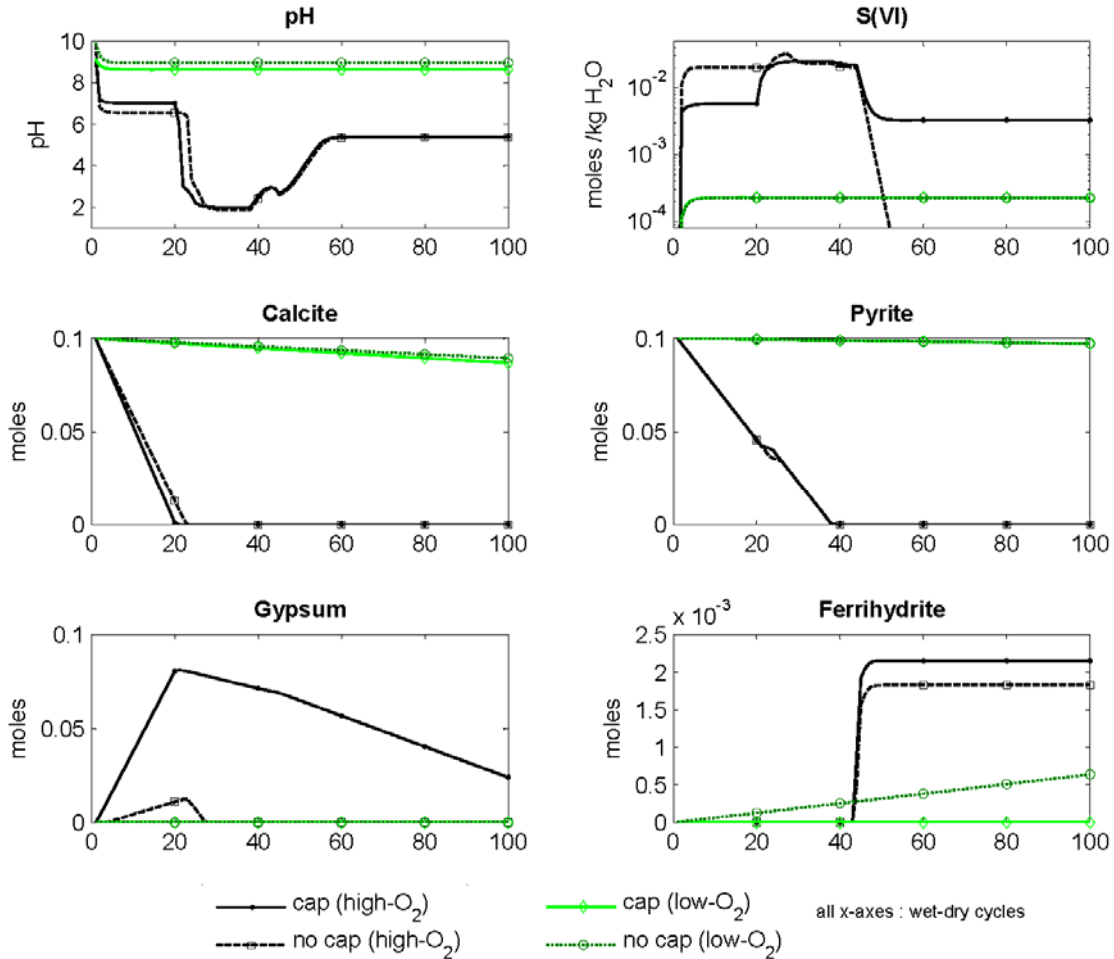
Fig. 2 Results obtained from the reference scenario ("High-O2) and an alternative scenario with lower oxygen ("low-O2"), for constant T=10 °C. "cap" indicates simulations performed using THERMO-ZNS thermodynamic database, while "no cap" indicates simulations with the Thermoddem database.

As such, it seems that capillarity has a selective control on ARD reactions and dynamics; specifically it affects sulphate dynamics through precipitation/dissolution of gypsum and other secondary minerals, while other processes associated to primary minerals, such as pyrite oxidation and calcite dissolution, are seemly less affected by capillarity.

4.2   Sensitivity analyses

We plot in Fig. 2a to Fig. 2f the results corresponding to the low-O_2 case (green lines), where the quantity of available oxygen is more limited than in the high- O_2 case at the beginning of each dry season; T=10ºC, and the amount of calcite is 0.1 moles. In this case, it can be observed that capillarity does not play a strong control on speciation. The behavior of pH and sulphate are almost identical for the two databases. No gypsum is generated and calcite consumption rate is also comparable between the two simulations.

This result is consistent with reduced pyrite consumption in the presence of lower oxygen concentrations: low acidity is produced and immediately buffered by calcite, which dissolves over wet-dry cycles (i.e. time) at a slower rate than in the previously analyzed case. It seems therefore that capillarity effects on the dynamic of pyrite oxidation are, to some extent, subordinate to the presence of oxygen.

The main difference stems from the behavior of ferrihydrite. While at higher $O_{2(g)}$ partial pressure ferrihydite precipitates after 48 wet-dry cycles for both capillary and non-capillary schemes, this mineral only precipitates in the no-capillary scheme at lower $O_{2(g)}$ conditions after a few wet-dry cycles and, quite surprisingly, does not precipitate (at least within 100 wet-dry cycles) in the capillarity scheme. This behavior can be explained considering that, in the low-O_2 scheme, a pH-Eh condition which is less favorable to Fe(III) develops when capillary constraints are taken into account. The calculated Fe(III) concentration are around 2.6×10^{-11} mol/kgw in the capillary scheme ($P = $ -100 MPa) and and 6.3×10^{-11} mol/kgw in the no-capillary scheme ($P = $ 0.1 MPa). Thus, despite a solubility constant (K_{sp}) of ferrihydrite which indicates that this mineral is more stable under isobaric capillary constraints (log $K_{sp} = $ 3.3, with $P = $ -100 MPa) than without capillary constraints (log $K_{sp} = $ 3.7, with $P = $ 0.1 MPa), the behavior difference in the aqueous solution leads to a final destabilizing effect of capillarity on ferrihydrite. Since the behavior of sulphate is similar in the two cases, this "anomalous" effect on ferrihydrite is under the idealizations of the model of secondary importance for the long-term evolution of ARD from WRD. However, in real systems, ferrihydrite could exert a pH-dependent sorption control on metal and oxyanion concentrations in drainage.

A further sensitivity analysis simulating a larger amount of calcite was performed on high-O_2 scenarios to gain further insights on the role of capillarity in this system in presence of a circumneutral environment (low-O_2 scenarios were not analyzed being insensitive to capillarity, as described above). We set 10 moles of calcite, an amount much larger than pyrite (0.1 moles) with $T=10°C$ as before. The capillarity-corrected simulations and those based on Thermoddem are not reported, being similar to the previously analyzed low-O_2 scenario: no gypsum is produced, consistent with the enhanced capacity of calcite to buffer pH.

Quite surprisingly, temperature had no effects on capillarity in both high-O_2 (Fig. 3) and low-O_2 (not reported) scenarios. Simulations at $T=0.1°C$ (blue lines) produced results almost identical to those at the reference $T=10°C$ (black lines) and $T=20°C$ (red lines). The sole exception is for the production of gypsum, which is slightly larger for simulations at lower T; yet, such a small amount of gypsum does not sensibly affect pH and sulphate production. Most importantly, the larger difference in gypsum between capillarity-controlled reactions with non-capillarity controlled reactions is maintained at all analyzed T. While temperature directly controls the impact of capillarity of the thermodynamic behavior of aqueous speciation reactions (Eq. 2), we can conclude that

temperature may not be a fundamental parameter to consider when analyzing the impact of capillarity on long-term ARD production from these settings. Yet, temperature does affect other processes that have not been accounted for here, such as temperature-

driven gas flow gradients (e.g. Harries and Ritchie, 1981; Lefebvre et al., 2001), and reaction kinetics, and therefore must be accounted for in general WRD studies.
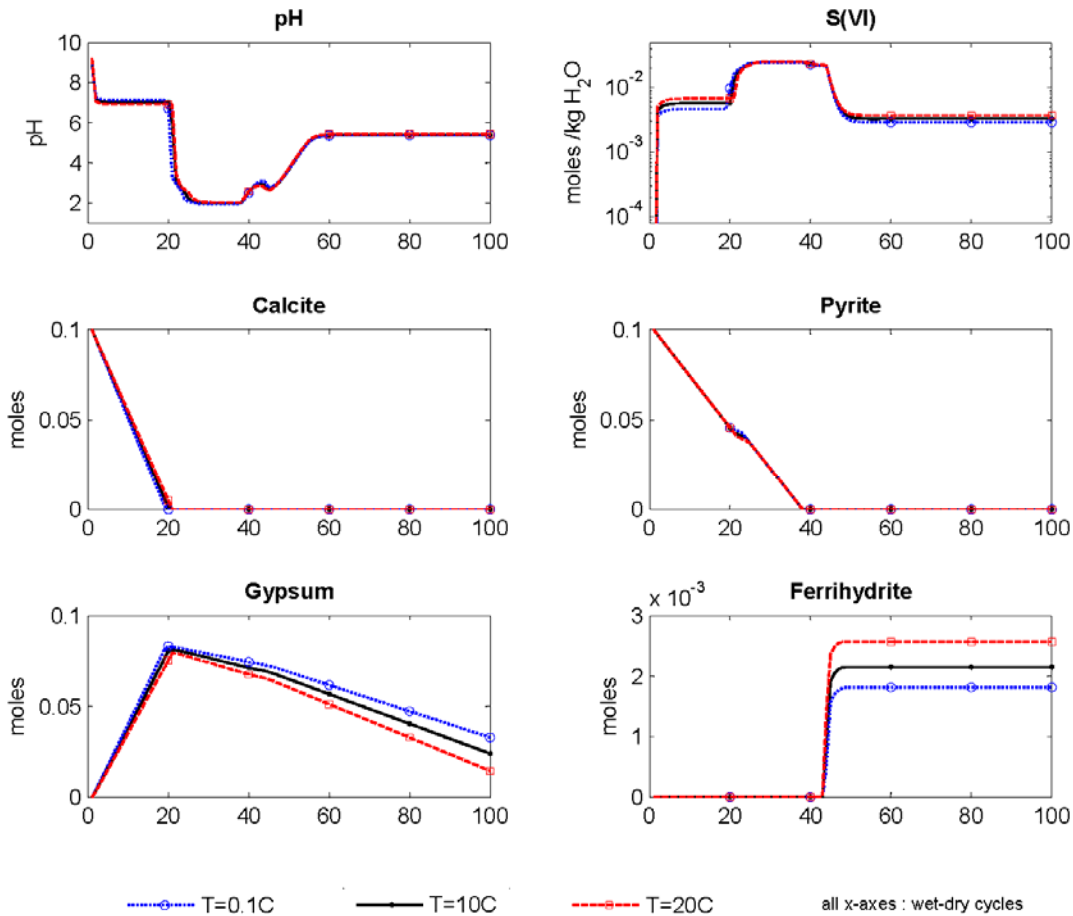

Fig.3 Results obtained from the reference and variable temperature. "cap" indicates simulations performed using THERMO-ZNS thermodynamic database, while "no cap" indicates simulations with the Thermoddem database.

5   Discussion

5.1   Why capillarity preferentially affects secondary minerals?

From the results of our numerical investigation, we observed that when secondary minerals are not produced capillarity has poor or no influence on the overall WRD

behavior, and dissolution/precipitation or oxidation of primary minerals seems to be insensitive to capillarity.

To provide an explanation to this behavior, we need to introduce the concept of "isobaric" and "anisobaric" environment of mineral formation. In typical geochemical models, minerals are assumed to react (e.g precipitate/dissolve) under the same pressure as pore water. This situation is termed "isobaric environment of mineral formation" (or interaction). On the contrary, when the mineral is at another pressure than that of pore water, the situation is termed "anisobaric environment of mineral formation" (or interaction). A classic example of an anisobaric condition is the formation of minerals in deep geological environments, where the lithostatic pressure may significantly differ from the hydrostatic pressure (Colten-Bradley, 1987) and thus minerals form at different pressures. An anisobaric situation can also occur in capillary systems. For instance, anisobaric conditions may ubiquitously characterize capillary gas-pore solution systems, as gases cannot undergo negative pressures (while capillary water does in the unsaturated zone). In certain circumstances, both isobaric and anisobaric conditions can coexist. For instance, specific minerals can form under the pore-water pressures, while others can have formed at lower or higher pressures. The status of coexistence of both conditions is termed "dual context' (Lassin et al., 2005). We refer the interested readers to Mercury et al. (2003) and Lassin et al. (2005) for additional details about these concepts.

In WRDs, it is reasonable to assume that the dual context may exist. Initial primary minerals (pyrite and calcite in our model) could have formed at pore-water pressures different from those characterizing the transient hydrostatic conditions within the unsaturated piles. On the other hand, secondary minerals (gypsum and ferrihydrite in our model) can precipitate at equilibrium with pore water and thus form under isobaric conditions.

It can be shown that in general isobaric conditions contribute more to stabilize minerals than anisobaric conditions. This is due to the condition-specific energetic contribution of each chemical compound to the final equilibrium conditions of a chemical reaction. We refer to Lassin et al. (2014) for details. Our results seem to confirm this fact, as capillarity does not significantly affect pyrite and calcite, when compared for instance with its stronger control on the formation of gypsum and ferrihydrite.

The amount of precipitating gypsum directly controls the long-term storage of sulphate in the outflowing waters. Thus, a necessary condition for capillary to significantly control the long-term geochemical behavior of WRDs could be the actual formation of this secondary mineral. To have sufficient amount of gypsum in WRDs, however, it is necessary that pyrite oxidation and calcite dissolution are sufficiently active to generate enough sulphate and calcium and cause gypsum precipitation. This process is very sensitive to the amount of primary minerals and to oxygen and carbon dioxide existing

within WRDs. Indeed, gypsum was not produced in low-O_2 scenarios (Fig. 2), either with (cap) or without (no cap) capillarity.

As such, we may conclude that the efficiency of gas transport mechanisms within WRDs can play a dominant factor for capillarity control of sulphate over long times because of its impact on the production of gypsum. This mechanism dominates for instance the impact of other factors, which were already identified as controlling the geochemical behavior of pyrite and calcite. Among them, we highlight the increased pyrite oxidation rate associated to an increased gas solubility of oxygen under capillarity conditions (described by Lassin et al. 2005), or the larger solubility of calcite at high capillary pressure (P=-100 MPa) than at lower capillary pressures (P=0.1 MPa). Indeed our model results confirm the existence of such behaviors; however, their impact is subordinated to gas transport. It should be emphasized this conclusion is strictly valid within the geochemical system analyzed in this work. In other systems, capillarity can become the most determining factor. As highlighted by Lassin et al. (2013, 2014) the changes in the individual or reaction thermodynamic properties due to capillary constraints are not sufficient to anticipate the response of a geochemical system to capillary perturbation.

Our work did not directly cover other interesting aspects of the impact of capillarity on WRDs. For instance, we infer from the work by Bouzid et al. (2011b) that in some circumstances, a primary mineral (like calcite) can partially dissolve in the anisobaric context and re-precipitate as secondary calcite in the isobaric context. Stabilization of calcite was also evoked by Zilberbrand (1999) who considered isobaric conditions in a context of drying soils, thus favorable to "secondary" calcite formation. In the long term, calcite precipitation/dissolution could significantly change the local pore geometry and, consequently, the hydrodynamic properties of the porous medium and the ARD hydraulic dynamics. Furthermore, according to the generalized approach developed by Coussy (2006), such processes could even impact the pore-scale mechanical behavior of the porous medium. These aspects could not be studied using the model framework developed in this analysis.

5.2 Implications for gypsum precipitation and passivation

When found as rims or coating layers on top of reactive minerals such as calcite, gypsum can reduce the buffering capacity of calcite in the long term. From our simulations, it is not possible to adopt a mechanistic approach to simulate the exact amount of gypsum that could cover calcite. However, we can provide an estimate of the impact of capillarity on the formation of gypsum.

The calcite to gypsum conversion reaction in the acid domain can be written as follows:

$$CaCO_{3(s)} + H_2SO_{4(aq)} + H_2O = CaSO_4{:}2H_2O_{(s)} + CO_{2(aq)}. \qquad (7)$$
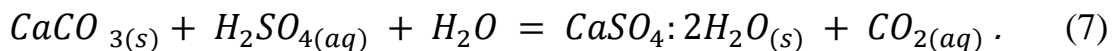
Using THERMO-ZNS, the equilibrium constant (K_r) of this reaction can be calculated either neglecting capillary effects or in a dual context (see Section 5.1).

The log K_r of this reaction is 6.67 at T=10°C, P=0.1 MPa (no capillary effects) and 7.62 at T=10°C, P=-100 MPa (with capillary effects). This increase of the log K_r represents a stabilizing effect of capillarity in favor of gypsum compared to the situation where no capillary constraints are taken into account, or are into play. In that sense, it appears that capillary promotes gypsum formation from calcite. Capillary conditions preferentially take place in fine-grained porous media (according to Young-Laplace and Kelvin laws); as such it can be expected that gypsum coatings on calcite grains would preferentially occur in fine-grained materials. This result qualitatively matches the findings by Booth et al. (1997).

To further support the importance of capillarity on passivation, one should recall that capillary forces are stronger under relatively dry conditions and in fine-grained porous media. The latter are able to retain more capillary water compared to coarse-grained porous media. Thus, while the local mobile pore-water/solid ratio in coarse-grained zones is expected to be low during dry periods, it can remain quite high in less mobile fine-grained zones throughout the year (e.g .Pettenati et al., 2008). Thus, all the mass of dissolved sulfate, stemming from oxidation of sulfides, could be locally involved in the gypsum equilibrium because of diffusion-limited mass transport in the low permeable zones. This issue may further enhance the repartition of gypsum over the calcite surface.

While these results shed new lights about the analysis of long-term passivation on carbonates in WRDs, additional studies are needed to better characterize passivation and to quantify long-term gypsum formation.

6 Conclusions

The different pressure of capillary water compared to free water can generate a potential difference in chemical energy required to achieve thermodynamic equilibrium (e.g. Mercury and Tardy, 2001), when compared to speciation occurring under water-saturated conditions. Capillary forces are typically higher in fine-grained sediments and under dry conditions. In a WRD context, fine-grained materials are ubiquitous and have a key control on hydraulic and geochemical processes associated with ARD (e.g. Strömberg and Banwart, 1999).

We analyzed the potential impact of capillarity on aqueous and water/rock geochemical reactions forming acid rock drainage and occurring in WRDs, by means of numerical simulations in a simplified geochemical system. We used a thermodynamic database adapted to aqueous speciation calculations under water-saturated conditions (Thermoddem) and modified it using the THERMO-ZNS code (Lassin et al., 2005) to

calculate capillarity-corrected equilibrium reactions. Although the conceptual and numerical system was idealized, the results provide useful insights into the effects of capillarity on ARD dynamics from WRDs.

According to our simulations, capillarity could play a fundamental role on ARD through its control on the precipitation of secondary minerals. Among them, gypsum seems to be the most important one, as it acts as a sulfate sink and can maintain long-term release of (relatively) larger sulfate concentrations over time. We showed that gypsum could be quite sensitive to capillarity when available calcite is low (poor pH buffering capacity) and oxygen and carbon dioxide content are sufficiently high to promote pyrite oxidation and calcite dissolution. These conditions can take place in highly ventilated systems and when primary minerals controlling acidity have been initially consumed (or passivated).

Theoretically, the selective behavior of capillarity on secondary minerals can be associated with the anisobaric/isobaric conditions of formation of minerals. Secondary minerals should preferentially precipitate in the "isobaric" configurations since they are stabilized by capillarity. On the contrary, the context for primary minerals is assumed to be anisobaric, which is rather destabilizing and thus favorable to dissolution. This differential situation leads to an energetic configuration that favors the development of a driving force, which stimulates the geochemical reactivity of the water/rock system. This fact can have important implications in the process of calcite passivation, which involves coating or rimming of calcite minerals by gypsum (and potentially other secondary minerals not studied in this work).

A strong impact of capillarity may not be ubiquitously present in WRD. For instance, it may not affect the long-term ARD when gas permeability is low and circumneutral environment is maintained for long time scales. At lower oxygen levels, when calcite still buffers acidity, no secondary minerals are generated and capillarity has no big impact on speciation dynamics, at least for the number of wet-dry cycles considered in our work (corresponding to approximately 100 years). Capillarity effects seem to be independent from the water temperature, although several other processes controlled by temperature were not accounted for in this work.

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