Water resources monitoring and mine water control in Portuguese old uranium mines

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Abstract

Environmental rehabilitation of old abandoned mines in Portugal in done since 2001 by EDM - *Empresa de Desenvolvimento Mineiro*, a state-owned company, of 175 abandoned mining areas, 61 of which in radioactive minerals and 114 in polymetallic sulphides. By the year of 2015, 95 mining areas have been intervened of a total of 175 and ten are with ongoing remediation works.

Monitoring the water environment is a relevant activity in the work developed in radioactive mines, started since 2002, which includes measuring *in situ* parameters and laboratory analysis of chemical and radiological parameters as total uranium, radium-226, sulphates, chlorides, manganese, calcium and sodium, these already identified in previous studies to be the best indicators of hydrochemical contamination related to the old uranium mining areas. Water resources monitoring plan covers upstream and downstream surface water samples, groundwater samples through wells, boreholes and piezometers in the surrounding mine area, together with the quality control of mine water before and after treatment. Per year a total of around 1260 water samples are collected in 61 radioactive mines. Denser monitoring plan in terms of sampling points and monitoring frequency is dependent on the level of contamination of each mine.

The main objective of this paper is to present some details and example results of the work performed by EDM regarding the water resources monitoring plan and control of mine water effluents implemented in the radioactive mines. One of the main focus of remediation design projects is the control and treatment of mine water using passive treatment systems. EDM is implementing this type of systems with demonstrated success, in some cases associated with groundwater natural attenuation processes for uranium, radium-226 and other metals.

Key words: Environmental monitoring, water resources, mine water control, passive treatment systems

Introduction

Portugal has an important legacy of old abandoned 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., a state-owned company, under a legal regime of concession assigned by the Portuguese State and approved by the Decree-Law Nº 198-A/2001. EDM is covering the environmental rehabilitation of 175 abandoned mining areas, 61 of which in radioactive minerals and 114 in polymetallic sulphides. In the radioactive mines the most relevant are Urgeiriça, Quinta do Bispo, Cunha Baixa, Bica and Vale de Abrutiga, all located in the Beiras Granitic Region (EDM, 2011), in the central part of Portugal. By the year of 2015, 95 mining areas have been intervened of a total of 175 and ten mining areas are with ongoing remediation works.

During the first years of the environmental concession the main areas of activity were the development of the inventory and detailed characterization studies of abandoned and degraded mining areas, followed by a risk ranking assessment, as well as the development of environmental remediation projects and its implementation tanking in to consideration the risk assessment prioritization.

The main environmental impacts in radioactive mines are acid water drainage, mostly a direct result from exploitation methods with static leaching and/or *in situ* and from ore concentrates production, from the radiations susceptible to produce air, soil and water pollution and the presence of waste dumps tailings ponds liable to produce chemical and radiological contamination by leaching phenomena, dust dispersal and radiation emissions. Common solutions in the remediation process are confinement and sealing of mining wastes and adequate mine water management, ensuring control and treatment either through active or passive systems, or both.

Actually, main strategic missions of EDM are the development of remediation works of the remaining mining sites, the development of safety actions and the development of medium and long term monitoring and maintenance actions before and after remediation in air, water, soils and sediments.

The objectives of the water monitoring plan are to obtain and maintain an integrated data base established for all the 61 radioactive mining areas of continuous records that will allow to compare water conditions before and after environmental remediation and to analyze the performance of the developed actions, also to ensure the accompaniment of active and passive treatment of mine effluents during and after post-remediation phases, and in the future during the transition phase from the active treatment to the new passive systems.

In this paper a few results examples of the water resources monitoring plan and the control of mine water effluents implemented in the radioactive mines are presented in terms of water quality and discharge flow and the water quality evolution in already rehabilitated mines regarding surface water, groundwater, active and passive treatment systems of mine water.

Methods / Monitoring Plan

Monitoring the water environment is a relevant activity in the work developed in radioactive mines, started since 2002, which includes measuring *in situ* parameters (pH, electrical conductivity, redox potential and temperature) and laboratory analysis of chemical and radiological parameters as total Uranium, U234 and U238 radionuclides, Radium-226 activity, sulphates, chlorides, manganese, calcium and sodium, these already identified in previous studies to be the best indicators of hydrochemical contamination related to the old uranium mining areas. Water resources monitoring plan covers upstream and downstream surface water samples, groundwater samples through wells, boreholes and piezometers in the surrounding mine area and in the upper and depth aquifers, together with the quality control of mine water before and after treatment. Piezometric levels and river flow are also measured at the water sampling locations.

Per year a total of around 1260 water samples are collected in 61 radioactive mines. Denser monitoring plan in terms of sampling points and monitoring frequency is dependent on the level of contamination of each mine area. Additionally continuous monitoring of *in situ* parameters (pH, electrical conductivity, redox potential, temperature, total suspended solids and discharge rate) is implemented in treated mine water before watercourse discharge.

In radioactive old mines 34 were already recovered including most of the old mines with more significant negative environmental and public health impacts and the environmental liabilities. At the end of 2015 there were ongoing efforts to conclude the remediation of another six radioactive mining areas and there were 21 remaining areas with remediation works to be carried out until 2022, when the concession contract expires. Table 1 presents the distribution scope of the monitoring plan per each mine.

***Table 1** Monitoring plan scope distribution per radioactive mines, in 2015*

Monitoring plan scope	Radioactive mines	Total
Mine water control and monitoring (ATS)	Urgeiriça, Cunha Baixa, Quinta do Bispo, Bica	4
Passive treatment systems (PTS)	Urgeiriça (*Shaft 4*), Cunha Baixa, Bica, Freixiosa, Vale de Abrutiga	5
Surrounding environmental monitoring pre- and post-remediation	Urgeiriça, Cunha Baixa, Bica, Vale D´Arca, Freixiosa, Carrasca, Vale de Abrutiga, Prado Velho, Senhora das Fontes, Other mines	34
Surrounding environmental monitoring pre-remediation	Quinta do Bispo, Castelejo, Mortórios, Other mines	21

The periodicity of the water samples collection as also the number of sampling locations is dependent on the historical quality data and environmental risk of those mines. The monitoring plan is revised before and after the remediation takes place. Table 2 presents the number of sampling places and samples collected in each mine, ranging from an more intensive plan in Urgeiriça with 264 water samples/per year to a lesser intensive plan in Vale d´Arca with 32 water samples/per year. Also 36 small mines or with less environment impacts and low risk mines are monitored, ranging from one to five sampling points with biannual periodicity.

Table 2 *Monitoring plan regarding water resources and mine water control in radioactive mines*

	Number of sampling places in each radioactive mine												
	A	B	C	D	E	F	G	H	I	J	K	L	M
Mine water control	2	2	2	-	2	1	-	-	-	-	-	-	-
Passive treatment	11	10	11	16	-	-	3	-	-	-	-	6	-
Groundwater	48	2	24	2	22	4	-	14	12	12	13	-	-
Surface water	6	18	3	-	2	7	3	6	4	4	3	2	57
	Number of samples in each radioactive mine per year												
	A	B	C	D	E	F	G	H	I	J	K	L	M
Mine water control	24	24	24	-	24	12	-	-	-	-	-	-	-
Passive system	132	120	132	192	-	-	12	-	-	-	-	24	-
Groundwater	96	4	48	4	44	8	-	28	24	24	26	-	-
Surface water	12	36	6	-	4	14	12	12	8	8	6	8	114
Sub-Total	264	184	210	196	72	34	24	40	32	32	32	32	114
Total	1266 water samples/year												

A-Urgeiriça; B-Cunha Baixa; C-Bica; D-Freixiosa; E-Quinta do Bispo; F-Castelejo; G-Carrasca; H-Vale de Abrutiga; I-Mortórios; J-Senhora das Fontes; K-Prado Velho; L-Vale d´Arca; M-Other 36 mines

Continuous monitoring of mine water

In addition to monitoring and to periodic quantification of the several parameters, based upon laboratory analysis, the need was felt to adopt a system that would allow a closer interaction with the phenomena occurring as a consequence of the ongoing control actions regarding the mine water treatment. For this purpose it was considered important to adopt a continuous monitoring system that would allow to control and possible correction in real time of the actions carried at the mine water ATS.

With the objective of following up in real time the process of neutralizing the liquid effluents generated in some of the radioactive minerals mining areas, EDM conceived and developed a monitoring system that allows determining and recording continuously some of the quantities and expedite parameters that qualify the conditions in which the treatment is processed and the conditions under which the treated mine water is fed into the water courses.

The central system installed in the head office of EDM in Lisbon, was conceived and commissioned in order to receive (from the remote system), process and store all the information relative to all the facilities for monitoring physical and chemical parameters, and equally to lodge and manage command applications and technically manage the facilities and equipment located next to such systems that comprise, in each location, a set of equipment and analytical instruments for the acquisition, grouping and transmission of data. All the collected information is subject to treatment and kept on record.

Water sample collection

Regarding conservation and preparation of water samples for laboratorial analyses, they are acidified with acid nitric (65%, v/v) to 1<pH<2 after collection for total metal analysis, major cations and uranium. For radium-226 they are previously filtered using a 0,45 micron glass fiber filter and then acidified with nitric acid (65%, v/v) to 1<pH<2. In case of this radionuclide only the dissolved form is analyzed. This is related to historical data and with the necessity to maintain comparable water samples results. Radiological analysis are performed by spectrometry by liquid scintillation supported in ultrasensitive spectrometer *PerkinElmer Quantulus*; with variable degree of uncertainty according the activity of radioisotopes, on average 15% of the calculated value. Metals and major cations are usually determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Compliance criteria

Compliance verification of the monitoring plan water quality results is performed accordingly to the water quality standards according to their uses (Portuguese Decree-Law nº 236/98, August 1st), namely Annex XVIII *Effluents discharge limits*; Annex XXI *Environmental objectives for surface water*; Annex XVI *Standard water quality used for irrigation*. Concerning radioactive elements compliance verification uses USEPA 40 CFR *Parts 9, 141, and 142 "National Primary Drinking Water Regulations Radionuclides, Final Rule";* 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 of 30 µg/l and 0,185 Bq/l, respectively. In case of discharge effluents monthly average limits are 2000 µg/l for total Uranium and 0,37 Bq/L for Ra-226.

Mine Water Active treatment system

Active treatment is performed in the following mining areas: Urgeiriça, Cunha Baixa, Quinta do Bispo and Bica. The active treatment system is based on addition of sodium hydroxide to increase pH, barium chloride to precipitate the radium and decantation ponds to precipitate metals. Water control before treatment includes mensal collection of mine water or leached and after treatment sample biweekly collection of composite samples meaning two samples per month. Before discharge in the watercourse *in situ* parameters are continuously registered (pH, electrical conductivity, temperature, redox potential, total dissolved solids and discharge rate). Figure 1 shows the temporal variation of discharge rate and conductivity average values at Bica monitoring station.

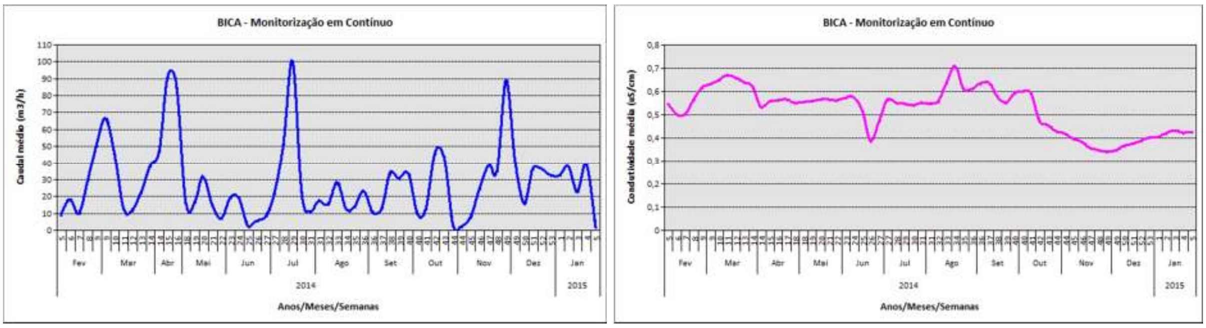

Figure 1 *Temporal variation of discharge rate and conductivity average values – continuous monitoring of treated mine water – Bica mining area*

Removal efficiency rates of active treatments were calculated based on most recent available laboratory results from chemical and radiological analysis and considering main contaminants and metals (Table 3). Removal efficiency varies from 60% to 100% for iron, 96% to 51% for manganese, 49% to 75% for Utotal and 85% to 96% for Ra-226.

Table 3 *Removal efficiency rates of active treatments systems (average values)*

Mining area/ data period	pH initial(final)	Removal efficiency	Iron (mg/L)	Manganese (mg/L)	Utotal (µg/L)	Ra-226 (Bq/L)
Urgeiriça	3,54(7,66)	RE (%)	100%	94%	74%	91%
(2012-2015)		C*i*(C*f*)	37,89 (0,12)	50,56(3,05)	522(137)	0,348(0,030)
Quinta do Bispo	3,69(7,91)	RE (%)	99%	76%	75%	96%
(2012-2015)		C*i*(C*f*)	41,1(0,31)	12,7(3,04)	2316(570)	0,494(0,021)
Bica	5,13(7,69)	RE (%)	98%	96%	49%	85%
(2014-2015)		C*i*(C*f*)	10,3(0,16)	2,49(0,09)	16,9(8,6)	0,274(0,040)
Cunha Baixa	5,00(8,15)	RE (%)	60%	51%	52%	97%
(2014-2015)		C*i*(C*f*)	0,68(0,27)	3,81(2,47)	1111(529)	1,070(0,029)

RE - Removal efficiency (%); C*i* - initial concentration; C*f* - final concentration, after active treatment

Thus, the discharge of treated mine water meets the regulatory standard limits for effluents discharge into watercourses, including the more restrictive limits the use for human consumption in case of Ra-226. Manganese concentrations are still one gram per liter superior to the legal effluent discharge limit value of 2 mg/L, nevertheless this is not considered a relevant exceedance because of the mining framework of the area and background geochemical composition of groundwater's.

An important aspect relating to mine water treatment is that normally it has gradually improved its quality over time, even before the interventions of environmental recovery they have started. This situation explains the lower concentrations of untreated mining water in case of Bica and Frexiosa. Figure 2 show for Bica mining area the temporal variation of pH and total Uranium in mining water, treated mining water and in downstream water course; after environmental remediation in 2013 concentrations of uranium in mine water decrease to <100 µg/l.

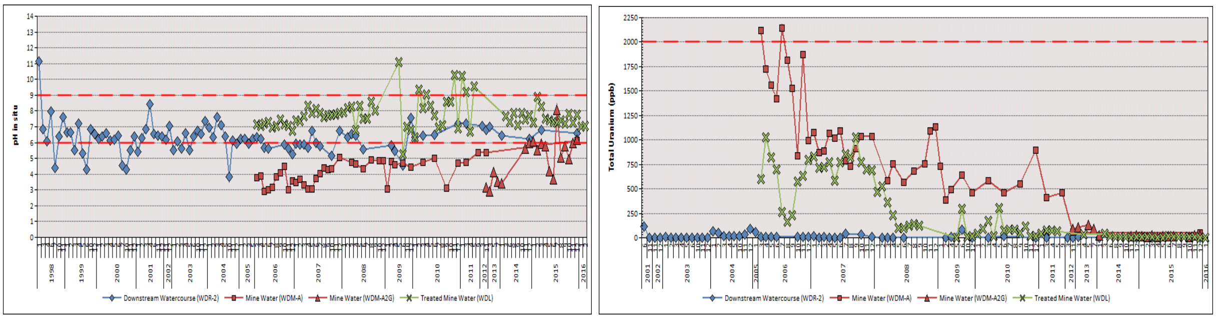

***Figure 2** Temporal variation of pH and total uranium in mine water before and after active treatment and in downstream watercourse – Bica mining area*

Mine water passive treatment systems

PTS are recently implemented in the following mining areas, with already concluded or ongoing environmental remediation actions: Urgeriça, Cunha Baixa, Bica, Freixiosa and Vale de Abrutiga.

In **Urgeiriça** a PTS was installed in 2012 in the old mine *shaft* nº 4 to decontaminate seepage water that outflows and as a result of the controlled mine flood. The monitoring results in the last three years proved that this system is efficient by promoting the decrease and significant removal of radionuclides and heavy metals concentrations to levels below regulatory standard limits (this issue is presented at IMWA2016 by Pinto *et al*. (2016) *Passive Treatment of Radioactive Mine Water in Urgeiriça Uranium Mine, Portugal*). Figure 3 presents the system removal efficiency by comparing initial and final average concentrations along treatment path (medium values in the first semester 2015). The calculated removal efficiency rates are greater than 90% for Fe, Mn, Utotal and Ra-226.

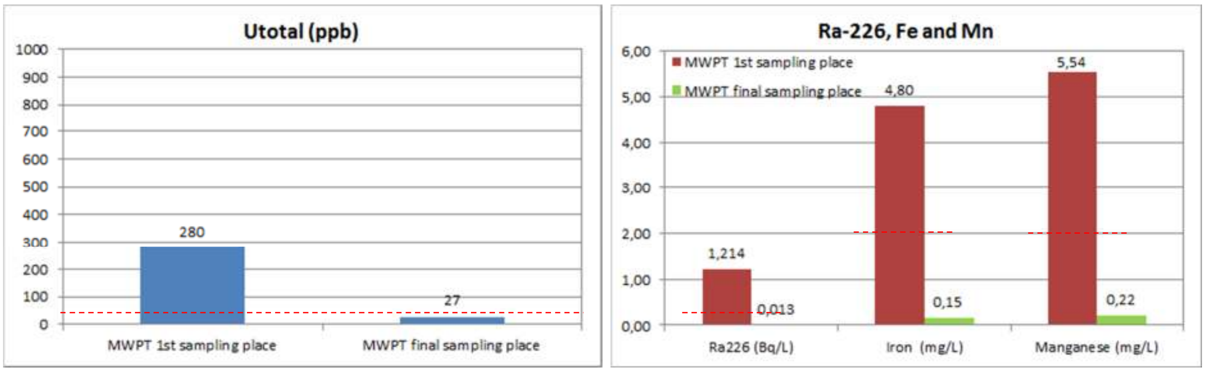

***Figure 3** Mine water PTS efficiency by comparing initial and final concentrations along treatment path (medium values in the first semester 2015) in Urgeiriça mine - Shaft4*

In **Cunha Baixa** the PTS started operating in March 2014 after environmental remediation works were completed. It is located in the old open pit where mine water from galleries outflows. It comprises various large ponds with aerobic treatment by aquatic *macrophytes*, anaerobic treatment with planted *macrophytes* and connecting sectors with limestone and barite. The primary results from monitoring data reveal the necessity of spatial increase the retention times of mine waters. So a complementary

PTS was constructed in 2016 and collection of water samples flowing by treatment tanks and ponds began in April, 2016. No results from this new passive treatment phase are yet available.

In **Bica** mining area the environmental rehabilitation took place from September 2011 to November 2013 and included the construction of a confined cell for heaps of leached material and sterile materials and the construction of ATS and also PTS. Mine waters drain preferably by a gallery located at a lower point. Mine waters and landfill leachate produced in the confined body are treated before discharge into the watercourse. The ATS is based on addition of sodium hydroxide to increase pH and barium chloride to precipitate the radium. After chemical treatment, the water is routed to a settling system comprising two ponds, which promote the sedimentation of radium and some metals. The PTS by physical-chemical and biological processes comprises a first tank that enables water circulation downwardly through a layer consisting of gravel, barite and activated carbon and a second tank with *macrophytes* in order to capture heavy metals that are still present in the water. The system has a number of *bypass* paths that allows conducting the water to different stages of treatment depending on its quality, which is continuously motorized by a monitoring station before watercourse discharge. The mine water quality has been subject to monitoring since 2002, when the underground galleries were flooded. Main elements present in mine water are uranium, radium, iron, manganese, sulfur, oxides and hydroxides of iron. Since this date it was possible to observe an improvement in the mine water quality, which is materialized by an increase of pH and conductivity decrease, which corresponds to a decrease in the acidity of water and a decrease of dissolved ions, in particular Fe and Mn. The PTS begins to work on its full mode since November 2014 and monitoring is done on a monthly basis (Figures 4 and 5). Figure 6 shows results of pH, Mn, Utotal and Ra-226 along treatment path, before watercourse discharge, with lower concentrations comparing to initial mine water concentrations.

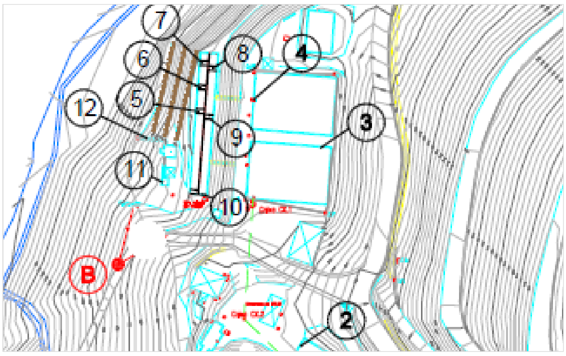

***Figure 4** Sampling points location at Bica PTS*

***Figure 5** Photo from the Bica PTS*

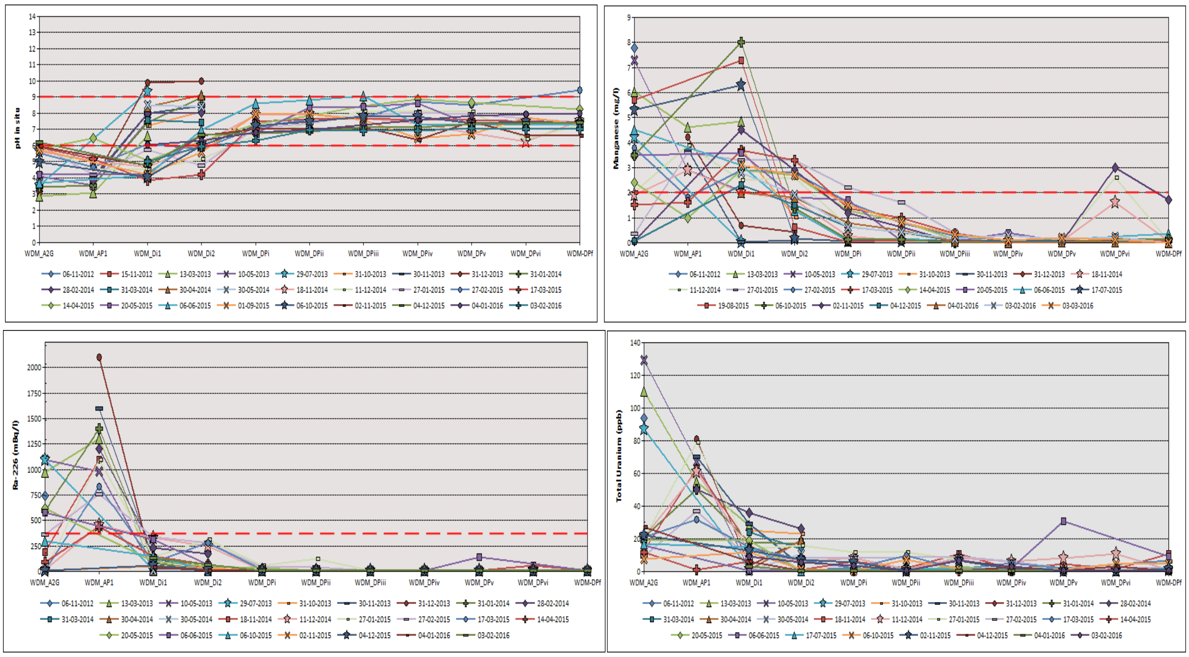

***Figure 6** Spatial and temporal variation in pH, Mn, Utotal and Ra-226 along PTS path - Bica mine*

In **Freixiosa** mining area the PTS was constructed in 2012 to treat seepage water with high concentrations of iron and some Ra-226. This seepage water naturally discharges in a small stream giving color to water due to iron oxides. The PTS is composed by a first stage with a cascade system and tanks that promote the precipitation of chemical species present in the effluent, namely the iron and manganese and a second stage with sequential seven decantation ponds, a barite tank and two *macrophytes* basins. At the end of the treatment pathway and before river discharge concentrations are low and below the regulatory values limits for Utotal, Ra-226, Fe and Mn.

In Vale de Abrutiga mining area it is under construction a new PTS to replace de old one that needed to be reformulated due to the appearance of new seepage water and also because it was clogged after six years.

Removal efficiency rates of PTS were calculated based on most recent available laboratory results from chemical and radiological analysis and considering main contaminants and metals (Table 4). The results have to be analyzed individually per mining site. In case of Urgeiriça removal efficiencies rates are >89% for the analyzed elements and compliance of regulatory limits is assured. In case of Bica and Freixiosa the same conclusion can be pointed out, but with exception for iron, initial concentrations are lower than in Urgeiriça-*Shaft4*. In case of Cunha Baixa contaminants removal did not produced the excepted results and the existing PTS was recently improved and enhanced.

Table 4 *Removal efficiency rates of passive treatments systems (average values from first semester 2015)*

Mining area	pH initial(final)	Removal efficiency	Iron (mg/L)	Manganese (mg/L)	Utotal (µg/L)	Ra-226 (Bq/L)
Urgeiriça (*Shaft4*)	6,37(7,47)	RE (%)	97%	96%	89%	99%
		C*i*(C*f*)	4,80(0,15)	5,54(0,22)	250(27)	1,214(0,013)
Bica	4,67(7,76)	RE (%)	98%	97%	89%	99%
		C*i*(C*f*)	10,48(0,22)	4,08(0,12)	45,5(4,86)	0,853(0,010)
Freixiosa	6,20(7,09)	RE (%)	90%	37%	89%	99%
		C*i*(C*f*)	6,46(0,67)	0,78(0,49)	8,97(1,00)	0,690(0,010)

RE - Removal efficiency (%); C*i* - initial concentration; C*f* - final concentration, after PTS

Groundwater and surface water monitoring

In terms of groundwater monitoring it is essential to previously determine the groundwater flow directions and to locate sampling points downstream and upstream from the mining area. Also groundwater monitoring must be performed before remediation actions are implemented, during the remediation and after works in the same locations. Special care must be taken to avoid piezometers destruction during the remediation works. An historical data base must be set up in terms of groundwater quality in a few piezometers that are correctly located and well-constructed and isolated regarding the aquifers that are monitored without interferences between them.

Figure 7 show for Cunha Baixa the spatial and temporal variation of total uranium concentrations in boreholes located downstream of the mining area. Is is important the note despite the variations the decrease in concentrations after the recovery actions. Also piezometric levels are measured in the groundwater monitoring points. Figure 8 shows historical series of depth to the water level measured in wells in the vicinity of Urgeiriça mine when the mine was flooded in 2003.

Meteorological Data

Meteorological data are gathered from two automatic stations located in Urgeriça and Cunha Baixa mining areas. Measured data are total precipitation, temperature, wind direction and velocity, solar radiation, evaporation and evapotranspiration calculation. All data is acquired in real time by telemetry. This type of data is used to calculate water balance in the study areas, especially for long term control and management of the PTS and to evaluate the discharge rates from seepage waters. Figure 9 shows an example of the data form Urgeiriça automatic meteorological station.

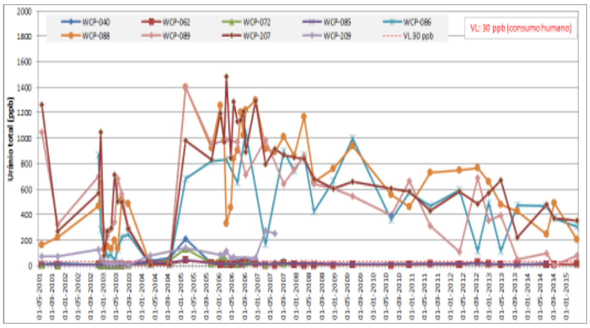

Figure 7 *Groundwater monitoring of total uranium - Cunha Baixa*

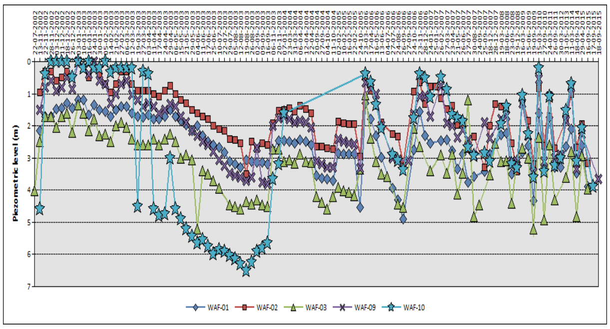

Figure 8 *Piezometric level – Urgeiriça*

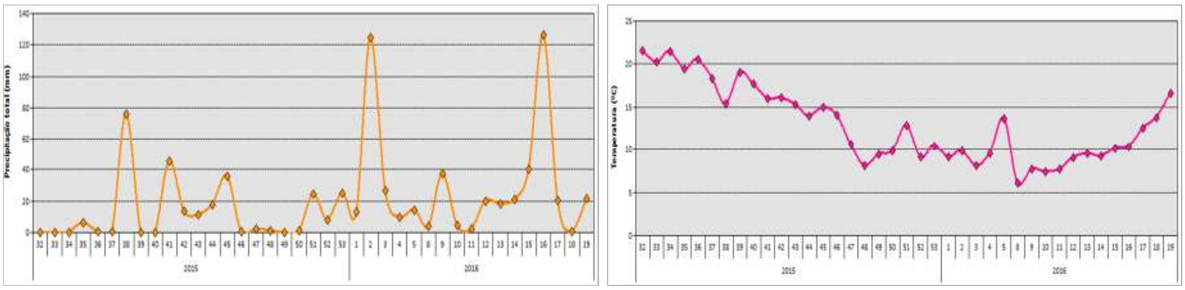

Figure 9 *Meteorological data from Urgeiriça mining area (precipitation and temperature)*

Conclusions

This paper briefly presents some details and results of the water resources monitoring plan and mine water control implemented by EDM in the 61 old radioactive mines located in Portugal, of which 34 are already recovered. Per year a total of around 1260 water samples are collected for chemical and radiological laboratory analyses and *in situ* parameters register. This activity is essential to compare the water conditions before and after the environmental remediation actions and to analyze its performance improvements in terms of downstream groundwater and surface water bodies. One of the main focus of remediation design projects is the control and treatment of mine water using passive treatment systems. Long term maintenance of these areas considerers a gradual transition from active treatment plants to passive treatment systems of mine water and leachates having as a perspective of more sustainable management post-remediation mining areas and also the decrease in contaminates concentrations. Preliminary results of removal efficiency rates of these systems are presented, although they have been recently implemented. EDM is implementing this type of systems with demonstrated success, in some cases associated with groundwater natural attenuation processes for uranium, radium-226 and other metals.

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