

Using Reactive Transport Modeling to Evaluate the Source Term: The First Challenge in the Remediation Actions to be Implemented in the Closeout of First Uranium Mining in Brazil

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ABSTRACT

This paper discusses the application of a reactive transport model as a powerful tool for the understanding of the hydrogeochemical processes that occur in one of the waste rock piles of the first uranium mine in Brazil, seeking to subsidize the appropriate choice of a remediation strategy. The Brazilian mine located at the Poços de Caldas plateau, in the state of Minas Gerais, generated approximately $27.2 \times 10^6 \text{ m}^3$ of waste rock. The waste rock pile object of this study presents a volume of $12.4 \times 10^6 \text{ m}^3$ and an area of $56.9 \times 10^6 \text{ m}^2$. Pyrite oxidation was found to be a critical factor in the mobilization of metals and radionuclides to environment. It was estimated that acid drainage generation will last for 600 years. The long time scale involved on the oxidation of pyrite materials implies the need for adoption of permanent remedial actions.

INTRODUCTION

The first uranium production center in Brazil began operation in 1982. After 13 years of a non-continuous operation, the mining activities were suspended definitively. Uranium was extracted by open pit mining. Operations gave rise to approximately $12.4 \times 10^6 \text{ m}^3$ of waste rock, while the mill process generated a volume of approximately $2.39 \times 10^6 \text{ m}^3$ of tailings. Regardless the fact that some studies developed in this area exist, a well-defined plan of action, aimed at the remediation and rehabilitation of the site, has not been implemented yet.

The main sources of pollutants to the environment are the tailings dam, the waste rock piles and the open pit. Pyrite oxidation was found to be the driving force in the leaching of metal and radionuclides into environment. It was estimated that acid drainage generation will last for 600 and 200 years from waste

rock piles and tailings dam, respectively [1]. Accurate prediction of the release rate of metal and radionuclides from these sources and their transport into the subsurface environment is a critical factor to the assessment of environmental impacts and to the development of effective remediation strategies.

In prevailing practices radiological assessment, the source term is evaluated by means of the assessment of dissolution rates and the solubility of radionuclides. This standard practice has obvious shortcomings, mainly because it cannot produce a realistic representation of the system under study. The alternative to overcome these shortages is using more sophisticated models that could represent real complex problems. Reactive transport codes are powerful tools in the evaluation of coupled thermal–hydrological–chemical processes and in the prediction of the long-term performance of remediation strategies. The difference between the predictions from these two approaches can be as high as several orders of magnitude. Generally, conventional approaches produce predicted values higher than the measured ones. On the other hand, the use of reactive transport model requires a good knowledge of the simulated hydrogeochemical system, along with the choice of appropriated algorithms that can represent the most important processes.

Documented descriptions of geochemical processes in waste rock piles (mining wastes) are not easily found. There is even more scarce information about processes that take place in pyritic wastes with potential of generating acid drainage, such as the problem addressed by the present project. In the last 30 years, the acid drainage from mining activities began to be recognized as a serious environmental problem, with extensive risks which had not deserved due attention, especially if management strategies are taken into account.

In this paper, we present the application of a reactive-transport model to simulate the transport of reactive multi-species solutes in heterogeneous, anisotropic, saturated-unsaturated waste rock pile system of the first uranium mine in Brazil. The model used to describe the complex hydrogeochemical processes that control the generation of acid drainage and the distribution of solutes between groundwater and waste rock matrix was the 2D finite-element hydrogeochemical transport model, HYDROGEOCHEM v.4 [2]

STUDY AREA

The studied waste-rock pile is part of the Poços de Caldas mining and milling complex, located at the southeast region of Brazil (Figure 1). Average rainfall rate is 1,700 mm/a which causes serious problems in terms of water management. It has been estimated that about US\$ 200,000 are spent annually to treat the acid waters originated in these waste-rock piles. Obviously the collect and treat strategy cannot be faced as a permanent solution.

The cumulative uranium production was 1,242 tons of U_3O_8 . In the development of the mine 44.8×10^6 m³ of rocks were removed. From this amount, 10 million tons were used as building material (roads, ponds, etc). The rest was disposed into two major rock piles, waste rock pile 8 (WRP-8) and 4 (WRP-4). Both piles are located at areas close to the mine pit. The WRP-4 was chosen as a study object because almost all the drainage coming from the pile is collected in only one holding pond, facilitating mass balance calculations. It is to be mentioned that a huge database from monitoring program carried out by the mine operator is available.

The WRP-4 was built in a valley near a Consulta's stream bed. The construction method of the pile consisted of end-dumping, i.e., the waste-rocks were dumped directly over the crest of the pile face from trucks. The bottom of the valley was previously prepared to receive the waste rocks. Deep drains were constructed to allow for the drainage of the infiltrating waters and a liner of compacted material was

placed to avoid percolation of water into the original land surface. The WRP-4 contains $12.4 \times 10^6 \text{ m}^3$ rocks, with a top area of 0.57 km^2 . Recently, four boreholes were drilled through the pile to allow for groundwater sampling and the measurement of the water level. Periodic determinations of contaminant concentrations in the infiltration and out-flowing waters as well as measurements of the discharge rates are performed by the mine operator.



Fig. 1. Site location

METHODOLOGY

- **Physical Characterization of the Pile**

In a coupled reactive transport model, confidence on the final results will depend, in a first place, on the accuracy with which the model is able to simulate the flow within the pile. One of the main parameters to be known is the hydraulic conductivity within the pile. A single value of hydraulic conductivity cannot be used to represent the entire WRP-4 and a range of values should be expected as a consequence of variations in particle size, rock characteristic, and construction methods. Due to the lack of financial resources, the field program was conducted on the top and slope surfaces of the pile. The sampling points were designed to give the best possible representation of the hydrological processes occurring inside the pile. The sampling grid was set along a cross-section located at a portion of the ancient stream bed over which the pile was built. The grid was composed by 12 sampling points. Six of them were fixed in order to form a transect, with 50 meters interval between each one of them. Three of these points were positioned at the top of the pile (P1, P2 and P3) and the others were located at the slope of the pile (B1, B2 and B3). In order to increase the consistency of the measurements at the top of the pile, two others points were positioned 10 m to the right and 10 m to the left of each one of these three points located at the top of the pile. The sampling grid is showed in the figure 2. For each sampling point non-deformed samples were visually described and collected using a ring sampler 0.0599 m thick and 0.0537 m of internal diameter. The collected samples were sent to the laboratory for further analysis. They involved

the determination of the basic hydrogeologic properties of the samples such as porosity, specific gravity, soil-water characteristic curves, and saturated hydraulic conductivity. Due to the highly heterogeneous and not consolidated characteristics of the material, non deformed blocks of waste-rock could not be collected for column tests in the laboratory. *In-situ* measurements of saturated hydraulic conductivity (K_{sat}), using the Guelph permeameter, were also taken.

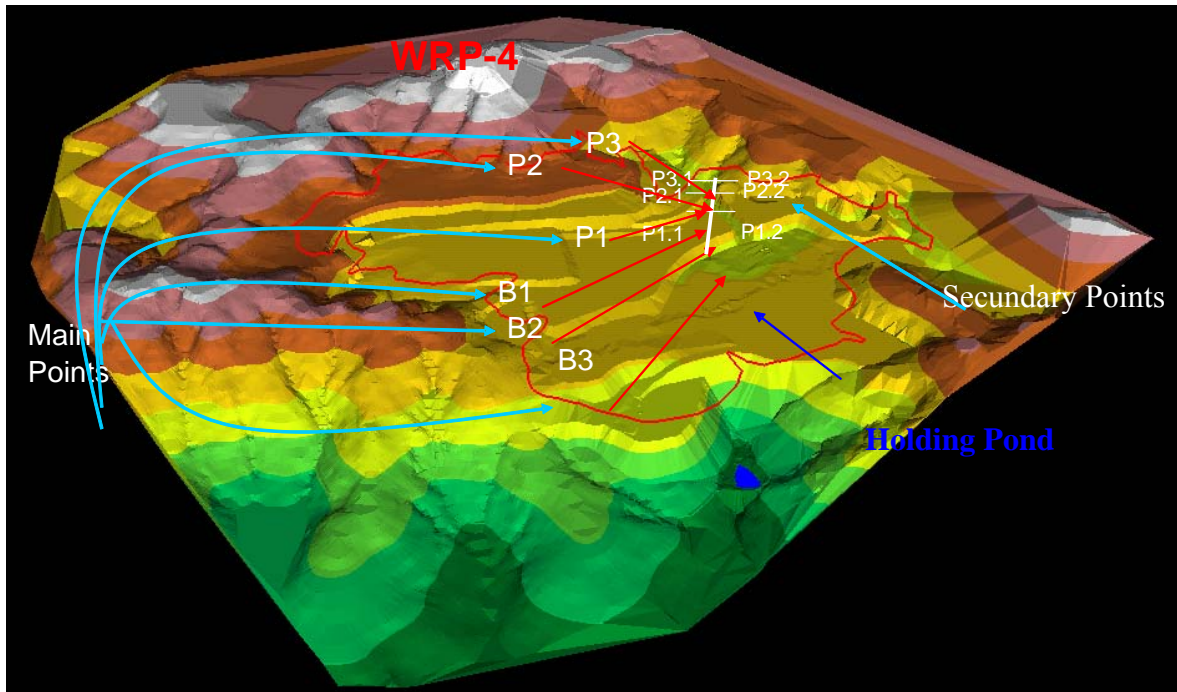


Fig. 2. Sampling grid

The main sampling points (B1, B2, B3, P1, P2 and P3) are spaced in intervals of 50 m, the secondary points (P1.1, P1.2, P2.1, P2.2, P3.1 and P3.2) are spaced 10 m of each main point. The red line delimits the area of the WRP-4.

- **Geochemical Characterization of the Pile**

The evolution of the geochemical system inside of the WRP-4 was described using the concept developed by [3] and [4] as inverse and forward methods of chemical modeling of natural waters. This strategy involves the sampling of water along a flow path. The progressive changes in the chemical and isotopic properties of this water would reflect the geochemical processes such as mineral dissolution and precipitation, ion exchange, gas exchange and oxidation-reduction reactions that occur in the system. This strategy was performed collecting water samples upward (spring of the stream) and downward (holding pond) of the pile.

The first obvious constraint of these processes is the chemical and isotopic data-set itself [5]. The data used in this paper were based on 10 years of the monitoring program carried out by the mine operator. Table I. summarizes the available data on the chemistry of effluent waters from the WRP-4 and of the stream water upward the pile.

Table I. Summary of Average Values Measured in Holding Pond and in the Stream Water Upward of the WRP-4

Parameters	Average values measured	
	Stream water	Holding Pond
Ph	6.26	3.38
Eh	410	508
pe	6.95	8.61
Concentrations (mgL⁻¹)		
Al	1.84	117
Mn	0.22	73
F	0.20	99
SO4	5.02	1,040
Ba	0.040	0.38
Ca	0.57	72
K	2.24	8.08
Fe	1.25	1.78
U	0.0015	6.51
Th	0.0020	0.19
Mg	0.098	5.90
Zn	0.028	153
Pb	0.00039	0.30
Cu	0.0030	1.16
Si	0.060	35.0
Activity Concentration (BqL⁻¹)		
Ra226	0.030	0.31
Ra228	0.038	0.29
Pb210	0.023	0.36

The other constraint is the tendency of the infiltration water to dissolve or precipitate minerals as reflected by the saturation indices that are obtained from speciation calculations based on the water analyses. The mass balance calculation between two points along the flow path is done by simultaneously solving a set of equations that relates the change in elemental composition to several possible reactions according to their assumed stoichiometry. In a sense, it is a matrix transformation from compositional changes in aqueous constituents to mass transfer changes in minerals, gases and redox conditions using the stoichiometry of the phases to make the transformation [4].

The mineral phases used in the inverse geochemical calculation were based on the mineral characterization of the pile [6], [7] and are presented in the Table II.

The computer program used to carry out the inverse geochemical modeling and speciation calculations was the PHREEQC v.2. The used database was that distributed with the code, *phreeqc.dat*, that is consistent with the database of other aqueous models such as *wateq4f.dat* of the WATEQ4F code [8], [9], and *minteq.dat*, of the MINTEQA2 code [10].

Table II. The Mineral Phases used in the Inverse Geochemical Calculation and the Reactive Transport Model

Mineral Phase	
K-Feldspar^{#,*}	KAlSi₃O₈
Kaolinite^{#,*}	Al₂Si₂O₅(OH)₄

Muscovite^{#,*}	KAl₃Si₃O₁₀(OH)₂
Fluorite^{#,*}	CaF₂
Hematite^{#,*}	Fe₂O₃
Uraninite^{#,*}	UO₂
Magnetite^{#,*}	Fe₃O₄
Pyrolusite[#]	MnO₂
Pyrite^{#,*}	FeS₂
Sphalerite[#]	ZnS
Gibbsite[*]	Al(OH)₃
Silica[*]	SiO₂

inverse geochemical calculation

*reactive transport model

- **Conceptual model of the WRP-4**

The reactive modeling of the source-term was divided into two parts: 1) the water flow modeling study, in which the water movement in the WRP-4 was determined and 2) the transport modeling study, in which the consequences of the water movement to the reactive transport of radionuclides and metals were investigated. These modules are integrated in one computational code called HYDROGEOCHEM, a Coupled Model of Fluid Flow, Thermal Transport, and Hydrogeochemical Transport through Saturated-Unsaturated Media - Version 4.0. [2]

The water flow model is a platform upon which the transport model was constructed. Consequently, an appropriate characterization of the flow inside of the pile is of fundamental importance to increase the confidence in the transport model.

Regarding the water movement the studied pile is located on a sloping land surface between a recharge (top of the pile) and a discharge area (where seepage water is collected into a holding pond). The primary source of water to the waste-rock pile is the precipitation. Part of the precipitated amount infiltrates the waste-rock and moves downward (in direction to the base of the pile). Another part can become runoff water over the surface of the pile. The water balance for the WRP-4 was calculated based on historical data of rainfall and outflow records. The average rainfall rate considered was 1,700 mm.a⁻¹. The estimated runoff and evaporation were 30% and 12% respectively. Based on these values, the infiltrating portion of the rainfall creates a water table inside the pile. Such fact is supported by the measurements of the water level in the piezometers installed in the pile. Measurements of water level values in the piezometer 01 (located at the ancient stream bed) showed variations less than 10% during the year, maintaining a saturated layer inside the pile 10 meters thick. This piece of information associated with the small variation of the pile outflow (less than 10% between dry and wet season), suggests the existence of a mechanism that regularizes the water level inside the pile.

Based on the above description the WRP-4 can be considered as a heterogeneous and unsaturated-saturated system containing waste rock layers which can steeply change in grain size. According to what is reported in the construction project of the pile the coarse grained material would be deposited in the base of the dump (with predominance of blocks of rock with diameter varying from 0.3m to 1.2m associated to the angle of slope (α) between 36° and 40°) being the finer grained material mostly found in the upper layers with (α) varying between 42° and 45° [11]. The probable segregation of the material with the depth allows us to propose that the saturated hydraulic conductivity may be higher close to the base of the pile. Some authors point-out that end-dumping construction method results in a distribution of particle

sizes grading from fine to progressively coarser proceeding from the level of the dump platform toward the base of the dump [12].

The field observations revealed three distinct particle size groupings, a fine upper zone, a very coarse toe zone and an intermediate zone between these two zones. The first layer consists of altered phonolitic rocks with different grain sizes involved by a fine matrix with significant fractions of silt and sand. The intermediate layer is composed by a combination of altered phonolitic and breccias rocks with a narrower grain size range (3 to 15cm) with a small amount of a fine matrix. Altered phonolitic rocks with a huge variation of grain sizes compose the base layer. It was possible to measure the existence of 2 cm wide channels between the blocks of rocks. The grain size segregation can be observed in the figure 3.

These layers are found adjacent to each other. This finding may suggest the possibility of preferential flow within the pile. [13] suggested that in unsaturated, layered systems such as waste rock piles, liquid water may be transported preferentially through the fine-grained material rather than the coarse-grained one. The authors recognize that this hypothesis contradicts conventional theory for flow in waste rock dumps. The importance of this idea is that this form of preferential flow may allow the waste rock pile to store water. In opposition to this idea it is reported that high-permeability channeling is thought to be a primary control on water movement through waste-rock piles [12]. Still the lack of field observation persists. It is clear however, that despite the above-mentioned difficulties in assessing moisture movement in waste rock piles, consideration must be given, among other issues, to the configuration and construction of the waste rock pile [13].

In summary it can be suggested that the entire base of the pile can be considered as a high-conductivity layer, rather than a discrete series of channels, acting as the primary conduit for much of the water movement inside the pile and consequently, minimizing the elevation of the water table.

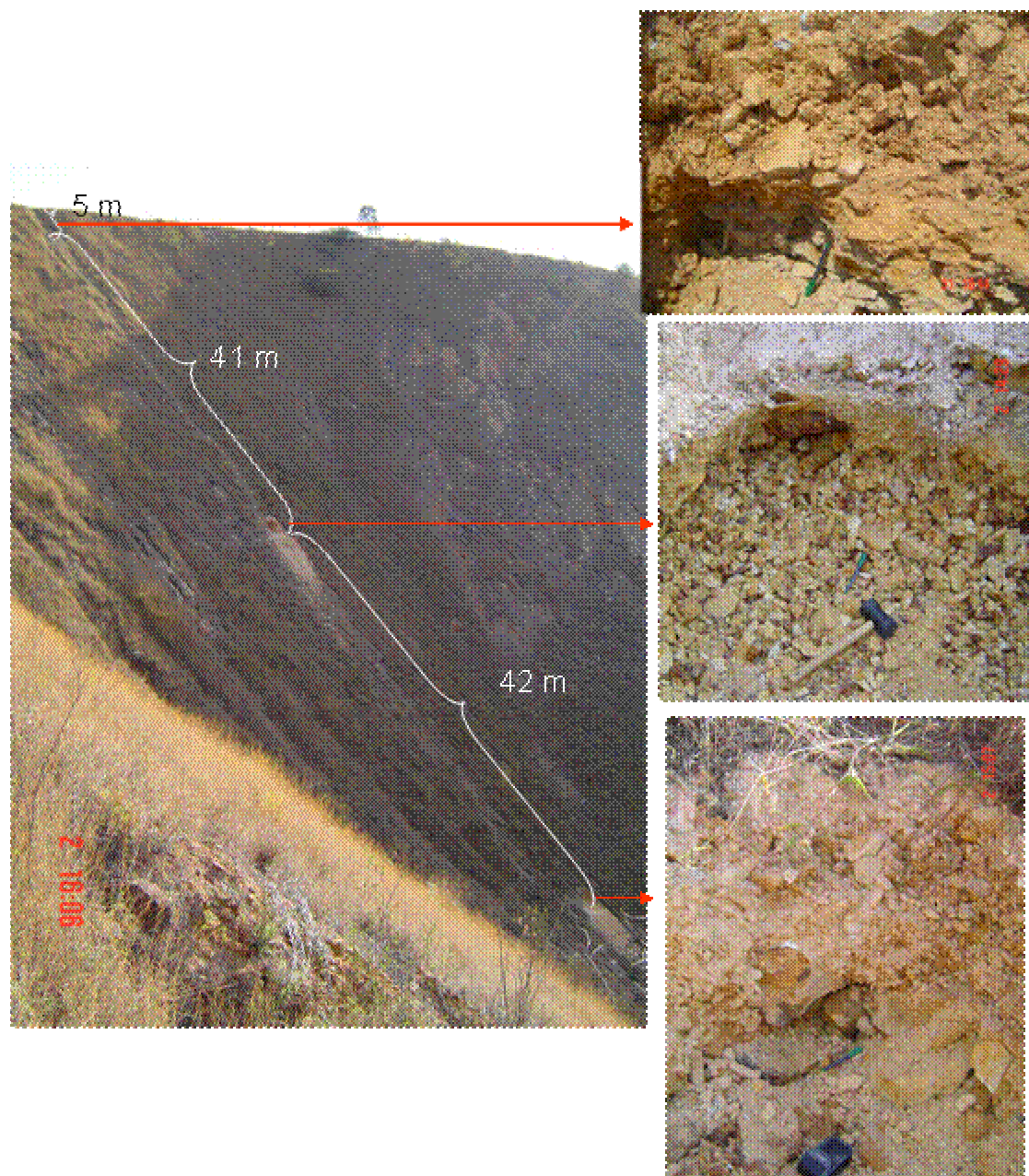


Fig. 3. Grain size segregation observed along the slope surface of the WRP-4 (Field program September;2004)

The geochemical reactions in unsaturated media as the WRP-4 occur primarily in the interfaces of the solids (minerals) with gases and aqueous solutions. The rates at which these reactions occur are controlled by the transport (or trapping) of reagents to and across the interfaces. These processes can be classified into Mass Transfer Processes involving the minerals present in the wastes and Rate Determining mechanisms which control the path of these reactions [14].

It is suggested that the oxidative dissolution of pyrite is the driving force in the leaching rate of metal and radionuclides from WRP-4 [1]. In general, four classes of mineral-fluid reactions are identified as contributing to acid and metal release and consumption: i) Oxidation of pyrite, releasing acid, major and

trace metals and sulphate; ii) Precipitation of oxyhydroxides releasing acid and consuming major and trace metals; iii) Dissolution/precipitation of sulphate minerals mediating the dissolved metal concentrations as well as total dissolved solids and iv) Dissolution of oxyhydroxides and silicates consuming acid. These processes (dissolution/precipitation) take place in a series of steps including adsorption/desorption, diffusion and surface chemical reactions. Precipitation still involves the additional initial step of nucleation. The slowest process in the sequence will determine the rate at which the reaction proceeds. This controlling process is determined by the properties and compositions of both the minerals and the solutions involved in the reactions.

In general, the models which describe the rates that control the pyrite oxidation focus on the O_2 transport (diffusion through the stagnant water layer, diffusion on surfaces or through the solid) and reaction (rate of reaction at solid surface sites) mechanism within particles of the pile. The bulk transport mechanism which delivers oxidant from outside the pile to reaction sites within the pile is often considered as being unimportant, with the consequent assumption that the oxidant concentration surrounding each particle of the dump is constant. This assumption may be valid in special cases (Chemical Plants) but, it is less likely to be true for natural weathering processes in pyritic mine wastes.

Several researchers sustain that the rate at which oxygen is supplied into the pile (assumed to be limited by the rate that that oxygen could diffuse through the pore space of the pile) represents the rate controlling oxidation reactions [15], [16] and [17].

However, consensus exists in the literature that the best way to represent the reactive geochemical processes that occur in mine waste (under generation of acid drainage) would be through a network of reactions that take into account the equilibrium and kinetic reactions.

The conceptual model of WRP-4 for the reactive geochemical system is based on equilibrium and kinetic reactions. The reactive system was completely defined by specifying chemical reactions and counting the total number of chemical species involved in the reaction. The standard equilibrium expression (with a suitable equilibrium constant) was used to represent all the fast reaction, such as the aqueous complexation reaction and precipitation of secondary phases. The slow reactions were represented by the kinetic expression and associated rate constants to address the dissolution reactions of key minerals present in the pile and the Fe^{+2} oxygenation. The reaction network that describes the evolution of the geochemical system can be observed in the Tables III and IV.

Table III. Equilibrium Reactions with Theirs Equilibrium Constant Associated Used in the HYDROGEOCHEM 4

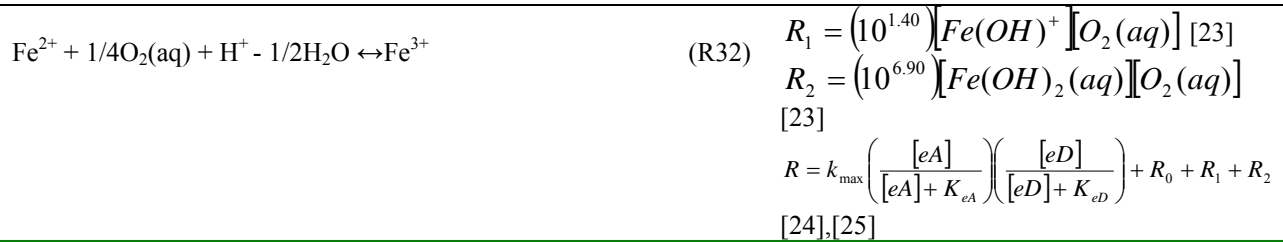
FAST REACTION – (EQUILIBRIUM EXPRESSION WITH EQUILIBRIUM CONSTANT)		
Reaction	#	Reaction Constant
Aqueous Complexation Reactions		
$H_2O(aq) \leftrightarrow H^+ + OH^-$	(R1)	$\text{LogKe} = -13.99$
$Al^{+3} + F^- \leftrightarrow AlF^{+2}$	(R2)	$\text{Log}_{10}K^0 = (7.8 \pm 0.07)$
$Al^{+3} + 2F^{-1} \leftrightarrow AlF_2^+$	(R3)	$\text{Log}_{10}K^0 = (12.73 \pm 0.11)$
$Al^{+3} + SO_4^{-2} \leftrightarrow AlSO_4^+$	(R4)	$\text{Log}_{10}K^0 = (3.9 \pm 0.2)$
$Al^{+3} + 2SO_4^{-2} \leftrightarrow Al(SO_4)_2^-$	(R5)	$\text{Log}_{10}K^0 = (5.9 \pm 0.5)$
$Al^{+3} + 3F^- \leftrightarrow AlF_3(aq)$	(R6)	$\text{Log}_{10}K^0 = (16.78 \pm 0.15)$
$Ca^{+2} + SO_4^{-2} \leftrightarrow CaSO_4(aq)$	(R7)	$\text{Log}_{10}K^0 = 2.31$

$\text{Fe}^{+2} + \text{SO}_4^{-2} \leftrightarrow \text{FeSO}_4(\text{aq})$	(R8)	$\text{Log}_{10}\text{K}^0 = 2.25$
$\text{Fe}^{+3} + \text{SO}_4^{-2} \leftrightarrow \text{FeSO}_4^+$	(R9)	$\text{Log}_{10}\text{K}^0 = 4.25$
$\text{Fe}^{+3} + \text{F}^- \leftrightarrow \text{FeF}^{+2}$	(R10)	$\text{Log}_{10}\text{K}^0 = 6.2$
$\text{Fe}^{+3} + 2\text{SO}_4^{-2} \leftrightarrow \text{Fe}(\text{SO}_4)_2^-$	(R11)	$\text{Log}_{10}\text{K}^0 = 5.38$
$\text{Fe}^{+3} + \text{H}_2\text{O} - \text{H}^+ \leftrightarrow \text{FeOH}^{+2}$	(R12)	$\text{Log}_{10}\text{K}^0 = -2.19$
$\text{K}^+ + \text{SO}_4^{-2} \leftrightarrow \text{KSO}_4^-$	(R13)	$\text{Log}_{10}\text{K}^0 = 0.85$
$\text{H}^+ + \text{SO}_4^{-2} \leftrightarrow \text{HSO}_4^-$	(R14)	$\text{Log}\text{K}^0 = 1.988$
$\text{UO}_2^{+2} + \text{SO}_4^{-2} \leftrightarrow \text{UO}_2\text{SO}_4$	(R15)	$\text{Log}_{10}\text{K}^0 = 3.15$
$\text{UO}_2^{+2} + 2\text{SO}_4^{-2} \leftrightarrow \text{UO}_2(\text{SO}_4)_2^{-2}$	(R16)	$\text{Log}_{10}\text{K}^0 = 4.14$
$\text{UO}_2^{+2} + \text{F}^- \leftrightarrow \text{UO}_2\text{F}^+$	(R17)	$\text{Log}_{10}\text{K}^0 = 5.09$
Precipitation of secondary phase		
$\text{Ba}^{+2} + \text{SO}_4^{-2} \leftrightarrow \text{BaSO}_4$ (Barite)	(R18)	$\text{Log}_{10}\text{K}^0 = 9.97$
$\text{Fe}^{+3} + 2\text{H}_2\text{O} - 3\text{H}^+ \leftrightarrow \text{FeOOH}$ (Goethite)	(R19)	$\text{Log}_{10}\text{K}^0 = 1.00$

Note: The Thermodynamic Data Base were based on [18]

Table IV. Kinetic Reaction and Rate Expression Included in the HYDROGEOCHEM 4

SLOW REACTION – (KINETIC EXPRESSIONS AND ASSOCIATED RATE CONSTANT)		
Reaction	#	Rate Law
The mineral dissolution were treated using empirical rate laws		
$\text{Al}(\text{OH})_3$ (Gibbsite) + $3\text{H}^+ \leftrightarrow \text{Al}^{+3} + 3\text{H}_2\text{O}$	(R20)	$R = -SA[1.067 \times 10^{-16} \times [\text{H}^+]^{0.992}]$ [19]
Fe_2O_3 (Hematite) + $6\text{H}^+ \leftrightarrow 2\text{Fe}^{+3} + 3\text{H}_2\text{O}$	(R21)	$R = -SA[1.029 \times 10^{-21} \times [\text{H}^+]^1]$ [19]
Fe_2O_4 (Magnetita) + $8\text{H}^+ \leftrightarrow \text{Fe}^{+2} + 2\text{Fe}^{+3} + 4\text{H}_2\text{O}$	(R22)	$R = -SA[1.417 \times 10^{-12} \times [\text{H}^+]^{0.279}]$ [19]
FeS_2 (Pyrite) + $8\text{H}_2\text{O} + 14\text{Fe}^{+3} \leftrightarrow 15\text{Fe}^{+2} + 2\text{SO}_4^{-2} + 16\text{H}^+$	(R23)	$R = SA \times (10^{-6.07}) \frac{[\text{Fe}^{+3}]^{0.93}}{[\text{Fe}^{+2}]^{0.40}}$ [20]
2FeS_2 (Pyrite) + $7/2\text{O}_2$ (gas) + $\text{H}_2\text{O} \leftrightarrow \text{Fe}^{+2} + 2\text{H}^+ + 2\text{SO}_4^{-2}$	(R24)	$R \cong S_{\max} (kg(S)dm^{-3}d^{-1})$ [1],[21]
2FeS_2 (Pyrite) + $7/2\text{O}_2$ (aq) + $\text{H}_2\text{O} \leftrightarrow \text{Fe}^{+2} + 2\text{H}^+ + 2\text{SO}_4^{-2}$	(R25)	$R = SA \left\{ (10^{-8.19}) \frac{[\text{O}_2(aq)]^{0.5}}{[\text{H}^+]^{0.11}} \right\}$ [20]
SiO_2 (Silica) + $2\text{H}_2\text{O} \leftrightarrow \text{H}_4\text{SiO}_4$	(R26)	$R = -\left(\frac{A}{M}\right) [(k_+ - k_- [\text{H}_4\text{SiO}_4])$ [22]
UO_2 (uraninita) $\leftrightarrow \text{U}^{+4} + 2\text{H}_2\text{O} - 4\text{H}^+$	R(27)	$R = -SA[2.593 \times 10^{-14}]$ [19]
$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (Kaolinite) + $6\text{H}^+ \leftrightarrow 2\text{Al}^{+3} + \text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$	R(28)	$R = -SA[1.396 \times 10^{-23} \times [\text{H}^+]^{0.777}]$ [19].
KAlSi_3O_8 (K-feldspar) + $8\text{H}_2\text{O} \leftrightarrow \text{K}^+ + \text{Al}(\text{OH})_4^- + 3\text{H}_4\text{SiO}_4$	(R29)	$R = -SA[7.627 \times 10^{-20} \times [\text{H}^+]^{0.5}]$ [19]
CaF_2 (Fluorite) $\leftrightarrow \text{Ca}^{+2} + 2\text{F}^-$	(R30)	$R = -SA[7.065 \times 10^{-21} \times [\text{H}^+]^1]$ [19]
$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ (Muscovite) + $10\text{H}^+ \leftrightarrow \text{K}^+ + 3\text{Al}^{+3} + 3\text{H}_4\text{SiO}_4$	(R31)	$R = -SA[1.976 \times 10^{-16} \times [\text{H}^+]^{0.37}]$ [19]
Fe⁺² oxygenation		$R_0 = (10^{-5.10}) [\text{Fe}^{+2}] [\text{O}_2(aq)]$ [23]

**Notes:**

1. SA is the reactive surface area of the mineral concerned (m^2 per m^3 media).
2. $[]$ denotes a concentration in units of mol per dm^3 of water.
3. S_{\max} = The maximum reaction rate. It was assumed that sulphide oxidation is the only process consuming significant amounts of O_2 , then the measured O_2 consumption rates can be used to determine the sulphide oxidation rates. The S_{\max} value used in the simulation was $2.00 \times 10^{-6} \text{Kg}(\text{S})\text{m}^{-3}.\text{d}^{-1}$ [1].
4. (A/M) = the relative interfacial area between the solid and aqueous phases/the relative mass of water in the system. k_+ is the dissolution constant and the k_- is the precipitation dissolution
5. k_{\max} = the maximum rate of the reaction = $5 \times 10^{-7} \text{Ms}^{-1}$ [24]. $[eA]$ = is the concentration of the electron acceptor (mol/L). $[eD]$ = is the concentration of the electron donor (mol/L) = $[\text{Fe}^{+2}]_{\text{tot}}$. All forms of dissolved $\text{Fe}(\text{II})$ are assumed to be bioavailable, so the electron donor concentration refers to total Fe^{+2} rather than the concentration of the free ion Fe^{+2} . K_{eA} = is the half-saturation constant associated with the electron acceptor = $1 \mu\text{M}$ [25]. K_{eD} = is the half-saturation constant associated with the electron donor = $1 \mu\text{M}$ [25].

All the dissolution reactions require an estimative of the surface area of the mineral available for reaction. Values for mineral surface areas were derived using the methodology proposed by [26], i.e. the surface area of an individual mineral was determined based on the assumption that its contribution to the surface area of the rock is proportional to its volume abundance in the rock. The average measured physical surface area of the waste rock is approximately constant per volume of rock and independent of the particle size distribution, i.e. $1 \pm 0.4 \text{ m}^2/\text{g}$ [26]. The Physical surface area of $9.09 \times 10^5 \text{ m}^2$ per m^3 media was estimated for the WRP-4, considering the average values of porosity (45%) and specific density (2.02 g/cm^3). This value is in agreement with others estimated values for waste-rock [26] and [27].

In summary, the conceptual model considers, for the sake of simplicity, that the WRP-4 is composed by two types of homogeneous materials representing the two main hydraulic domains; one with low hydraulic conductivity (representing the average of the values measured in situ in the top surface of the pile = $9.271 \times 10^{-4} \text{ cm/s}$) and other one with high hydraulic conductivity (that represent the limit of the guelph permeameter = 10^{-2} cm/s). It was based on a 2D vertical Cartesian cross-section of the pile 700 m wide and 20 m high. The chosen section is intended to allow for the best representation of the preferential water flow inside the pile, since this section follows the topographical slope of the valley..

The conceptual model also assumes the follow conditions:

- (1) The flow system is in a steady state, i.e., a constant rainfall rate is maintained at the pile surface during the entire duration of the simulation. This rate represents the measured average value of the rainfall rate at the site minus the runoff and the evaporation rates,
- (2) Porosity and permeability are not affected by pile consolidation, neither by mineral precipitation or dissolution
- (3) The aqueous complexation reactions and the precipitation of secondary phase are fast (equilibrium-controlled) processes if compared to the flow field;
- (4) The dissolution of minerals and the oxygenation of Fe^{+2} are governed by slow reaction and are described by rate laws.

SIMULATION OF THE WRP-4

The discretization of the waste rock pile (WRP) domain was made via a triangular finite element mesh, including a total of 30,828 elements and 16,969 nodes.

It was assumed that the initial distribution of the pressure head inside the WRP-4 was known. This condition was obtained by simulating the steady-state version of the Richards' equation subjected to time-invariant boundary conditions. Three different boundary conditions were imposed: (1) the base of the pile was considered impermeable; (2) the top and the slopes of the pile were considered subjected to the rainfall infiltration, evaporation and runoff; (3) a small boundary segment located at the toe of the pile was considered as groundwater outflow.

The initial chemical composition of all pollutants in the infiltration water that enters the WRP-4 was based on average data obtained from the monitoring program carried out by the mine operator (these results are shown in Table I – stream water). This quite simple approach is considered adequate to model the overall pile behavior and calculate the long-term evolution of pile effluent compositions.

Numerical simulations were performed for a period of 1 year to obtain a quantitative description of the system's time evolution in order to predict the spatial distribution of groundwater heads, moisture content, velocity field and concentration of all the chemical components (dissolved, precipitate, sorbed or ion free).

RESULTS

• Field Observations

Data from the measurements with the Guelph permeameter showed that at the pile surface saturated hydraulic conductivity (K_{sat}) values varied by one order of magnitude ($2.06 \times 10^{-4} - 1.04 \times 10^{-3}$ cm/s). Measurements of K_{sat} in the slope of the pile were only possible to be accomplished at sampling point B1. Due to the coarse-grained characteristics of the material, it was not possible to accomplish the measurements with the Guelph Permeater in sampling points B2 and B3. However, saturated hydraulic conductivity greater than 10^{-2} cm/s can be suggested as taking place at those locations because this is the highest of hydraulic conductivity that can be measured by the Guelph permeameter).

Few works are found in the literature discussing the variability of the hydraulic conductivity in waste-rock piles [12]. One of them reported hydraulic conductivity values ranging from 10^{-2} to 10^{-5} cm/s [28]. Values were reported in the same range coming from two mine sites; the South Dump of the Doyon mine site in Canada and the Nordhalde dump of the Ronnenberg mining district in Germany [29]. The values of K_{sat} reported in this paper fall within this range.

• Laboratory Analyzes

It has been reported [30,31] that values of hydraulic conductivity obtained in the laboratory are generally smaller when compared with those measured in the field. The comparison between field and laboratory values obtained in this work is presented in Table V. The difference between the average values obtained in the field and in the laboratory was observed to be around 30%, being higher in the laboratory.

Table V. Values of the Hydraulic Conductivity Obtained in Field and in Laboratory

Sampling Points	Hydraulic Conductivity (cm/s)	
	Laboratory	Field
Top Surface of the Pile		
Point 1 (P1)		
P 1	3.03×10^{-3}	3.75×10^{-3}
P 1.1	1.74×10^{-3}	3.12×10^{-4}
P 1.2	1.10×10^{-3}	
Average	1.95×10^{-3}	2.03×10^{-3}

Point 2 (P2)

P 2	6.35×10^{-4}	1.04×10^{-3}
P 2.1	6.20×10^{-3}	5.17×10^{-4}
P 2.2	7.51×10^{-3}	2.06×10^{-4}
Average	4.78×10^{-3}	5.88×10^{-4}

Point 3 (P3)

P 3	4.03×10^{-4}	3.12×10^{-4}
P 3.1	2.33×10^{-4}	
P 3.2	1.83×10^{-3}	3.30×10^{-4}
Average	8.23×10^{-4}	3.21×10^{-4}

Slope Surface of the Pile

B 1	6.94×10^{-3}	9.50×10^{-4}
B 2	2.38×10^{-3}	
B 3	9.70×10^{-4}	
Average	3.43×10^{-3}	9.50×10^{-4}

Individual soil-water characteristic curve was determined, from large pressure plate apparatus technique, for each sampling point. The results reveal that it is not possible to characterize different groups of materials inside the pile by means of this strategy. This finding contradicts the evidences presented so far and can be explained by the fact that samples collected by the ring sampler don't represent adequately the heterogeneities found in the pile. This problem could have been overcome if experiments in laboratory with non-deformed blocks were made. The difficulties generally found in collecting non-deformed waste-rock samples as well as in the appropriate characterization of waste-rock pile property functions has led the scientific community to develop new technologies aimed at determining the constitutive relationships of unsaturated materials [32]. Figure 4 shows the hydraulic property functions used in the simulation.

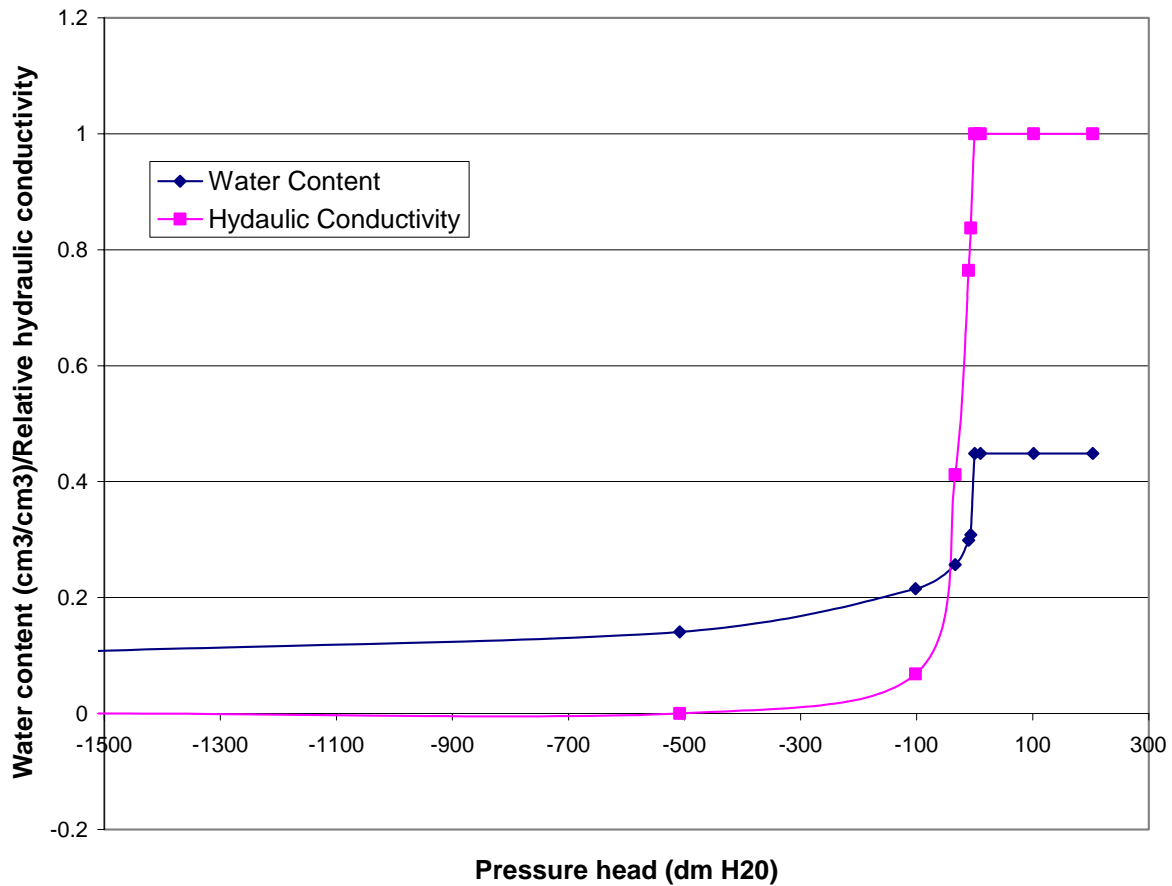


Fig. 4. Hydraulic property function used in the simulation

- **Simulation**

The estimated outflow of the pile ($223.3 \text{ dm}^3/\text{d.dm}$) is in good agreement with the measured data ($222 \text{ dm}^3/\text{d.dm}$). This result demonstrates the ability of the model in reproducing the water budget appropriately.

The modeled data indicate that the velocity field presents a huge variation, with values varying from 0.5 cm/d to 130 cm/d . However, most of the pile presents small values of velocity, of about 10 cm/d . The highest velocities were found in the constriction areas at the bottom of the pile. The comparison between modeled values with measured ones is impossible to be done due to the lack of field observations. The preliminary results of the velocity field distribution inside the WRP-4 are shown in the Fig. 5.

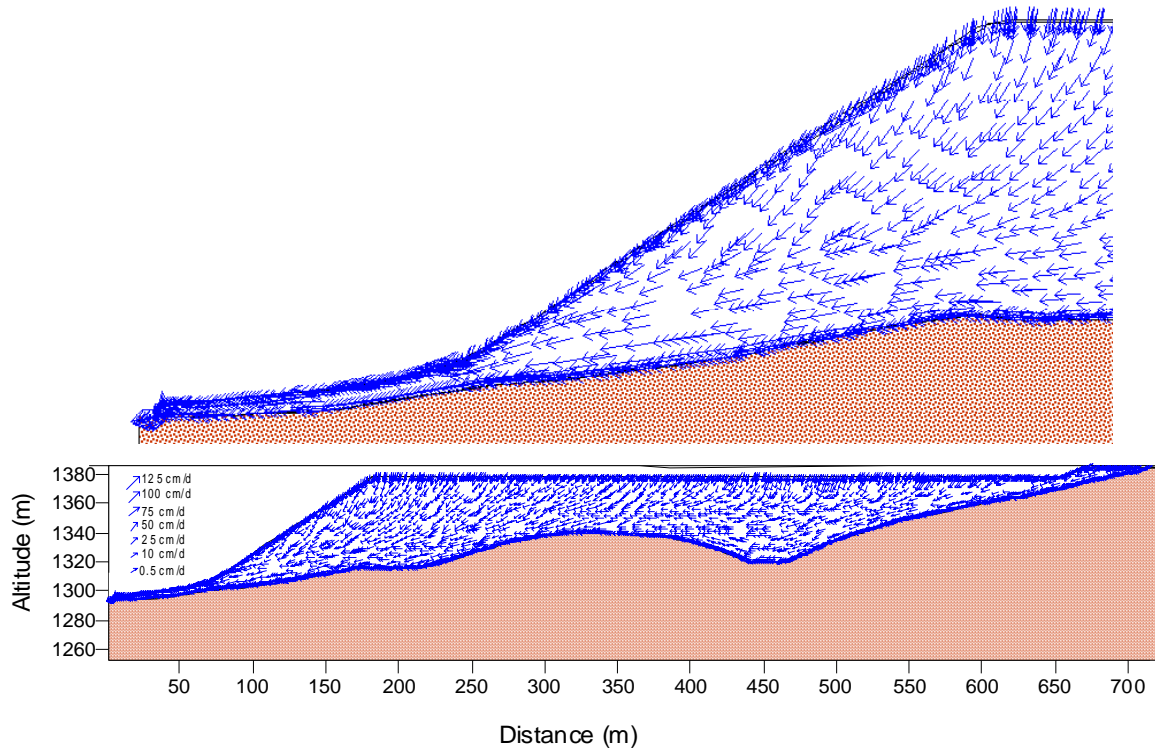


Fig. 5. Distribution of the velocity field inside of the WRP-4

The estimated results of the pressure head shows that almost all the pile is under unsaturated conditions (Figure 6). The maximum value of the saturated layer given by the model is 35 m. This value is almost four times higher than the measured water level inside the pile as previously reported in this paper. This difference can be explained by the fact that an impermeable boundary condition was used in this simulation.

Despite this difference, it can be accepted that the model is simulating well the water behavior inside the pile.

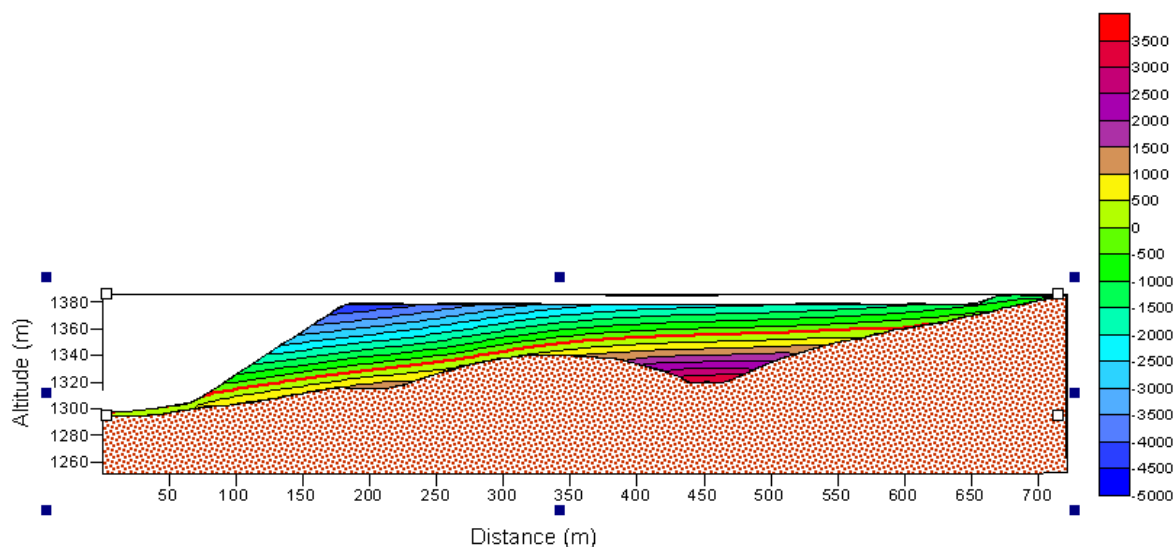


Fig. VI. Distribution of pressure head inside the WRP-4 (in cm)

The geochemical evolution of the seepage water of WRP-4 was interpreted by examining mass balance calculation. The mass balance and mass transfer results can be observed in the Table VI.

The results of geochemical evolution show that the most important geochemical processes which occur in WRP-4 are: K-feldspar and Albite dissolution; Kaolinite dissolution; Pyrite oxidation; Barite solubility equilibrium; Silica precipitation; Goethite precipitation; Manganese oxide dissolution; Fluorite and calcite dissolution.

Table VI. Mass Balance and Mass Transfer Results Computed by the Model. Results in mol/kg of Substance Dissolved (positive) or Precipitated (negative values).

Phase		Mole transfer (mol/kg)
K-Feldspar	$KAlSi_3O_8$	1.56×10^{-1}
Kaolinite	$Al_2Si_2O_5(OH)_4$	2.06
Fluorite	CaF_2	2.09
Barite	$BaSO_4$	-3.2×10^{-3}
UO ₂	UO_2	2.74×10^{-2}
O ₂ (g)	O_2	21.0
Goethite	$FeOOH$	-5.80
Quartz	SiO_2	-4.01
MnO ₂	MnO_2	1.33
Pyrite	FeS_2	5.81
Redox mole transfer		
	Fe(2)	5.78×10^{-3}
	S(-2)	1.16×10^{-2}
	U(4)	2.74×10^{-5}

CONCLUSION

Measurements of hydraulic conductivity in the field and in the laboratory were different from each other but to an extension of no more than 30%, if average values are taken into consideration. The conceptualisation of the pile as being composed by only two types of layers (with different values of hydraulic conductivity) did not prevent the model to predict accurately the water balance inside the pile. The overestimation of the saturated layer thickness at the base of the pile produced by the model may be attributed to the boundary conditions that were used in the simulation. However, it is likely that this won't be of primary impact in the prediction of pollutant concentrations in the drainage. The pile conceptualisation did not allow for the proper prediction of potential preferential flow paths inside the pile, however it must be considered that the unsaturated nature of the system, will favour the oxidation of pyrite by air oxygen that diffuses into the pore spaces of the rocks. In this way, the primary role of the infiltrating water into the pile would be to maintain a sufficient level of humidity and to flush the pollutants downwards. The preliminary results suggest that the use of equilibrium/kinetic geochemical models should be coupled with hydrology model to produce a realistic representation of the system under study. On the other hand, the use of coupled model (or reactive transport model) requires a good knowledge of the simulated hydrogeochemical system that implicates in a vast data site characterization. The application of this kind of model to real cases is still a challenge; however, such codes are becoming useful tools in the assessment of the potential for contamination of this source and in the evaluation of the design strategies for remediation of the waste rock pile.

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