



# Acid mine drainage as an important mechanism of natural radiation enhancement in mining areas

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**Abstract.** Acid mine drainage (AMD) is a world wide problem that occur whenever sulfidic material is present in association to the mined ore. The acidic waters generated by the process of sulfide minerals oxidation can mobilize important amounts of pollutants and cause significant environmental impacts. The composition of the drainage will depend, on a very large extent, on the mineralogy of the rocks. The purpose of this paper is to demonstrate that acid mine drainage has the potential to enhance the natural levels of environmental radioactivity. The paper revises some strategies to be used in the diagnostic of the problem. General mathematical formulations that can assist on the prediction of the duration of the problem, and the definition of the size of the oxidizing zones in a waste dump are given. A study case on a waste dump of the Poços de Caldas Uranium Mining Site, Brazil is also presented.

## 1. INTRODUCTION

In several mining sites around the world, the presence of oxidising sulfides in waste rock and in the tailings is the cause of most important potential environmental problem. Oxidation products can include hydrogen sulfide, partially oxidized oxianions, such as thiosulphate and polythionates, iron sulfate in solution, elemental sulfur, various jarosite compounds, sulfuric acid, and heavy metals [1]. Radionuclides are recognized as being of concern when uranium ore is mined. Several works have reported the occurrence of acid mine drainage in uranium mining site [1,2,3]. Two of the most famous mining sites to present this problem are the Rum Jungle Mining Site in Australia and the Poços de Caldas Mining Site in Brazil. However, the presence of radioisotopes in acid mine drainage may also be of relevance in non-uranium mining sites, specially when uranium occurs in higher concentrations than the average concentration generally found in the crust. Any acid formed from pyrite oxidation will, to some extent, react with other gangue minerals within the solid sample. The basic reaction to be considered is:



The composition of the resulting solution will be dependent on the other minerals present in the rock (or tailings). Some examples are:

- $\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2$  (calcite dissolution)
- $\text{CaMg}(\text{CO}_3)_2 + 2\text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{MgSO}_4 + 2\text{H}_2\text{O} + 2\text{CO}_2$  (dolomite dissolution)
- $\text{KAl}[\text{AlSi}_3\text{O}_{10}](\text{OH})_2 + \text{H}^+ + 3/2\text{H}_2\text{O} \rightarrow \text{K}^+ + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \text{ (s)}$  (muscovite dissolution)
- $\text{KAlSi}_3\text{O}_8 \text{ (s)} + \text{H}^+ + 9/2\text{H}_2\text{O} \rightarrow \text{K}^+ + 2\text{H}_4\text{SiO}_4 + 1/2\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \text{ (s)}$  (K-feldspar dissolution)

The rate of dissolution of the minerals and, ultimately, the composition of the drainage will be controlled by a series of kinetic and equilibrium reactions.

There are other points to be considered. These waters can not be released into the open environment because of the low pH. Treatment of these waters generally involves their neutralization with lime, aiming to increase the pH to something around 7.0. Due to the amount of pollutants present in the drainage, a highly contaminated sludge will be formed. This material will need to be disposed off with some care because it may pose undue health risks to the members of the general public.

## 2. PREDICTING THE OCCURRENCE OF ACID MINE DRAINAGE

It has already been demonstrated that acid mine drainage may mobilize and introduce in the environment significant amount of radionuclides. The first step to be achieved then is to predict the occurrence of acid mine drainage and assess the load of pollutants involved on the process.

The first step in assessing the acid forming potential of a mining site is to carry out an acid-base account on various samples. In essence, this involves static laboratory procedures that evaluate the balance between acid generation processes (oxidation of sulfide minerals) and acid neutralizing processes (dissolution of alkaline carbonates, displacement of exchangeable bases, and weathering of silicates). The values arising from the acid-base account are referred to as maximum potential acidity (MPA) and acid neutralizing capacity (ANC), respectively. The difference between the MPA and ANC values is referred to as the net acid producing potential (NAPP). The following procedures are suggested in order to investigate the potential for acid generation [4]:

- pH and electrical conductivity (EC): measured on water extract (1:2, solid:water) after 24 hours;
- Total sulfur content of solids;
- Acid neutralizing capacity (ANC) of solids: determined by the addition of acid to a known weight of sample, then titration with NaOH to determine the amount of residual acid;
- Net Acid Producing Potential (NAPP) of solids: calculated from the total sulfur and ANC results;
- Net Acid Generation (NAG) of solids: determined by the hydrogen peroxide oxidation method;
- Kinetic (or monitored) net acid generation (NAG) tests: determined by the hydrogen peroxide oxidation method with reaction kinetic monitored by continuous recording of pH and temperature. After reaction, the NAG liquor is filtered (0.45  $\mu\text{m}$ ), being sub-samples analyzed for acidity, multi-elements, and radionuclides;
- Multi-element composition of solid: determined directly using a combination of ICP-mass spectroscopy (ICP-MS), ICP-optical spectroscopy (OES), atomic absorption spectrometry (AAS) and radiochemical analysis.

### 3. THE GLOBAL OXIDATION RATE (GOR) AND THE INTRINSIC OXIDATION RATE (IOR)

The Global Oxygen Consumption Rate (GOR) in a waste rock dump can be equated to the oxygen flux through the surface of the dump if the gas transport can be considered one-dimensional. The total oxidation rate, in units of  $\text{kg}(\text{O}_2)\text{s}^{-1}$ , can be found by integrating the GOR over the total surface area of the dump. An additional step is the evaluation of the Intrinsic Oxidation Rate (IOR). The IOR is simply the rate of consumption of oxygen by the material in the waste under the conditions that apply to that material. The most practical units to use are  $\text{kg}(\text{O}_2)\text{m}^{-3}\cdot\text{s}^{-1}$ . The IOR depends on a number of parameters such as temperature, particle size distribution, physical form of pyrite, Eh, pH,  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio and the bacterial ecology and numbers. The GOR can be related to IOR by means of equation 2 [5].

$$\text{GOR} = \text{IOR} * L \text{ (equation 2)}$$

Where, L is the average height of the dump.

Ideally, oxidation is initially confined to an upper discrete zone in the dump. There would be no oxidation below this region because oxygen entering from above is consumed by this upper zone of sulphidic material. The extent of this region may be calculated by means of equation 3 [5]:

$$X = (2 * D * C_o / \text{IOR})^{1/2} \text{ (equation 3)}$$

Where X = extent of the region of oxygen consumption (m), D = diffusion coefficient of  $\text{O}_2$  in the dump ( $\text{m}^2\cdot\text{s}^{-1}$ ), and  $C_o$  = oxygen density in air ( $\text{kg}\cdot\text{m}^{-3}$ ).

The time that would be necessary for the whole oxidation of the pyritic material in the dump can be calculated by means of equation 4 [5]:

$$T = (E * d_{rs} * L^2) / (2 * C_o * D) \text{ (equation 4)}$$

Where, E = mass of oxygen used per mass of sulfur consumed, and  $d_{rs}$  = bulk sulfur density.

The time involved on the duration of acid mine drainage generation may vary. However, it is likely to be about hundreds of years. This implies on the fact that if the problem is detected and, in the case that it already exists in a determined site, permanent remedial actions will have to be adopted.

#### 4. A STUDY CASE ON THE URANIUM MINING SITE OF POÇOS DE CALDAS AND IMPLICATIONS TO OTHER NON-URANIUM MINING SITES

Mining operations at the mining site of Poços de Caldas (Brazil), gave rise to two major waste rock piles – WRP 4 and 8. The first will be object of this study since all the drainage from the pile is collected in a holding pond. Table 1 shows the average concentrations of some pollutants in the drainage from WRP-4.

Table 1. Average, Maximum and Minimum Concentrations of Pollutants in the Acid Drainage of WRP-4 (n=21)

Pollutant	Mean	Minimum	Maximum
<sup>226</sup> Ra (Bq/L)	0.29	0.14	0.58
<sup>238</sup> U (Bq/L)	175	71	315
Al (mg/L)	96	61	161
F (mg/L)	99	5.1	167
Mn (mg/L)	75	6.6	105
pH	3.30	2.9	3.7

The most significant observation that can be made from the values in Table 1 is the disequilibrium between <sup>226</sup>Ra and <sup>238</sup>U giving a Ra/U ratio of 0.0017. This can be explained by the fact that radium (co) precipitates with Ca/BaSO<sub>4</sub> formed in the process of the gangue dissolution. Table 2 shows the result from a column leaching experiment carried out with rocks from WRP-4. A pilot column 1 m high and 0.5 m in internal diameter was filled with rock collected in the waste rock deposit area. Distilled water was introduced at the top of the column at a rate intended to reproduce the local rainfall records. Water samples were collected daily and analyzed for the relevant natural radionuclides. Three sub-samples of the material in the column were taken for total analysis of radionuclides before and after the leaching process. The solid material was homogenized and submitted to total digestion in Teflon containers with a mixture of HNO<sub>3</sub>/HF/HClO<sub>4</sub>.

Table 2. Radionuclide Activity Concentration in the Solid Material in the Column Before and After the Leaching Experiment

Sample	<sup>238</sup> U	<sup>234</sup> U	<sup>230</sup> Th	<sup>226</sup> Ra	<sup>210</sup> Pb	<sup>210</sup> Po
Before	4,203	4,090	4,066	5,845	5,120	6,600
After	1,633	1,570	2,273	4,660	4,223	5,236
Ratio	0.38	0.38	0.55	0.79	0.82	0.79

The results show clearly that uranium isotopes are leached at the same extent, while <sup>230</sup>Th occupies an intermediate position and Ra, Pb and Po are leached in a lesser extent. It can also be observed that disequilibrium already exists in the rock before the leaching experiment and is reflected in the WRP drainage

It is reported by the mining operator that  $8.9 \times 10^5 \text{ m}^3$  of acidic waters are pumped annually from the holding pond that collects the drainage from WRP-4. The average sulfate concentration in the drainage is 1,010 mg/L. It can be estimated that  $9.0 \times 10^5 \text{ kg(SO}_4\text{)}\text{a}^{-1}$  are produced as a result of pyrite oxidation in the WRP. The oxygen consumption rate can be readily related to a sulfate generation rate by means of equation 1. The GOR in the waste rock pile can be equated to the oxygen flux through the surface of the pile if the gas transport can be considered one-dimensional. As a result, the total oxidation rate can be found by integrating the GOR over the total surface of the dump ( $56.9 \times 10^4 \text{ m}^2$ ). For the present case the GOR can be assumed as equal to  $2.9 \times 10^{-8} \text{ kg(O}_2\text{)}\text{m}^{-2}\text{.s}^{-1}$ . The IOR can be calculated by means of equation 2. A value equal to  $1.3 \times 10^{-9} \text{ kg(O}_2\text{)}\text{m}^{-3}\text{.s}^{-1}$  is obtained. This value is a typical low rate one, generally found in waste rock dumps [5]. The oxidizing region can be estimated by means of equation 3. The calculate value of X is 45 m. Taking into account that the pile

height is about 90 m, two oxidizing regions may be imposed to the system. The time that would be necessary for the whole oxidation of the pyritic material in the dump can be calculated by means of equation 4. It can be pointed out that more than 1,000 years will be necessary for the consumption of all the pyritic material in the dump. This is quite a long time and will impose the application of permanent remedial actions.

Presently, the acid drainage is treated with lime. Table 3 shows the results of radioisotope concentrations in the sludge, resulting from the neutralization of acid waste rock drainage.

Table 3. Radioisotope Activity Concentrations in the Sludge of the Poços de Caldas Uranium Mining Site Acid Waste Rock Treatment (Bq/kg)

$^{238}\text{U}$	$^{226}\text{Ra}$	$^{210}\text{Pb}$	$^{232}\text{Th}$	$^{228}\text{Ra}$
14,350 +/- 7,875	370 +/- 245	384 +/- 671	371 +/- 444	579 +/- 1,877

The uranium concentration is two orders of magnitude higher than the other radionuclides and shows a correlation with the disequilibrium reported for the acid drainage itself as reported in table 1.

The origin of the water collected in the holding pond (and subsequently pumped to the treatment unit) is the rainfall infiltration through the dump and the water infiltration through the toe of the dump (the dump is placed in an ancient river course). It has been demonstrated that it will take more than 1,000 years for the pyritic material in the dump to be fully oxidized. Since the drainage collected in the holding pond is maintained basically by natural processes, there is no reason to believe that the water balance will be changed in the future. It can be estimated that 12 t/year of  $^{238}\text{U}$  and  $2.44 \times 10^{10}$  Bq/year of  $^{226}\text{Ra}$  will be produced annually by the chemical treatment of these drainages. Taking into account that this treatment is being undertaken for more than 10 years, it can be estimated that, at least, 120 t  $^{238}\text{U}$  and  $2.4 \times 10^{11}$  Bq  $^{226}\text{Ra}$  have already been produced as a consequence of the treatment of acid drainage from the WRP-4. These figures correspond respectively to 34% and 5% of the total amount of  $^{238}\text{U}$  and  $^{226}\text{Ra}$  deposited at the tailings dam of Poços de Caldas Mining Site. If a tailings dam deserves a lot of attention in terms of commissioning and closeout strategies in terms of radiation protection issues, there is no reason to accept that a different approach shall be used for the proper management of this sludge.

In two mining sites investigated in the project reported in [6], a gold and a coal mining site,  $^{238}\text{U}$  uranium concentrations in the acid mine drainage from both installations were respectively equal to 30 and 100 Bq/L. The last value is quite similar to the average  $^{238}\text{U}$  concentration observed in the acid drainage of the uranium mining site of Poços de Caldas. The explanation for that may rely on the fact that, despite the higher  $^{238}\text{U}$  concentrations in the waste rock of Poços de Caldas Mining Site, it may occur in a less mobile state in comparison to what is observed in the Pyritic Waste Piles of the coal mine. Moreover, pyrite concentration in the spoils from the coal mine is about 20% while in the Poços de Caldas waste rock piles the average pyrite concentration is ten times lower (say 2%). The conclusion on this issue is that sludge from non-uranium mining sites may have significant amounts of radionuclides. As a result, it is mandatory that this material needs to be disposed off with care. Moreover, in some cases, as it happens in the Gold Mining Site of Jacobina (countryside of Brazil), the lack of a regular water supply (the mining site is located at a very dry region with precipitation records below 500 mm/year) makes the inhabitants use any available water. Thus, direct consumption of water with elevated levels of radionuclide concentrations shall not be disregarded at all.

## 5. REMEDIATION AND OVERALL STRATEGY TO DEAL WITH THE PROBLEM

It has been demonstrated above that, acid mine drainage may lead to the enhancement of natural radiation in the environment. It has also been reported some general actions that may be used to predict the occurrence of acid drainage resulting from mining operations; to predict the extension of oxidizing regions in waste rock piles and to estimate the duration of the process. These strategies are useful in predicting the occurrence of the problem and are very helpful in the planning of the overall management strategies. However, the remediation of existing sites needs also to be addressed.

In a general way, it can be considered that a dump already formed has an inert cover (maybe a capping layer) over it. Figure 1 summarizes a series of process occurring in the waste dump environment. Initially, oxygen will diffuse through the capping layer and react with the uppermost layer of rock. Oxygen penetration into the rock will depend on the thickness of the cap, the values of the diffusion coefficients and the intrinsic reaction rate. It can be assumed that an oxidation zone will be established; above the top of the zone there will be no reactive sulfur and below the zone the oxygen concentration will be zero. Within the zone, oxidation will proceed at uniform rate until sulfur is consumed, which will happen at the same time at all points in the zone. The oxygen will then diffuse through this newly created inert zone and establish a new oxidation zone, taking a negligible time to reach a new equilibrium. As this process repeat itself the inert or depleted layer will increase in thickness, being a sum of a series of former oxidation zones.

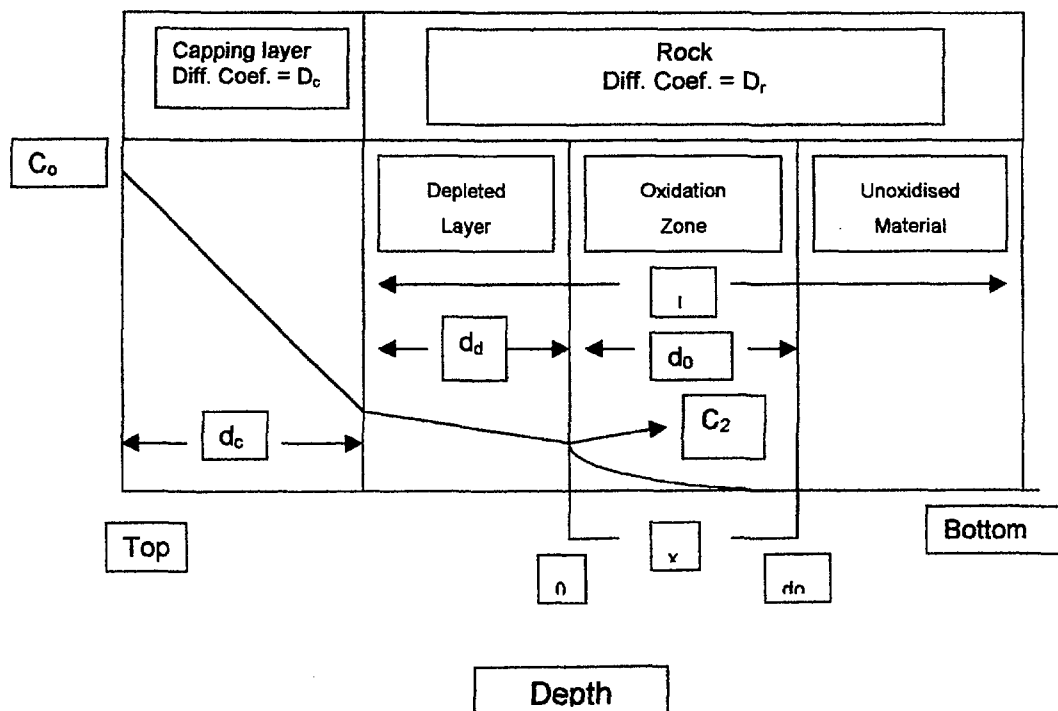


Figure 1. Schematic representation of the oxidation process in a waste rock dump.

A general strategy in the permanent remediation of a waste rock dump is the covering with a material presenting a low oxygen diffusion coefficient. It is reported that the reduction factor will depend much more on the properties of the covering layer than on the properties of the dump forming material (this include the IOR). The practical problem to be solved is to design an appropriate cover and guarantee the cover integrity along the time.

A cover of an inert material of  $X_c$  thickness and oxygen diffusion coefficient  $D_c$  generates the equation 5 [5]:

$$GOR = (2C_0D \cdot IOR)^{1/2} ((a + n)^{1/2} - (a + n - 1)^{1/2}) \text{ (equation 5).}$$

Where  $a = (X_c/D_c)^2 ((IOR \cdot D)/2C_0)$ .

This equation has been applied to the WRP-4 of the Poços de Caldas Uranium Mining Site. The composition of the drainage was simulated for three different cover thickness (0,5; 1,0 and 2,0 m) of varying oxygen diffusion coefficients ( $1.0 \times 10^{-8}$ ;  $1.0 \times 10^{-9}$  and  $1.0 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ ). The obtained results are shown in table 4. It can be seen that the best option relies between the options 4 and 5. From this stage on there will be no gain of effectiveness of the remediation applied.

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