Heterogeneous Oxidation and Hydrogeochemical Numerical Simulation in a Uranium Waste Rock Pile

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Abstract

This study investigates the hydrogeological and hydrogeochemical processes in Waste Rock Pile 4 (WRP4), located in the Poços de Caldas Alkaline Complex, Brazil, aiming to understand acid rock drainage (ARD) generation and contaminant transport. Formed during the operation of Brazil's first uranium mine, WRP4 exhibits complexity due to its chemical composition, particle size distribution, and interactions between gaseous, aqueous, and solid phases. Using integrated numerical models of groundwater flow and geochemical reactions, the study demonstrates that sulfide oxidation, primarily in the pile's oxidized zone, is the main mechanism driving ARD generation, resulting in acidic pH and high concentrations of metals and sulfate.

The hydrogeological model confirmed the principal groundwater flow direction from the Osamu Utsumi (OU) pit toward WRP4, with the pit significantly contributing to the system, especially during low-recharge periods. The hydrogeochemical model, developed using PHREEQC software, indicated that the internal drainage of WRP4 is predominantly influenced by the oxidized zone, with additional contributions from the pit lake. Mineral dissolution within the pile and precipitation of others, such as iron and manganese, were observed due to variations in redox conditions.

The results underscore the importance of monitoring and environmental rehabilitation strategies to mitigate ARD impacts. Incorporating mineralogical data and gas partial pressures in future models is recommended to enhance simulation accuracy. This study provides a valuable foundation for managing uranium waste rock piles, contributing to the protection of water resources and the environment.

Keywords: Acid rock drainage, numerical modeling, aqueous geochemistry, hydrogeology, uranium

Introduction

The geochemical and hydrological processes that occur in low-grade ore piles and waste rock piles share similarities, but the complexity of studying waste rock piles is amplified by factors such as size, geometry, chemical composition, particle size distribution, and the difficulty of controlling system conditions. This study focuses on the Waste Rock Pile 4 (WRP4), a uranium waste rock pile established in the 1980s during the operation of Brazil's first uranium mine, located in the Poços de Caldas Alkaline Complex, Minas Gerais. The WRP4 represents a waste disposal structure that requires an integrated approach to understand the associated groundwater flows and geochemical processes. Defining groundwater flows, combined with geochemical concepts, is important to understanding the dynamics of contaminant transport and the generation of acid rock drainage (ARD), which can negatively impact water resources and the environment.

Previous studies, such as those by Franklin (2007), Abreu (2013), and Alberti (2017), advanced the understanding of oxidation criteria and patterns in the WRP4, as well as the dynamics of flow and chemical reactions. However, none of these studies presented a numerical approach that integrated hydrogeological and hydrogeochemical models. This study aims to fill this gap by implementing and calibrating numerical models of groundwater flow and geochemical reactions, with the goal of providing a more accurate representation of the processes occurring in the WRP4. The integration of these models allows for a more robust analysis of the interaction between water flows and geochemical processes, contributing to the development of effective monitoring and environmental rehabilitation strategies.

Background

The Osamu Utsumi Mine, formerly Campo do Cercado Mine, is located near Caldas in the Poços de Caldas Alkaline Complex, Minas Gerais, Brazil. Discovered in the 1970s, uranium mining began in 1982 at the Caldas Ore Processing Unit but ceased in 1995 due to limited mineralogical understanding, achieving only 22% of its projected capacity (Cipriani 2002). Currently, INB and CNEN are engaged in environmental rehabilitation efforts.

The Poços de Caldas Alkaline Complex, the largest in South America (800 km^2, 33 km in diameter), formed during the Mesozoic and hosts uranium-, thorium-, and REE-rich lithologies, including tinguaite and phonolites (Fraenkel 1985). Uranium mineralization occurs as hydrothermal deposits in fractures and cavities or as secondary formations in redox zones, associated with pyrite, galena, sphalerite, fluorite, and barite (Franklin 2007).

The region has a tropical highland climate (16–25 °C), with 1,700 mm annual precipitation, mainly from October to March. Mining activities altered hydrology, including constructing WRP4 over Consulta Creek Valley, burying natural drainage. Bottom drains with boulders (200–1,000 mm) were installed and covered with fine-grained waste rock and clay. Additionally, a 500-meter diversion channel, lined with compacted clay, redirects Consulta Creek to the Taquari River, incorporating a retention dam for flow regulation (Franklin 2007).

Hydrogeochemical conceptual modeling

The conceptual hydrogeochemical model for the waste rock pile (WRP4) examines interactions between gaseous, aqueous, and solid phases, focusing on sulfide oxidation and metal leaching due to acid rock drainage (ARD). The pile has complex hydraulic and geochemical properties, with oxidizing conditions in the north and reducing conditions in the south, influenced by the Consulta Creek drainage system (Abreu 2013; Alberti 2017). Atmospheric oxygen enters through the slopes and is consumed by oxidation (Abreu 2013).

WRP4 spans 570,000 m^2 and holds 12 million m^3 of material, consisting of stripping material and Body B, a tubular breccia ore body. The matrix contains pyrite, fluorite, uranium minerals, molybdenum, and zirconium, with minor galena, sphalerite, and barite. Infiltration tests on the 150–200 mm clay cover confirmed low permeability. Samples were collected during the dry and rainy seasons in 2013 to 2015, and the following parameters were analyzed: Dissolved Oxygen, Turbidity, Eh, pH, Electrical Conductivity, Ca, K, Na, Mg, F, Cl, SO4, NO3, HCO3, CO3, Fe, Mn, Cd, Zn, Ba, Ti, Pb, V, Sr, Mo, Cu, Ni, Cr, Co, Hg, Si, Al, As, Y, Zr, U, Th, Ra226, Ra228, Pb210, and Rn in seven monitoring wells installed in bedrock (Alberti 2017), as shown in Fig. 1. The samples from the Osamu Utsumi pit and BNF showed mixtures of old and new water, indicating contributions from both subsurface flows and direct precipitation infiltration, suggesting a connection between WRP4 and the pit, supported by hydrochemical and isotopic similarities (Alberti 2017).

Pit waters show acidic pH at the surface, transitioning to alkaline and reducing conditions at depth. Acidic discharge fluctuates with precipitation, with peak contaminant concentrations after dry periods, consistent with the unreacted core model (Braun *et al.* 1974). pH remains acidic year-round, indicating continuous ARD generation (Abreu 2013). Geochemical assessments (paste pH, MABA, NAG) confirm advanced oxidation. The results suggest a moderate to low capacity for neutralizing acids, as indicated by the NP/AP ratio, and potential for acid generation under specific conditions, as shown by NAGpH values and sulfur content (Table 1). While sulfur content is not high, it suggests that acid drainage could occur, especially in areas with low NP/AP ratios and lower pH values.

Mineralogical analyses (ED-XRF, XRD, SEM-EDS) identified feldspars, muscovite, kaolinite, gibbsite, hematite, and goethite in the waste rock (Abreu 2013). Sulfur-rich samples showed Fe-S associations, indicating pyrite/pyrrhotite oxidation, while surface samples contained Fe oxides and aluminosilicates, reflecting advanced weathering. Pyrite oxidation drives ARD formation, while monazite and other rare earth-bearing minerals weather preferentially.

Hydrogeological conceptual modeling

The geotechnical structure under study was constructed over a lateritic soil layer ranging from 5 to 10 m in thickness, which tends to have a lower hydraulic conductivity than the saprolite layer beneath it due to the presence of clay minerals. This saprolite layer ranges from 10 – 20 m in thickness before transitioning into the underlying rock mass.

Regarding hydrogeological behavior, groundwater flow occurs primarily through two distinct pathways: (i) a shallow, unconfined flow within the granular lateritic and saprolitic materials, which can exhibit significant seasonal variability due to precipitation and evapotranspiration, and (ii) a deeper, structurally controlled flow regime governed by the fracture network within the rock mass. Table 2 resumes the aforementioned descriptions in addition to a range of expected hydraulic conductivity for this kind of material according to geological description of the area.

In a specific manner, the groundwater behavior in the study area is characterized by a principal flow through the fractures of the aquifer system, from the OU Pit toward the WRP4 as can be observed

Table 1 *Acid generation potential and sulfur content of waste rock materials (Abreu, 2013).*

	NP/AP	NAGpH (kg H_2SO_4 eq/t)	Sulfur content (%)
Max.	4.48	6.09	0.16
Min.	0.04	3.02	0.03
Med.	1.03	4.45	0.09

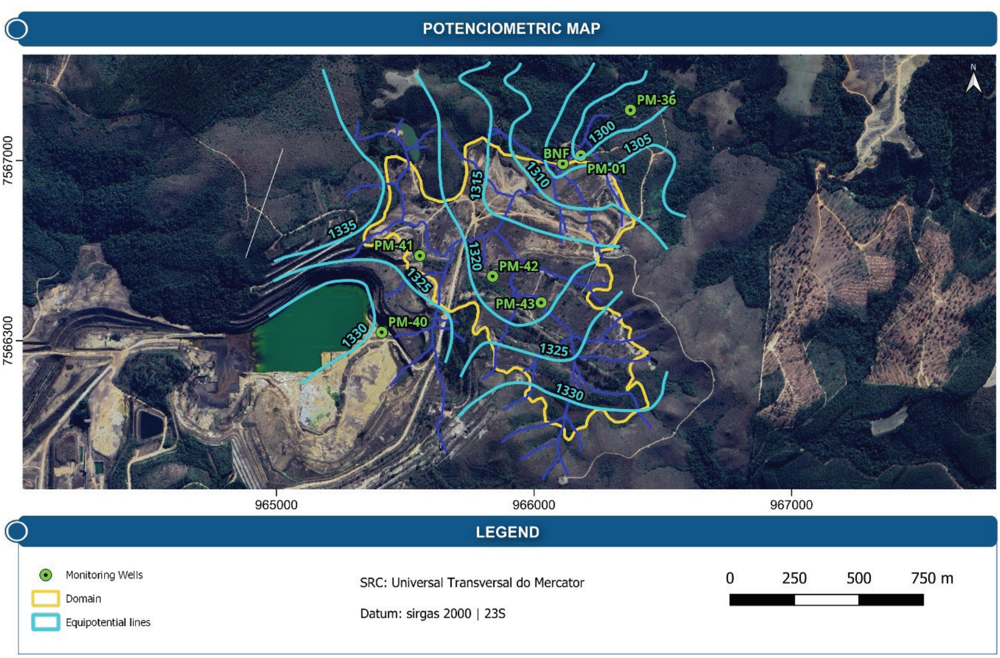

Figure 1 *Potentiometric map of study area.*

Table 2 Description of principal hydrogeological units.

Hydrogeological unit	Hydraulic conductivity (m/s)	Average thickness (m)	Type of flow
Lateritic soil	4.7E-9	5 – 10	Intergranular
Saprolite	5E-6	10 – 20	Intergranular
Rock mass	1E-7	-	Dual porosity
Waste rock pile	5E-7	50	Intergranular

Table 3 Hydrogeological monitoring data.

Monitoring well	Hydraulic head (m)	Date
PM-01	1292.9	December/2013
PM-10	1329.8	December/2013
PM-38	1327.1	December/2013
PM-39	1333.1	December/2013
PM-40	1334.0	December/2013

in the potentiometric map (Fig. 1). This interpretation was based on hydraulic head monitoring and the identification of discharge areas. Regarding the flow behavior within the dry stack, instrument PM41 (monitoring 1351 m) suggests the possible existence of a hydrologic divide between the pile and the pit. However, it is well known that dry stack tailings can create perched aquifers due to their compacted nature and low hydraulic conductivity. These perched aquifers may temporarily store infiltrated water, allowing for localized flow and gradual percolation into the underlying fractured aquifer system. Therefore, it is likely that PM41 is primarily monitoring superficial water rather than deeper groundwater flow. Furthermore, the potentiometric map confirms this interpretation, as it indicates that PM41 is influenced by shallow water rather than the regional groundwater system. Given this, PM41 may not provide relevant data for assessing regional groundwater flow patterns and can be considered less critical for evaluating the hydraulic connection between the OU Pit and the WRP4.

Understanding how much water infiltrates from the OU Pit toward the WRP4 is crucial for assessing the potential impact on groundwater flow and water quality. Quantifying the infiltration rate will help determine whether significant hydraulic interaction occurs between these structures, providing essential information for managing groundwater resources and evaluating potential environmental risks.

Hydrogeological numerical modeling

To further investigate the hydrogeological behavior of the study area, a two-dimensional numerical model was developed and calibrated under steady-state conditions. The calibration process relied on hydraulic head data from monitoring wells PM01, PM10, PM38, PM39, and PM40 (Table 3). As mentioned previously, PM41 was excluded from the calibration due to its shallow depth and focus on superficial water, which does not represent the deeper groundwater flow system.

The main objectives of the numerical model were to validate the conceptual understanding of the principal flow direction and quantify the contribution of water from two sources: flow from the OU Pit and effective recharge into the aquifer system. As can be observed in Fig. 2, the model helped confirm the general flow pattern described in the conceptual model. Specifically, it demonstrates that both the open pit and the dry stack pile contribute to the drainage system at the base.The quantification of water contributions revealed the following results under different recharge scenarios (Table 4). It is worth mentioning that the recharge rates were adopted through calibration in terms of water level and flow rate.

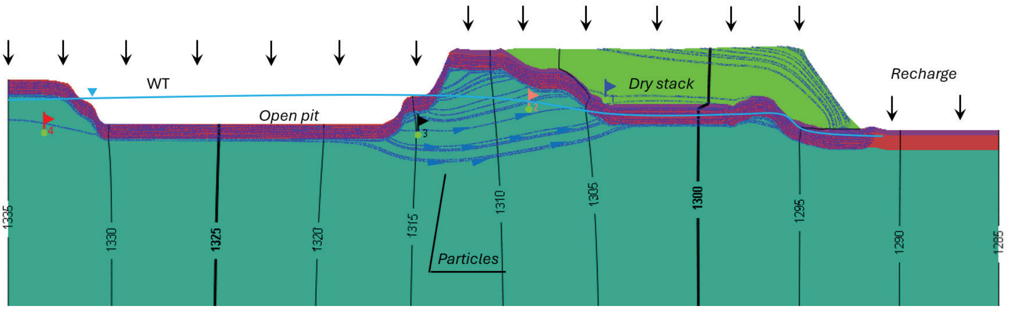

Figure 2 *2D Hydrogeological numerical model, pathlines (blue lines) and water table (sky blue line).*

Table 4 *Osamu Utsumi pit contribution.*

Recharge Rate (mm/year)	Contribution from the OU pit
100	18%
50	27%
25	35%

Table 5 *Observation points in the surrounding areas.*

Observation point	Hydraulic head (m) – 25 mm/year	Hydraulic head (m) – 50 mm/year	Hydraulic head (m) – 100 mm/year
1	1303	1305	1308
2	1308	1309	1311
3	1315	1316	1318
4	1333	1334	1334

These results show that as the recharge rate decreases, the relative contribution of water from the OU Pit increases, highlighting its importance as a significant source of groundwater under low-recharge conditions. This relationship reflects the strong hydraulic connection between the pit and the surrounding aquifer system, particularly in drier periods when natural recharge is limited. Results regarding the piezometric level in the surroundings of the study area were also studied, based on variations of the previously adopted recharge rate and the observation points shown in Fig. 2. Thus, Table 5 compiles the results in terms of hydraulic head.

The model provides a robust tool for understanding groundwater dynamics in the study area and serves as a foundation for future simulations to evaluate different management scenarios and assess the long-term impacts of hydraulic connectivity between the OU Pit and the WRP4. It is worth mentioning that the hydrogeological system was not assessed in transient regime.

Hydrogeochemical numerical modeling

The hydrogeochemical numerical modeling were performed using the software PHREEQC. The simulations involved mixing groundwater from three distinct site areas: the oxidized zone, the non-oxidized zone, and the mine's open-pit lake. According to the conceptual model, these zones influence the hydrogeochemical composition of the internal drainage of the BNF pile, which exhibits high metal concentrations, elevated sulfate levels, and acidic pH. The results of the hydrogeochemical numerical modeling indicate that the high concentrations observed in the BNF internal drainage originate predominantly from the oxidized zone, with contribution of the OU pit. The proportion of these contributions may vary depending on seasonality and precipitation.

Mixtures were simulated considering two scenarios, according with the OU pit contribution (Table 6): one with 65% of the contribution from the oxidized zone and 35% of the OU pit another with 82% of the oxidized zone and 18% of the OU pit. Based on these different proportions, the numerical modeling suggests that some dissolution is occurring within the pile, as indicated by the higher concentrations of aluminum, arsenic, and sulfate in the BNF drainage compared to the monitoring wells. Additionally, a decrease in potassium, manganese, and iron concentrations is observed in the BNF internal drainage relative to the monitoring wells, suggesting mineral precipitation. The numerical modeling results indicate a positive saturation index for $Fe(OH)_3$ (1.65), pyrolusite (3.35), barite (0.61), jarosite (10.59), and alunite (8.27), suggesting that these minerals may precipitate at the pile's outlet. This process may be driven by differences in redox conditions between the pile's interior and the bottom drain outlet.

As a next step to improve the modeling, it is recommended to incorporate mineralogical data and the partial pressure of gases. These parameters will provide more precise information, allowing for a more accurate representation of reality.

Conclusions

This study investigates the hydrogeological and hydrogeochemical processes in Waste Rock Pile 4 (WRP4) at the Poços de Caldas Alkaline Complex, Brazil. By combining groundwater flow and geochemical reaction models, it reveals that sulfide oxidation and acid rock drainage (ARD) in oxidized zones play a key role in contaminant transport. The OU pit contributes significantly to groundwater flow toward WRP4, especially in dry periods. High metal and sulfate concentrations, along with low pH in the pile's drainage, are mainly driven by the oxidized zone and further influenced by the OU pit. The findings support better environmental management and suggest incorporating mineralogical and gas data in future models.

Table 6 *Results from numerical modelling. [1]Median concentration of the parameters for the oxidized zone, [2]Median concentration of the parameters for the non-oxidized zone, [3]Median concentration of the parameters for the OU Pit, [4]Relative proportion of the effluent originating from the oxidized zone, [5]relative proportion of the effluent originating from the OU Pit.*

Parameter	Oxidized zone[1]	Non-oxidized zone[2]	OU Pit[3]	Results from numerical modelling 65%[4] 35%[5]	Results from numerical modelling 82%[4] 18%[5]	BNF
pH	4.76	6.63	5.33	4.63	4.61	4.00
Al (mg/L)	93.17	1.066	8.01	70.57	86.70	121.77
As (mg/L)	1.25	1.66	1.25	1.25	1.25	2.52
Ba (mg/L)	0.03	0.31	0.06	0.04	0.04	0.04
Ca (mg/L)	166.37	16.58	49.4	125.69	145.64	78.02
Fe (mg/L)	93.16	7.24	8.8	63.77	78.15	43.63
Mn (mg/L)	94.34	5.77	9.75	64.88	79.30	71.42
SO_4 (mg/L)	939.46	59.62	186.7	677.57	805.93	944.32
Zn (mg/L)	10.43	0.08	1.05	7.16	8.76	0.03
K (mg/L)	839.55	6.98	21.05	554.24	693.69	5.73
Mg (mg/L)	11.91	2.43	3.14	8.86	10.35	8.19
Na (mg/L)	2.57	16.9	0.815	1.96	2.26	1.31
Si (mg/L)	15.21	7.03	11.22	13.84	14.52	13.35

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