

Passive Treatment of Radioactive Mine Water in Urgeiriça Uranium Mine, Portugal

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Abstract

Environmental remediation of old uranium mine sites in Portugal in particular the importance of finding alternatives in water treatment processes has led to the research of passive treatment techniques in order to establish and improve long term sustainability. As so, this kind of innovative technology gathering in the same site chemical, physical, phyto and bioremediation has become a pilot ground or study area in Portugal.

The paper is focused in the main features of the applied techniques and their use on specific infrastructures to control uranium and radium contaminated effluents and seepage control. The aim of this paper is to, based upon three years of water samples analytical data, to better understand the behavior and efficiency of Mine Water Passive Treatment (MWPT) Systems alternatively to Active Treatment Systems (ATS) as well as to develop and systematize MWPT systems. Regardless the variation in the beginning of the MWPT's parameters concentrations, the results show that this kind of treatment on mine water or seepage, throughout the system stabilization in less than 2 years, highly reduces concentrations of radioactive elements mainly Uranium (total) from 487µg/l to nearly 11µg/l, with a 98% efficiency, and Ra₂₂₆ with 99% efficiency, varying 1Bq/L to <DL, 0,01Bq/l. Metals Fe-oxides and Mn are also reduced from ~6mg/l in the first passive treatment pond to values below detection limits in the final pond (<1mg/L). Metalloids mainly Mg²⁺ and K⁺ show stable concentrations with values up to 15mg/l and 10mg/l, respectively, along passive treatment. Ca²⁺ and Na⁺ show also stable values up to 100mg/l and 40mg/l, respectively.

Keywords: Remediation, Uranium, Mine water passive treatment, seepage control.

Introduction

Portugal has an important legacy of degraded former mining sites with clear environmental and public health impacts and safety problems. Since 2001 they are being subjected to environmental rehabilitation operations by EDM- *Empresa de Desenvolvimento Mineiro, S.A.* under a legal regime of concession assigned by the Portuguese State and approved by the Decree-Law N° 198-A/2001. EDM is covering the environmental rehabilitation of 175 abandoned mining areas, 61 of which in radioactive minerals and 114 in the Polymetallic mines set. In the radioactive ore mines the most relevant are Urgeiriça, Quinta do Bispo, Cunha Baixa and Bica mines, all located in the Beiras Granitic Region. By the year of 2015, 95 out of 175 mine sites have been intervened. Actually main strategic areas of EDM were to develop the remediation works of the remaining mining sites, the development of safety actions and medium and long term monitoring/maintenance operations in air, water, soils, sediments.

EDM started the Urgeiriça Environmental Remediation works in 2001 and started with the underground mine flooding at controlling at the same time in the surroundings 252 monitoring points (wells, piezometers, sediments, soil and streams) measuring in situ parameters (pH, electrical conductivity, EC, redox potential, Eh and temperature, t) and laboratory analysis of chemical and radiological parameters such as total uranium, Ra₂₂₆, sulphates, chlorides, manganese, calcium and sodium as hydrochemical contamination indicators.

In the meantime EDM started in this site some experiments with small pilot scale projects of passive treatments using some natural neutralizing and fixing agents such as barite, limestone, expanded clay and proportional flows with the purpose of scale up for large scale projects. Additionally the projects were upgraded with species of bioaccumulation heavy metals macrophytes (phytoremediation) taking in consideration the work of Favas et al (2013), and with the natural creation of adapted aquatic ecosystems for uranium and other metals reduction bacteria.

The results of final heavy metals concentrations were promising and led to final passive treatment projects, where the hydraulic retention times were optimized regarding the higher winter flows and lower temperatures. Therefore EDM implemented in 2012 the first MWPT with several decantation stages settling

remediation efficiency supported by a tight chemical analysis and monitoring program, first on a weekly basis and then monthly till now.

The results associated with groundwater natural attenuation processes and hot-spot contamination containment led to the generalization of passive treatment projects in other old uranium mining areas. Afterwards, and after the stabilization of the groundwater, the need of low flow seepage water control arose letting to the use of some other tests supported by independent structures in the passive treatment filled with activated carbon and also with some physical specific plastic frames for the growth of uranium bacteria.

In fact the streamlined passive treatments with lower associated operational costs, has led to the decline of chemical active treatments importance in EDM's context. Optimization of these passive systems can lead to an improvement in terms of associated maintenance costs and rehabilitation projects sustainability.

Study Area

Geographical and Geomorphological setting

The Urgeiriça Uranium mine is located in the parish of Canas de Senhorim, in the SE part of the municipality of Nelas, around 20 km south of Viseu in the center of Portugal, **Figure 1**. The parish has a population of 3500 and a population density of 136/km².

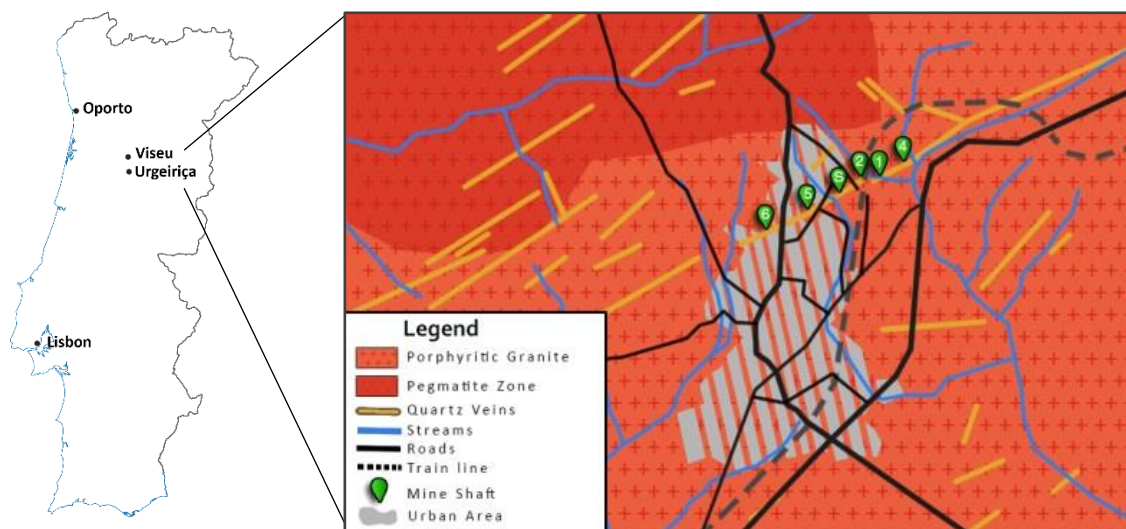


Figure 1 Localization of the Urgeiriça Mine and simplified geological map of the area

The geomorphology of the area is characterized by smooth reliefs, the highest point being located at 400 m and the lowest in the stream called “*Ribeira da Patanha*” sitting at 340 m. It belongs to the Iberian Plateau, which is tectonically stable. The study area is bordered by stream which is part of the Mondego watershed. The biggest depressions in the terrain are associated with streams presenting a dendritic pattern. The area is sparsely populated, being a suburban and agricultural area, forested by small bushes, pine trees, olive trees and eucalyptus. The local climate is a moderate Mediterranean climate.

Geology and Mineralizations

Geologically the area belongs to the geotectonic Central Iberian Zone in the Iberian massif. Hercynian Granites are predominant in the region, a porphyritic medium to coarse grained two mica granite, as it can be seen in **Figure 1**. The granites are considerably altered and the general area is very fractured, having three important faults associated with the mine, a horizontal fault, and two vertical ones, and various smaller ones. Veins are extremely common, with the dominant strike direction of N60°E.

The exploration was related to the mineralization of one of this vein, trending N60E – 75SE, up to 3 m thick and 7km in length, 2km of it were economically viable. The vein formation is related to the unconformity of *Variscan* granites. The orebody's origin is related to alpine movements that reactivated Hercynian faults and shear zones. According to Rich et al. 1977, volatile rich, high pressure and temperature hydrothermal fluids dissolved country rock, increasing the pH. This factor, combined with lower temperatures which decrease the solubility of UO₂ changed the valence state of Uranium from U⁺⁶ to U⁺⁴ which in turn led to the precipitation of Uranium minerals in those shear zones. The most significant mineralizations could be found in the most fractured areas.

The vein main association of minerals is microbotryoidal sooty picheblend and uraninite (UO₂), Pyrite (FeS₂), marcasite (FeS₂) and jasper quartz (SiO₄) as gangue, and sporadically galena (PbS) and chalcopyrite (CuFeS₂). The wall rock alteration is frequent, mainly sericitization, cloritization, hematization, jasperization and kaolinisation (Portugal et al. 1971).

Mining activity

The mine began its exploration of Radium Salts in the year 1913. Later during WWII the production shifted towards Uranium due to the demand at the time. In 1951, the Chemical Treatment Plant (CTP) was constructed, allowing Urgeiriça to be a hub for the reception and processing of uranium from mine sites of the *Centro* region, which at the time accounted for 61 uranium mining sites, with an output capacity of 125 t/year of U₃O₈.

The exploration methods were adapted throughout time. The site began as an underground mine using the Cut-and-Fill technique, with the empty stope being filled with gangue and low grade ore. In 1967 it reached its peak depth at 19 levels, roughly 500m deep and 1km in length. After it was concluded that the mineralization was depleted, small scale tests to recover residual uranium resources left behind were implemented. These tests consisted in using Sulphuric Acid to mobilize Uranium to an effluent that would be pumped out to the surface, using an ionic exchange system the uranium content could be extracted, a process denominated *in-situ* leaching. In 1969 the first four levels of the mine were destined to try out leaching *in-situ* on a bigger scale, taking advantage of a horizontal fault at that level. In 1971 the classical exploration was over and *in-situ* leaching was generalized to all floors and lasted until the mine was closed in 1991 (J. Cordeiro Santo 1983).

Methods

Procedures

Mine flooding

In 2001 the pumping of contaminated groundwater to the active treatment plant was interrupted in order to flood the mine in a controlled and progressive way as it can be seen in **Figure 2**. The objective was to understand the behavior of the groundwater related to the diminishing of oxidation/reduction reactions, creating an anaerobic environment restraining metals mobilization. Within two years of systematic water monitoring control, the water level reached its highest level. As so, in 2003 the groundwater level stabilized at the level between -12m and -8m and the natural hydrodynamic equilibrium was reached.

As the groundwater level rose throughout the mine galleries it started to exit only in the old mine shaft nº4 as expected, being collected, characterized and treated in the existent ATS. This spring is the only place where groundwater from the mine galleries outflows. By that time, some experiments were implemented, in the form of a passive treatment pilot plant, to research on the possibility to decontaminate this seepage water with these type of systems. Afterwards, while the main circuit was built, a second seepage water started to exit next to the former one.

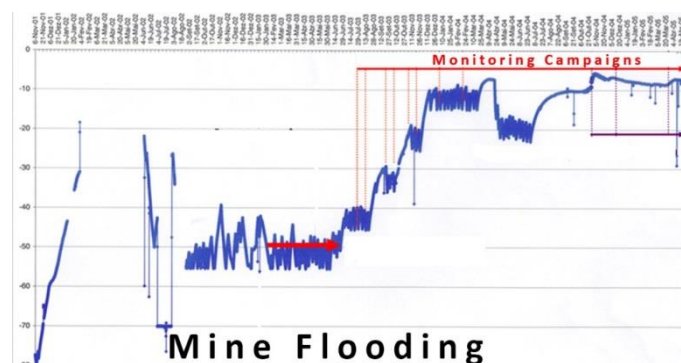


Figure 2 Mine flooding piezometric evolution

Structure of the Urgeiriça mine MWPT pilot plant

The MWPT pilot plant (Figure 3) used consisted in a small basin with decantation sectors filled with limestone gravel, expanded clay and barite acting as Permeable reactive Barriers (PRB's) in a total proportional volume related to the hydraulic retention time of existing active treatment basins, around 20 and 40 days, winter and summer, respectively. The final chemical analysis results led to decreasing concentrations of radioactive elements such as U_{total} and Ra²²⁶, Fe-oxides and Manganese.



Figure 3 Mine water passive treatment pilot plant

Mine water passive treatment project

The main features of the MWPT final project lay down on 6 ponds initially, 3 of concrete with a volume of nearly $V=1000\text{m}^3$, and other 3 up to 1700m^3 as wetlands with macrophytes. Afterward, the system was upgraded to treat the second seepage, with 3 additional concrete ponds of 100m^3 each, the last of which was divided into 3 as a pilot to test a PRB's with activated carbon filtration. The sampling locations were defined as WAP_i for the first decantation pond, ii for the second, and so on with the last point being WAP_f , the supplementary circuit was named WAP_{bi} , WAP_{bii} , WAP_{Biii1} , WAP_{Biii2} , WAP_{BiiiCA} (Figure 4.1).



Figure 4 - MWPT layout

The existing hydraulic retention time ensure the needed conditions to promote the oxidation and the precipitation of the main contamination elements, allied to the existence of bacteria and macrophytes which improve water quality. The final project was assembled with previously established hydraulic and physical data as shown in Figure 5.

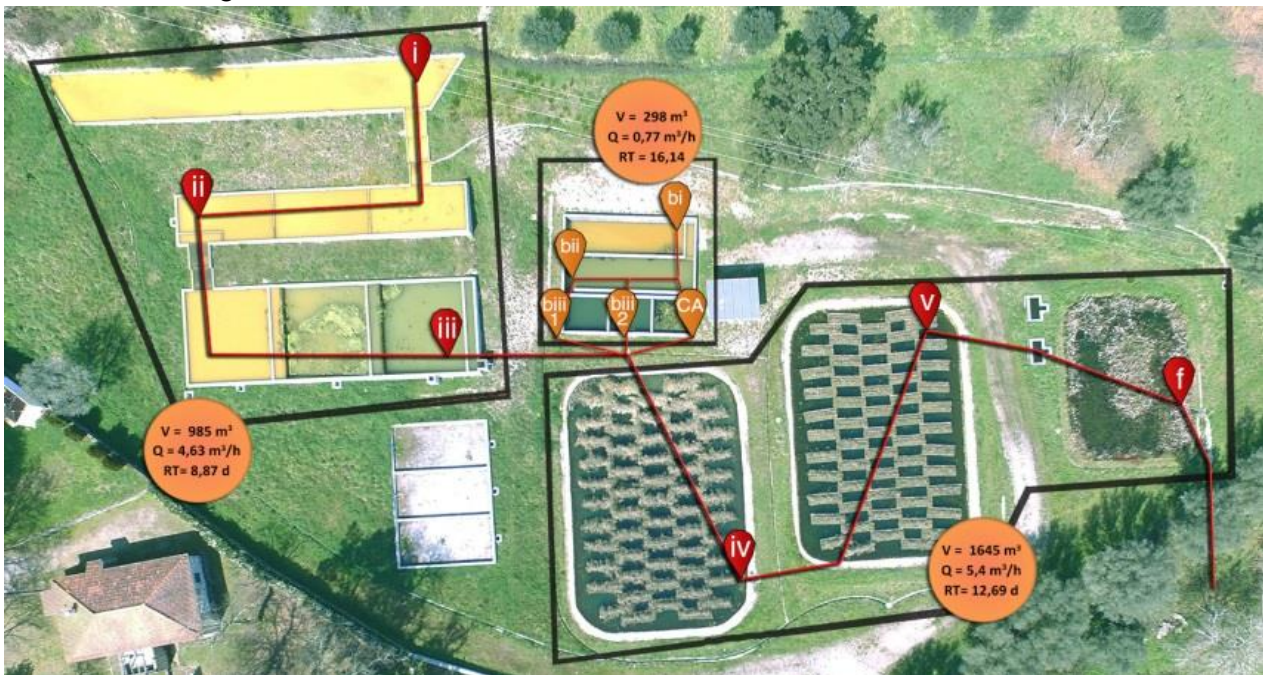


Figure 5 - MWPT layout and hydraulic data, V =Volume; Q =Flow; RT =Retention Time

The hydraulic data shows that the flow of the 2nd seepage treatment is six times lesser than the discharge from the main pathway. The historical discharged values are $0.9\text{m}^3/\text{h}$ (minimum) and $7.2\text{m}^3/\text{h}$ (maximum) with a mean value of $4.0\text{m}^3/\text{h}$ for all MWPT. The data used (Figure 5) report to field sampling.

Field sampling and sample treatment

Water samples for chemical analysis were collected in each of the MWPT ponds since September 2012 until present days with a frequency of at least once a month, accounting for 42 series of samples investigated in this study. In the beginning of the monitoring (2012) several chemical and physical parameters were analyzed, however since 2014, most of the trace elements were historically bellow the detection limit, the monitoring was focused in major cations (Ca, K, Na), major anions (HCO_3^- , Cl^- , SO_4^-), radionuclides (U_{total} , Ra_{226} , U_{234} , U_{238}) and trace elements (Fe, Mn).

The water samples were stored and transported in clean and sterile plastic bottles. For the determination of metals the samples were acidified with (65%) HNO_3 , being afterwards processed in a certified laboratory. Field parameters (pH, EC, Eh and t) were measured *in situ* at the same time in each sampling site. pH and t were measured using a pH-Electrode Sentix 940 probe from WTW, EC was measured using Tetracon 925 probe from WTW.

Results and discussion

Former studies indicates that bacteria alongside with macrophytes (phytoremediation) upgrade precipitation and coagulation processes being the macrophytes used in this case *Juncus efusus*, *Iris pseudacorus*, *Typha latifolia* and *Carex aquatilis*. The common bacteria present in these kind of contaminated waters tend to use organic matter as electron donors by promoting the removal of uranium from water by reducing U^{6+} to relatively insoluble U^{4+} (Zhang *et al.* 2012), favoring its precipitation. Bacteria studies are still being undertaken in order to maximize their growth.

This MWPT layout favors the oxidation and increase of pH and Eh which in turn increases the mobility of U forms. In general, and in less than two years, the system entered in a chemical balance and reached its equilibrium, as we can see in the charts below.

The standard water quality legislation used for compliance verification was the Portuguese Decree-Law nº 236/98, of 1 of August, Annex XVIII referent to discharge limits of effluents. Concerning radioactive elements we used USEPA 40 CFR Parts 9, 141, and 142 *National Primary Drinking Water Regulations Radionuclides*; USEPA CFR440.32 “*Effluent limitations for mine drainage from open pit and underground uranium mines*”. The used references, mainly drinking water regulations for Uranium and Radium, point out the observance of water limit for discharge at values of 30 $\mu\text{g/l}$ and 0,185 Bq/l, respectively. The waters in the MWPT can be classified as calcium bicarbonate according to the Piper diagram.

After the statistical analysis of the data the evolution of concentrations of each parameter were analyzed not only on a temporal evolution basis but also throughout the spatial sequence inside the MWPT.

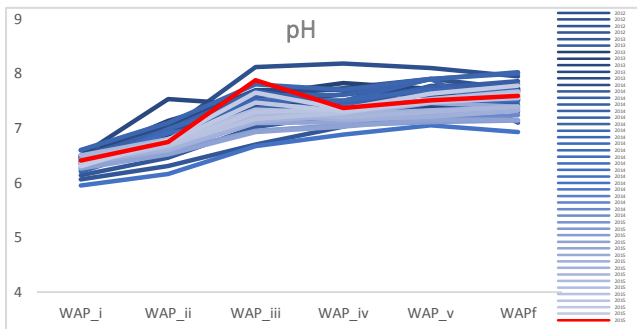


Figure 6 Spatial evolution of pH

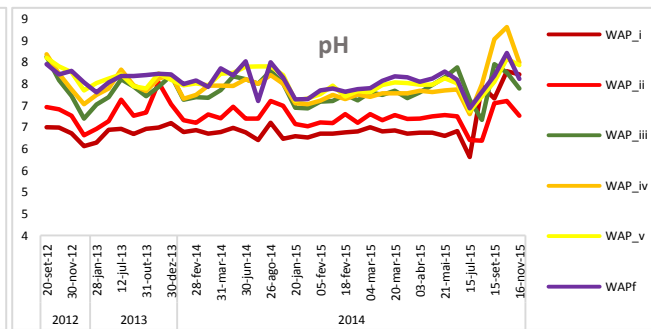


Figure 7 Temporal variation of pH

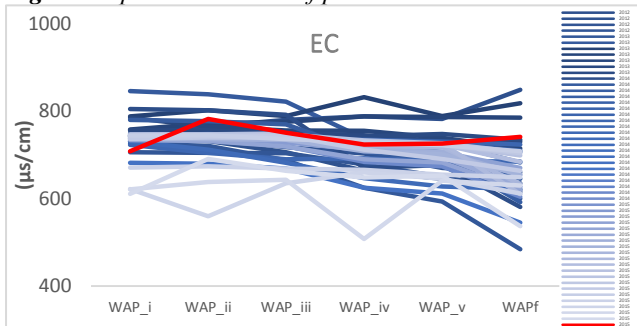


Figure 8 Spatial evolution of EC

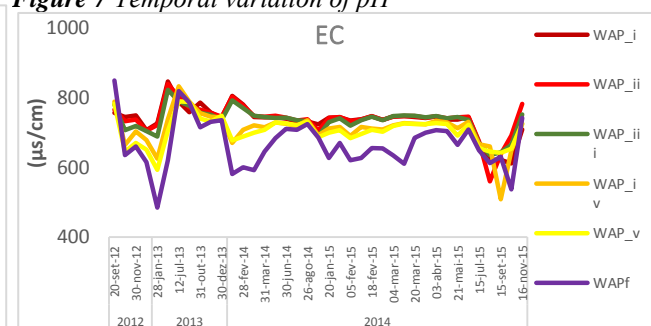


Figure 9 Temporal variation of EC

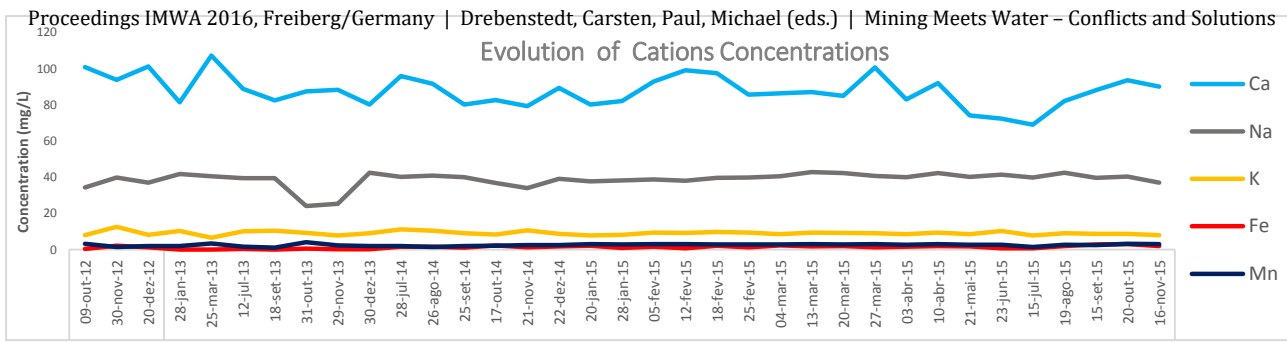


Figure 10 Temporal variation of average concentrations in MWPT of Ca, Na, K, Fe and Mn in $mg.L^{-1}$

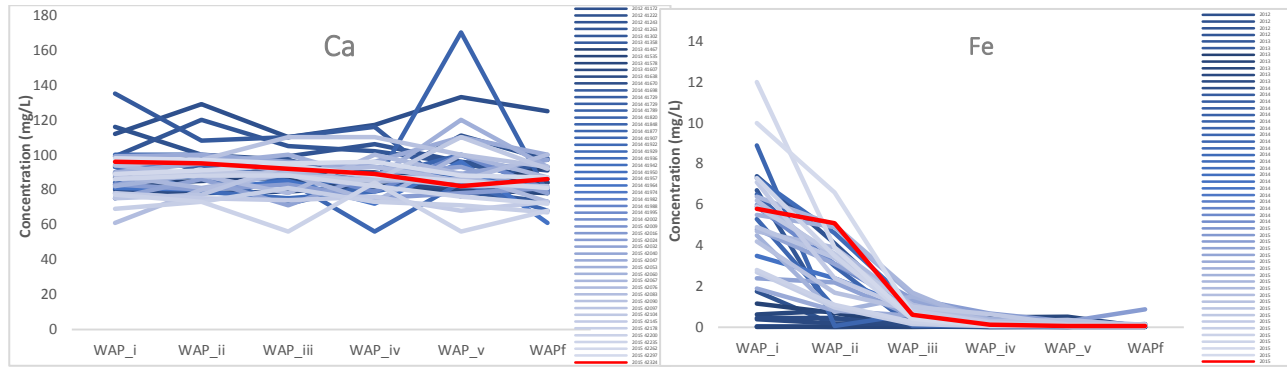


Figure 11 Spatial evolution of concentrations of Ca in $mg.L^{-1}$

Figure 12 Spatial evolution of concentrations of Fe in $mg.L^{-1}$

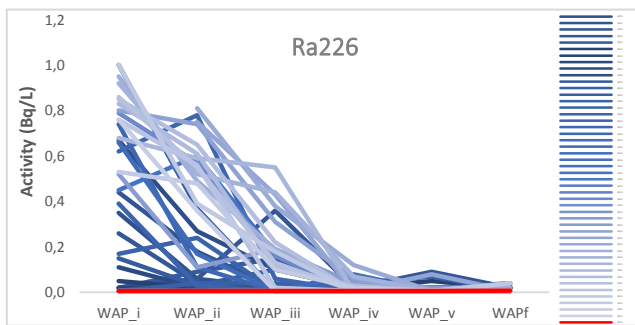


Figure 13 Spatial evolution of Ra-226 activity in $Bq.L^{-1}$

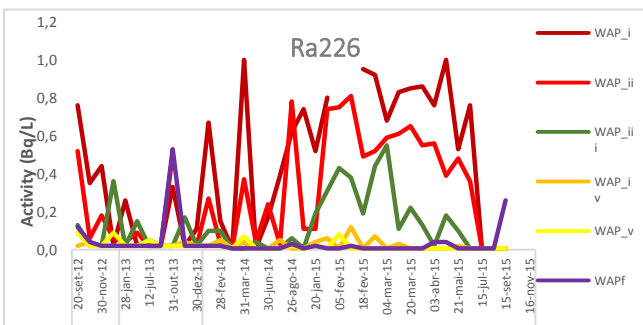


Figure 14 Temporal variation of Ra-226 activity in $Bq.L^{-1}$

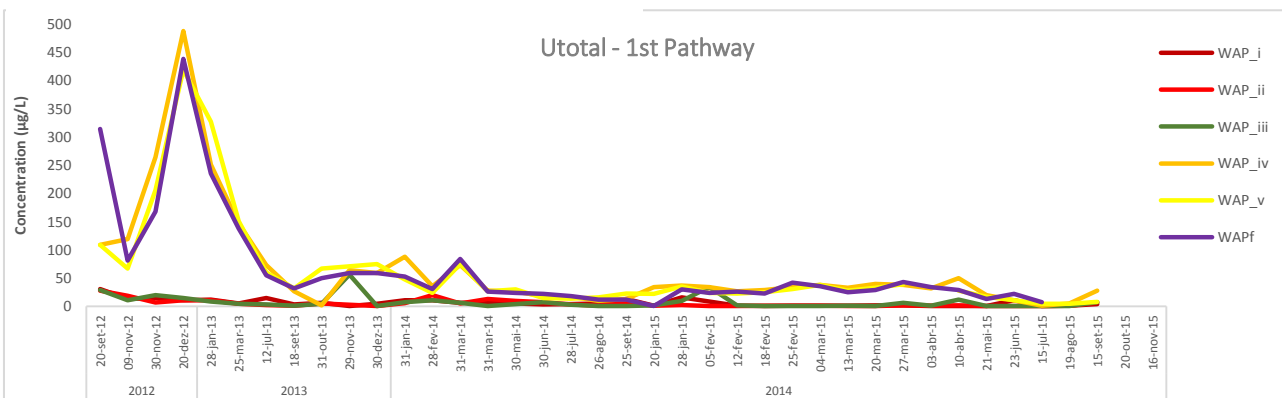


Figure 15 Temporal variation of U_{total} concentrations in $\mu g/L$, in the 1st pathway (2012-2015)

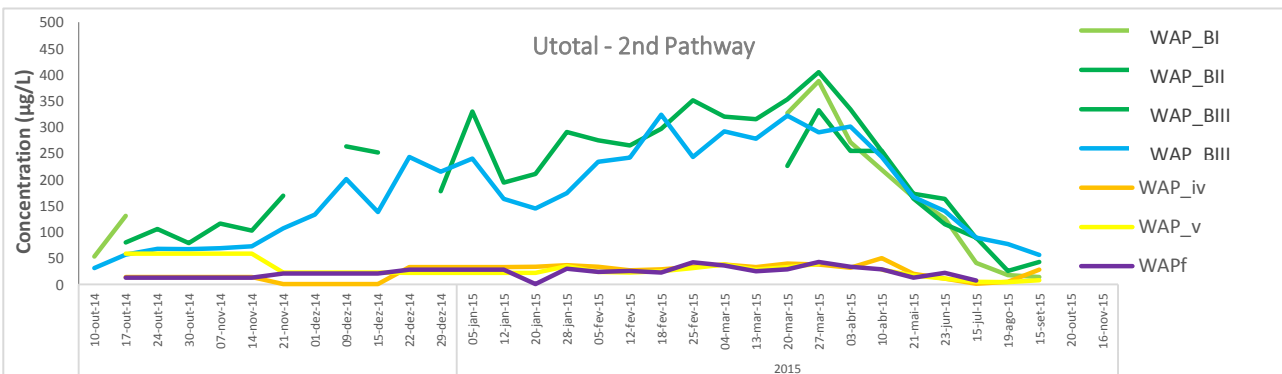


Figure 16 Temporal variation of U_{total} concentrations in $\mu g/L$, in the 2nd pathway (2014-2015)

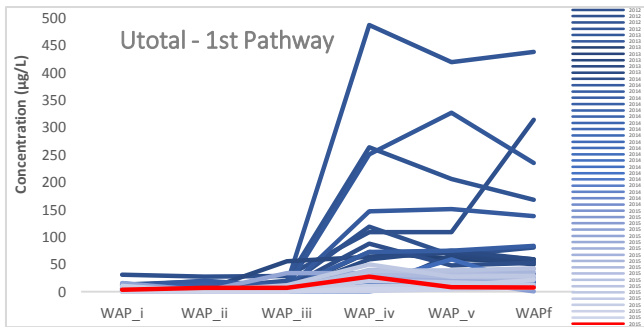


Figure 17 Spatial evolution of U_{total} concentrations in $\mu\text{g/L}$, 1st pathway

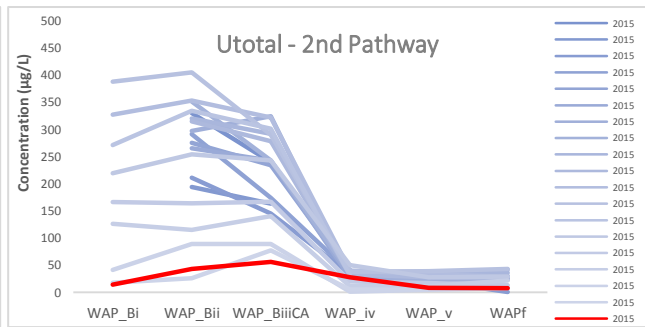


Figure 18 Spatial evolution of U_{total} concentrations $\mu\text{g/L}$, 2nd pathway

The graphs with spatial evolution are organized according to color series, being the darker colors the oldest series and the most recent samples the lightest. The last series of collected samples taken are marked in red.

The following conclusions were taken from the water quality monitoring results:

Physical Parameters - pH values are within 5.9 – 7,7 ranging from slightly acidic to alkaline (**Figure 6**). Both, Eh and pH values, increase spatially throughout the system, while EC decreases (**Figure 8**). Temporal variations can be observed in EC (**Figure 9**), while pH presents a more or less stable behavior (**Figure 7**).

Cations (Ca, Na, K, Fe, Mn) - In general, these elements have been stable during the monitoring period, as presented by **Figure 10** with the average concentrations of these elements along all the sampling points. However, spatial distribution during that same period present two different behaviors: Ca, Na and K maintain stable values during the whole system, being in **Figure 11** presented the evolution of concentrations of Ca. Whereas Fe-oxides (**Figure 12**) and Mn, present a diminishing behavior until WAPiii (third stage) of the system, varying from ~8 mg/L to under detection limits.

Anions (HCO_3^- , Cl^- , SO_4^-) – Regarding temporal evolution of the concentrations of the sampling points: Bicarbonates present a slightly increase over time (300mg/L), sulfates fluctuate from 200-100 mg/L while chlorides tend to stabilize ~50 Mg/L. Spatially, both chlorides and sulfates tend to stabilize throughout the MWPT, bicarbonates on the other hand present a similar behavior to Fe and Mn showing lower concentrations in the late stages of the system.

Radionuclides (Ra^{226} , U_{total} , U^{234} , U^{238}) – Spatially, Radium has been behaving in comparable way as bicarbonates, Fe and Mn do, with progressively lower activities as the MWPT progresses (**Figure 13**). Temporally has a stable behavior during the period with range values of $1 \text{ Bq}\cdot\text{L}^{-1}$ to <DL (0,01 Bq/L) (**Figure 14**). Total Uranium and its isotopes are similar in their performance. Temporal variation of the concentration of U_{total} has been decreasing in both pathways, 1st (**Figure 15**) and 2nd (**Figure 16**) which present a decline over time. However, spatially while 2nd pathway presents a diminishing behavior (**Figure 18**), in the 1st pathway an atypical behaviour can be observed with its concentration slightly increasing in the stage n^o4, WAP_{IV}, of the MWPT (**Figure 17**), decreasing afterwards to values below the ones verified in the initial stages. Most definitely this behavior has to do with two different factors, the first being the entrance of low flow seepage water (2nd pathway) with higher U_{total} concentrations than the initial ones of the first pathway (WAP_i to WAP_{iii}), and the second being the contribution of equilibrium between dissolved (U^{+6}) and particulate (U^{+4}) forms of uranium.

Conclusion

The monitoring results of the constructed MWPT in the last three years shows that this system is efficient by promoting the decrease and significant removal of radionuclides and heavy metals concentrations to levels way below regulatory standard limits.

Analyzing the temporal variation of the different patterns we can see that there is a general tendency overall for the diminishing concentrations (U_{total} and EC) over time, and a group of parameters that have been stable during the whole process.

When examining the evolution of the parameters within the MWPT flow path, we can distinguish three groups, based upon their behavior. The first group (EC, Ra^{226} , Fe, Mn, Bicarbonates) have a similar behavior, in which their values decrease as the treatment progresses. The second group (Eh, pH) increase their values in the late stages of the MWPT, and in the last group (Ca, K, Na) they remain with stable values through the system.

Our data seems to indicate that:

- The MWPT has been objectively efficient in terms of removing contaminants from the aqueous phase, within the most important parameters, Uranium (total) from 487µg/l to nearly 11µg/l and Radium from 1Bq/L to <0,01Bq/l, with an efficiency of up to 98% and 99%, respectively, in terms of temporal variation. Concerning spatial variation we have, from the latest series, an efficiency of nearly 90%, ranging ~250µg/l to nearly ~27µg/l.
- When compared with the Active treatment plant, at this efficiency rates, while the WMPT requires a higher monitorization time, it represents lower operational and maintenance associated costs, therefore being a clear option to replace the active treatments.
- There was an improvement in all water quality parameters, both temporally and spatially reaching uranium and Ra-226 values below USEPA standards for drinking water of 30 µg/l and 0,01 Bq/L, respectively.
- The system reached its chemical stabilization in a period of less than 2 years.
- The diminishing concentrations of Fe, Mn are mainly due to their precipitation in the first stages.
- The main mechanisms involved in the precipitation and mobilization of Uranium are thought to come from the increase pH/Eh, complexation with bicarbonates, organic matter and sulfates.
- Present data seems to indicate that Eh increase causes mobilization from U^{+4} which is in particulated uranium form into dissolved U^{+6} .
- The 2nd pathway has higher Uranium concentrations and Eh, with a significantly lower flow (6 times smaller), which contributes to the increase of the dissolved uranium in WAP_{IV}.
- While phytoremediation, specifically placed in stages WAP_{IV}, WAP_V and WAP_f, and bacteria growth also play a role in the system, it has not been assessed so far the bioremediation influence.

More investigation is undergoing to clarify these hypothesis and improve on the efficiency of the system, by analyzing sediments, plants and rocks in the vicinity of the MWPT and to test pilot the increase of Eh in an earlier stage of the MWPT forcing rapid U mobilization and subsequently its earlier precipitation with more hydraulic retention time to lowering the Eh to a more reduced aquatic environment.

Acknowledgements

The authors acknowledge the technical support of various EDM collaborators. We are very grateful to Prof. Alcides Pereira (University of Coimbra) and Prof. Eduardo Silva (University of Aveiro) for the comments and suggestions that supported this work.

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