Environmental Assessment for the Decommissioning of a Uranium Waste Rock Pile

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ABSTRACT

The Osamu Utsumi uranium mine (Minas Gerais, Brazil) operated between 1977 and 1995. Today, INB (Indústrias Nucleares do Brasil) and CNEN (Comissão Nacional de Energia Nuclear) work in an attempt to recover the areas impacted by mining and mineral processing activities. In this paper, acid effluents and surrounding waters from a uranium waste rock pile were characterized. Hydrochemical computer modeling (PHREEQC 2) and spectral analysis of transient data were used. Superficial and groundwater samples were collected from the massive waste rock, bedrock, and surrounding areas. Results indicate the existence of two oxidation patterns within the waste rock. At the western region, waters coming from the massive waste exhibit low pH, high total dissolved solids and high levels of sulfate, iron and aluminum, which are characteristic of acid drainage. These ions are supersaturated or close to the saturation limit. The waters of the wells located to the east exhibit characteristics of natural waters and are saturated in iron oxides. Transient data analysis showed that manganese, uranium, and sulfate in the effluent have a delay of three months with respect to the peak rainfall during the rainy season. Under conditions of supersaturation, acid drainage products precipitate in the porous medium, they are washed out during periods of peak flow and then transported to the output point. The pH has a prolonged effect until the next rainy season, explaining the slight variations from 3 to 4, over the hydrological year. Spatial variations in oxidation within the pile and the residence time of water and discharge of reaction products should be used in the remediation design of this pile.

Keywords: acid rock drainage, decommissioning, hydrogeochemical modeling, waste rock pile, uranium.

INTRODUCTION

Mineral oxidation of sulphide ores is the main mechanism to generate acid rock drainage. These minerals, once exposed to ambient weather conditions, Eh and pH, and biological agents can generate acidity. Chemical species containing sulfur are the primary source of acidity. The formation of acid effluent is commonly associated with the occurrence of sulfide minerals such as pyrite (FeS_2), chalcopyrite ($CuFeS_2$), arsenopyrite (FeAsS), sphalerite (ZnS) and galena (PbS) (MEND/CANMET, 2009).

The sulfate ion (SO_4^{2-}) is the most oxidized sulfur form in natural waters. Dissolution of sulfated minerals can reduce the pH of the medium. The formation of acid rock drainage from pyrite follows reaction 1, where 2 moles of protons (H^+) are produced for each mole of the mineral:

$$FeS_{2(s)} + 3{,}5O_{2(g)} + H_2O_{(l)} \rightarrow = Fe^{2+}_{(aq)} + 2SO_4^{2-}_{(aq)} + 2H^+_{(aq)} \tag{1}$$

The oxygen from the air can oxidize sulphide minerals within waste rock piles. Sulphide oxidation is favored as greater is the availability of oxygen at the surface of the mineral. The oxidation produces a variety of secondary mineralogical phases, changing the characteristics of the solid phases, which can be leached upon contact with the aqueous phase of the system.

This paper presents a geochemical characterization of the water circulating through a uranium waste rock pile and adjacent regions. The studied uranium waste rock pile, named Bota-Fora 4 (BF4), is located in the ore Treatment Unit of Caldas (UTM), under management of the Indústrias Nucleares do Brasil (INB), in the city of Poços de Caldas, Minas Gerais, Brazil. The region where the project is located is named Campo do Cercado. The activities of mining and ore processing were closed in 1995, and currently the area lies in decommissioning and implementation of a plan of reclamation process. Poços de Caldas plateau consists in a round caldera of approximately 33km in diameter along the axis northwest-southeast, and extends over around 800km², constituting the largest alkaline complex of South America. Outer ring that forms the caldera has altitude between 1500-1700m, and the inner mountains have an average altitude of 1300m. The ring structure of the caldera is Mesozoic origin, composed of volcanic rocks (alkaline) and plutonic rocks, containing significant amounts of U, Th and rare-earth elements (REEs) (Holmes et al., 1990; Schroscher and Shea, 1991).

Uranium mineralization has been classified into three distinct ore bodies, named A, B and E, according to the concentration of uranium. The body A presents average uranium content of 600ppm. Structurally, it has been described as a monogenic volcanic gap formed by enclosing angular rock fragments of tinguaite. The body B has average uranium content of 680ppm, and it has been described as a large mass of holes, arranged in a matrix tube. The matrix showed a tinguaite rock texture with minerals like pyrite, fluorite, uranium minerals, molybdenum and zirconium. In small amounts galena, sphalerite and barite were found. The Body E has an average grade of 1000ppm uranium, and it consists of a package of host rocks, non-brecciated, containing secondary mineral phases arising from the action of redox phenomena (Gerência da Minas de Caldas, 1988 apud Souza, 1995; Cipriani 2002).

The Bota-Fora 4 (BF4) was built on the valley of Consulta stream, adjacent to the pit mine area, burying natural drainage. The valley was previously prepared with deep drains to receive waste rock. A diversion channel (approximately 500m length) was excavated in natural terrain along the

left flank of the valley. The channel was covered with a compacted clay layer to prevent infiltration of water from the stream in the pile (Souza, 1995; Franklin, 2007). Upstream of Consulta stream deviation channel, a basin was constructed in order to regularize the flow. Downstream of the pile, Nestor Figueiredo basin (BNF) was built to catch the acidic effluents generated in BF4. The Bota-Fora 4 (BF4) has $12.4 \times 10^6 m^3$ and occupies an area of $56.9 \times 10^4 m^2$. The waste rock pile contains cover material of the mine and sterile sorting of body B (Figure 1).
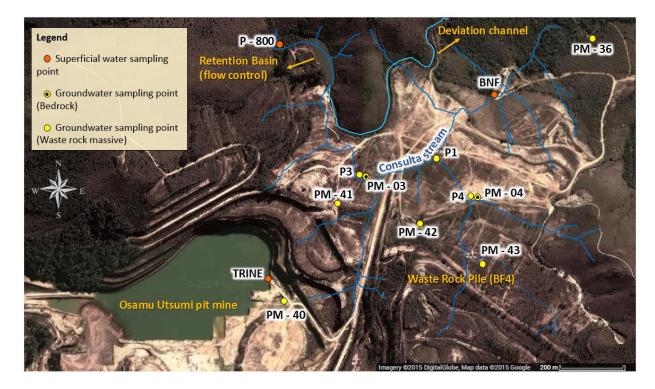

Figure 1 Partial view of the uranium exploration site with emphasis on Osamu Utsumi pit mine, waste rock pile (BF4) and water sampling points (adapted from Google maps, 2015).

METHODOLOGY

Water sampling and chemical analysis

Two sampling campaigns were carried out during the dry season, in August 2011 and July 2012. The sampling method used to collect the surface waters and the procedures for the preservation of the samples followed NBR 9898 standard (ABNT, 1987). Figure 1 shows the sampling points of surface and groundwater. For groundwater sampling, disposable bailers samplers produced in high-density polyethylene (HDPE) with 19:35 mm in diameter and 970mm in length were used. The following parameters were measured in all water samples: pH, total dissolved solids (TDS), redox potential (ORP), temperature and electrical conductivity (in situ, with the aid of a multiparameter meter manufacturer Myron L. Company, Ultrameter IITM model 6P). Table 1 shows the parameters and analytical methods used.

Table 1 Methods used in chemical analysis.

Ion	Analytical method	Ion	Analytical method
Na	Atomic Absorption	Al	ICP-OES
K	Atomic Absorption	Mn	Atomic Absorption
Mg	Atomic Absorption	F^-	Potentiometry
Ca	Atomic Absorption	SO_4^{2-}	EDXRF
Fe	Atomic Absorption	Alkalinity	Titration

Time series of discharge of acid drainage and its chemical composition, monitored monthly during 30 months from January 2007 to June 2009, were selected for spectral analysis (Fig. 2, Fig. 3 and Fig. 4). Time series for U, Mn, SO_4^{2-}, pH, acid discharge and precipitation (Fig. 5) were used. Selected chemical species have relevance for the treatment of effluents and for understanding the process generation of acid rock drainage.
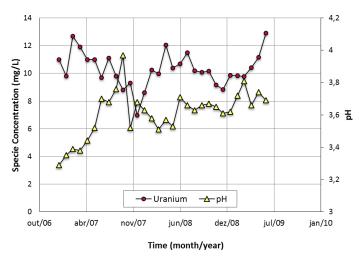

Figure 2 Time series of uranium and pH monitored from January 2007 to June 2009
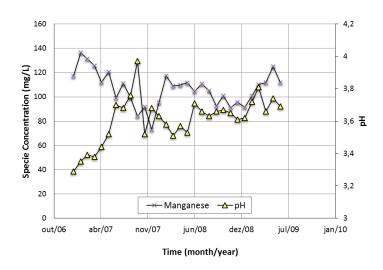

Figure 3 Time series of manganese and pH monitored from January 2007 to June 2009
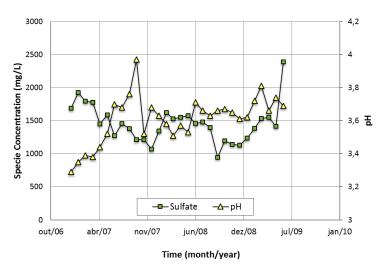
Figure 4 Time series of sulfate and pH monitored from January 2007 to June 2009
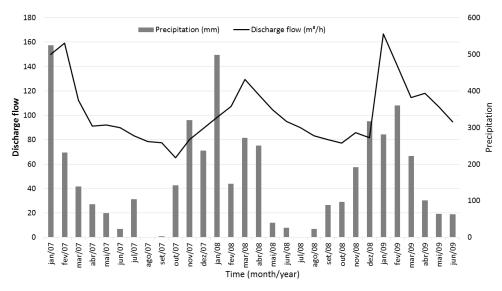

Figure 5 Time series of discharge flow of acid rock drainage and precipitation from January 2007 to June 2009

Data processing

The ionic concentration in the water is the product of geochemical reactions between the aqueous phase and the geological medium under certain environmental conditions. For evaluating the chemical evolution of water quality and the probable chemical reactions, a computational hydrogeochemical modeling was carried out using the software PHREEQC 2 (Parkhurst and Appelo, 1999).

Finally, the set of monitoring data of discharging acid drainage was analyzed by means of autocorrelation functions and cross-correlation. The former function considers the relationship between successive terms of a single time series and provides information on the duration of the

influence of an event in the system. The later function connects the sets of input and output, and indicates how they are correlated. The gap between zero and the maximum of the cross-correlation function, called delay, indicates how stress propagates thought the system.

RESULTS AND DISCUSSION

Computer modeling indicated a supersaturation of the samples of P1, P4 and PM-04 in chemical species containing iron (hematite, goethite and magnetite) and close to saturation limit of ferrihydrite. P1, P4 and PM-04 are also close to the saturation limit in relation to carbonated phase (calcite and aragonite). Non-precipitation of goethite in PM-41 and PM-43, unlike what happen in P1, P4 and PM-04, takes place at the higher pH, which favors the preferential formation of hematite (Tremocoldi, 2003). The preferential precipitation of magnetite compared to hematite takes place under reducing conditions, which is a characteristic of groundwaters.

Samples of the monitoring wells P3, PM-03, PM-40, TRINE and BNF are close to limit of saturation with respect to calcium sulfate (anhydrite or gypsum). PM-40 and P3 capture water from the bedrock of the terrain, below the BF4, have greater similarity in relation to the others. These samples are supersaturated in magnetite and close to the saturation limit in goethite and siderite. P3, PM-03, PM-40, TRINE and BNF are saturated in magnetite. This behavior highlights the trend of leach mineralogical phases containing iron, as expected in acid drainages. In addition, PM-03 and P3 samples, located side by side, are supersaturated in uranium, leading to precipitation of U_3O_8, U_4O_9 and uraninite. The sample of groundwater PM-36, located downstream of the waste rock pile did not show supersaturation in the evaluated phases. The control sample P-800 of surface water upstream of BF4, was supersaturated on hematite, goethite and magnetite.

Autocorrelation results presented similar buffer time, i.e., the duration of the influence of an event for all parameters analyzed, as showed on Table 3. Table 4 and 5 present the results for the cross-correlation. They present the response time of a phenomena (precipitation or discharge) and the signal propagation time in the system, i.e., how long the input phenomenon will affect the output phenomenon. According to the cross-correlation, the discharge on BNF (input parameter) is positively correlated to the chemical parameters (output). This implies that the increase in flow provides an increase in the concentration of U, Mn and sulfate, and a reduction of the pH (increase in H^+ concentration).

During the dry season, secondary phases are precipitated and/or adsorbed in the pores of the pile. With the onset of the rainy season, these species are leached and their peaks occur during this period. This period coincides with the seasonal dry and wet periods, explaining the formation of acid rock drainage throughout the hydrological year.

Such analysis allows us to infer on the hydraulic and geochemical behavior of the pile. After the onset of the rainy season, the pile will reflect an increased flow after 1.2 months. After three months, the pile will start to discharge the stored water in previous refills. The response of the system to the rainy season lasts about 4.8 months, i.e., nearly until the next rainy season. This explains the occurrence of discharge even during dry season. With the beginning of the discharge, the chemical species will be released after 3 months. It implies that these contaminants were leached and subsequently stored until their release in the medium. The release of contaminants

implies in a reduction of the pH. Contaminants as ferric ion is very effective to maintain low pH conditions due the low solubility of ferric hydroxide and to the release of protons by the hydrolysis reaction. It effect extends until the next rainy season.

Table 3 Autocorrelation function results.

	Buffer time (month)	Correlation
U	2.5	0.7
Mn	2.5	0.6
SO_4^{2-}	2.5	0.6
pH	3.0	0.7
Discharge flow	3.0	0.5
Precipitation	3.0	0.6

Table 4 Cross-correlation function and the time series of precipitation as the input parameter and the series of discharge as output parameters.

	Response to precipitation (month)	Precipitation effect (month)	Correlation
Discharge flow	1.2	4.8	0.7

Table 5 Cross-correlation function and the time series of discharge as the input parameter and the series of concentration of U, Mn, SO_4^{2-} and pH as output parameters.

	Response to discharge (month)	Discharge effect (month)	Correlation
U	2.5	5.4	0.7
Mn	2.5	5.8	0.6
SO_4^{2-}	2.5	5.4	0.6
pH	3.0	6.8	0.7

CONCLUSIONS

Two distinct hydrochemical patterns were identified. The western region of the cell, adjacent to the mine pit, preferably oxidizes and generates more acid effluent compared to the eastern region. The transient analysis of the discharges of Mn, U and sulfate in the acid mine drainage showed a positive correlation with flow, indicating that these species are precipitated and/or adsorbed in the pore media during dry periods and have their peak discharge after the beginning of the rainy season, indicating the occurrence of a leaching process. The pH has prolonged effect over 6 months, which explains the presence of acid drainage throughout the year hydrology.

The behavior of chemical species observed in the spectral analysis of monitoring data is corroborated by the results obtained by computational modeling. Acidic effluents are presented

supersaturated or near the saturation limit for Mn containing species, U and sulfate. It is highlighted by the occurrence of Mn concentrations close to saturation limits. The leaching process and subsequent saturation of aqueous species of Mn in the water appears as a phenomenon occurred independently of the formation of acid rock drainage.

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REFERENCES

ABNT - Associação Brasileira de Normas Técnicas (1987) *NBR 9898; Preservação e técnicas de amostragem de afluente líquidos e corpos receptores - Procedimento.*Rio de Janeiro, 22p.

Cipriani, M. (2002) *Mitigação dos impactos sociais e ambientais decorrentes do fechamento definitivo de minas de urânio.* Campinas: Instituto de Geociências, Universidade Estadual de Campinas, 332p. (Tese, Doutorado em Administração e Política de Recursos Minerais).

Franklin, M.R. (2007) *Modelagem numérica do escoamento hidrológico e dos processos geoquímicos aplicados à previsão da drenagem ácida em uma pilha de estéril da mina de urânio de Poços de Caldas – MG.* Rio de Janeiro: COPPE, Universidade Federal do Rio de Janeiro, 337p. (Tese, Doutorado em Engenharia Civil).

Gerência da Mina de Caldas. (1988) *Síntese dos trabalhos: Relatório Interno*. Indústrias Nucleares do Brasil.

Holmes, D.C.; Pitty, A.E.; Noy, D.J. (1990) *Geomorphological and hydrogeological features of the Poços de Caldas caldera and Osamu Utsumi mine and Morro do Ferro analogue study sites, Brazil.* Technical Report TR 90-14, Swedish Nuclear Fuel and Waste Management Co., 55p.

Mend/Canmet – Mining and Mineral Science Laboratory. (2009) *Prediction manual for drainage chemistry from sulphidic geologic materials.* MEND Report 1.20.1.

Parkhurst, D.L; Appelo, C.A.J. (1999) *User's guide to PHREEQC. Version 2. A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations.*US Geological Survey, Denver.

Schorscher, H.D.; Shea, M.E. (1991) *The regional geology, mineralogy and geochemistry of the Poços de Caldas alkaline caldera complex, Minas Gerais, Brazil.* Technical Report TR 90-10, Swedish Nuclear Fuel and Waste Co., 36p.

Souza, V.P. (1995) *Drenagens ácidas do estéril piritoso da mina de urânio de Poços de Caldas: interpretações e implicações ambientais.* Dissertação de Mestrado, Universidade de São Paulo, Dept. de Engenharia de Minas. 141p.

Tremocoldi, W.A. (2003) *Silicate and iron oxide mineralogy of the clay fraction of soils developed from basic rocks in São Paulo state.* Taubaté: Rev. Biociênc. v.9, n.1, p15-22