The Carnoules mine. Generation of As-rich acid mine drainage, natural attenuation processes and solutions for passive in-situ remediation

F.ELBAZ-POULICHET, UMR Hydrosciences, CNRS-University Montpellier I&II, IRD, Montpellier, France, felbaz@univ-montp2.fr
O.BRUNEEL UMR Hydrosciences, CNRS-University Montpellier I&II, IRD, Montpellier, France, obruneel@msem.univ-montp2.fr
C.CASIOT, UMR Hydrosciences, CNRS-University Montpellier I&II, IRD, Montpellier, France, casiot@msem.univ-montp2.fr

ABSTRACT: The former Carnoules Pb-Zn mine (Department of Gard, France) has produced 1.5 Mt of solid waste containing pyrite and associated metals and metalloids including arsenic and thallium. The tailings are stored behind a dam. Upon oxidation they generate acid ($pH \leq 3$) water containing up to 350mg/l of arsenic, 750 to 2700mg/L of iron, sulphate (2000-7500mg/L) and a few mg/L of heavy metals (Pb, Zn, Cd). The water surges at the bottom of the dam forming the Reigous Creek.

For the last ten years, the physicochemical, biological, mineralogical and hydrological characteristics of the site have been monitored by the Hydrosciences laboratory with the aim of understanding the processes responsible for the release of pollutants in the tailing stock and of reducing pollution in the mining creek. The results of this study indicate that, unlike at other sites, pyrite oxidation takes place at the bottom of the tailing stock at the entry of oxygenated underground water. The bacterial populations that are present in the tailings and may catalyse the oxidation reactions were identified. About 20 to 30% of the arsenic initially present in the spring water in the form of As(III), precipitates with Fe in less than 30 meters. This leads to the formation of ochre precipitates containing 20% of arsenic around bacterial structures. Several organisms (bacteria and euglena) that mediate Fe and As oxidation in the creek and thus contribute to accelerating arsenic retention in the solid phase were identified. On the basis of these results and pilot plant experiments, solutions for passive in-situ bioremediation are proposed.

1 INTRODUCTION

The history of mining activity has resulted in a significant waste legacy, which represents a threat for the environment. Major accidents, most often resulting from the breaching of an effluent retaining dike, can cause major pollution accidents like in England where the outburst of the Wheel Jane tin mine in 1992 resulted in severe contamination of the Carnon River and the Fal Estuary by toxic metals (Younger et al, 2005). More recently, the breaking of a dam retaining wastes from the Aznallcollar mine in Spain resulted in the contamination of the Guadiamar River (Achterberg et al., 1999), an affluent of the Guadalquivir, which drains the Donana national park (UNESCO world reserve).

These well-publicised disasters should not mask the silent reality of chronic and long lasting environmental pollution generated by mine drainage. In many cases mining waste can continue to adversely affect the environment for centuries after the abandonment of the mine itself, contaminating the soils in the immediate vicinity but also being dispersed by both surface and ground waters. Although precise quantification of the scale of this pollution is difficult, Johnson and Hallberg (2005) estimated that, in 1989, approximately 19,300 km of rivers and 72,000 ha of lakes and reservoirs throughout the world were severely affected by mining effluents.

Mine drainage results from the oxidation of pyrite and other sulphide minerals generally associated with coal and metal-bearing mineral deposits. They are most often acidic and contain high concentrations of metals and metalloids (including arsenic)

The Carnoules mining site (town of Saint Sebastien d'Aigrefeuille, France) provides an example of the unwanted legacy of mining activity. After a review of the history of the site including critical episodes, we summarize the studies that have been carried out for decades to better understand the link between chemical, biological and hydrodynamic processes which control the generation of acid mine drainage (AMD). We then examine a potentially low cost method of passive in-situ bioremediation of water.

2 THE HISTORY OF THE CARNOULES MINE (SAINT SEBASTIEN D'AIGREFEUILLE, FRANCE)

2.1 The exploitation

The extraction of Zn-Pb at Carnoules (Fig.1) officially started in 1730. At the beginning of the 20th century, the volume of the mining waste was estimated at 38 000m^3. Between 1951 and 1963 Pennaroya and then Metaleurop mining companies extensively exploited the ore. In 1961, during exploitation, the breaking of a dam retaining the water was responsible for major pollution of the Reigous Creek and the Amous River. Subsequently, the mining company cleaned the site and reinforced the dam.

After receiving official authorisation (departmental decree), the mine officially closed on October 24, 1963. It has generated a total of 1 500 000 tons of wastes, split into two tailings of respectively 460 000m^3 and 115 000 m^3, the first being located at the source of the Reigous Creek.

2.2 From mine closure (1963) to now

In 1963, the residents of the Amous River basin formed an association. Their fight was legitimated by the publication of a report by Faucherre (1964) attesting that the river water was toxic for both animals and humans. The Penarroya mining company rejected any responsibility by arguing that water pollution had already been present before 1951. In 1968, the company sold the site to a Belgian notary.

In 1970, a quantitative model of the acidification process, and the mechanism of dissolution and deposition of the chemical elements was proposed by Michard and Faucherre (1970). To our knowledge, this was the first scientific publication on the consequences of the oxidation of the sulphide wastes from the Carnoules mine.

In September 1976, the tailings partially collapsed due to a violent Mediterranean thunderstorm. This was followed in October 1976 by the sudden evacuation of the 100 000 m^3 of water initially contained in a lake that had formed in the tailing stock. The accident was responsible for the pollution of water and soil in the entire Amous valley.

The accident also highlighted a juridical imbroglio where both the administrative authorities and Pennaroya and later Metaleurope tried to pass on to each other responsibility for the former mining installations and for the cost of the security works that needed to be undertaken to prevent further dissemination of the pollution. In 1980, in the absence of any consolidation of the tailings, another thunderstorm resulted in further pollution of the downstream river network.

In 1982-1983, the wastes were gathered in a single tailing stock with a capacity of about 550 000 m^3, behind a concrete dam (Fig.1). The tailings were covered with an impermeable layer of clay, then arable soil and vegetation. However, this did not prevent acidic and As-rich water (pH=2-3) from emerging at the base of the dam and continuing to pollute the Reigous Creek and the Amous River. In addition, due to corrosion of the concrete by the wastes, the pipes channelling the water under the tailing stock exploded. This resulted in the formation of slashes, exposing the pyrite to air and water. In September 2002, after another violent Mediterranean storm (600 mm of rain in less than 24 h), Departmental authorities ordered Metaleurope to consolidate the tailing stock. The administrative tribunal successively cancelled previous two decrees. In the end, security works were undertaken in 2005. They were financed by local and national communities, water authorities and emergency funds provided by the European Commission after the September 2002 flood. However, these works were merely physical and did not prevent Acid Mine Drainage (AMD) which still continues today.

3 MECANISMS OF AMD GENERATION AND TRANSFER PROCESSES

3.1 Site description

Today the tailings (1.5 MT of spoil material, 6-20m thick and covering 54,375m^2) are stored behind a 35-meter-high dam. They are covered by a 30-cm-thick clay cover that has allowed the spontaneous establishment of a plant association comprising *Pinus maritimus*, heathers, and mosses. The tailings are composed of very fine grained material (<30µm on average). Quartz is the main mineral component. The tailings also contain 5-10% of arsenic-rich pyrite (2-4% As) and small amounts of galena and barite.

This material is deposited in the middle of and across the upstream part of The Reigous Creek at the site of its natural spring (Fig.1). The surrounding runoff waters are collected by concrete ditches running along the borders of the tailing surface. These waters flow into a small shaft and then down the gradient to the Reigous Creek through a concrete pipe that crosses the tailings. Rainwater is collected along the surface of the tailings by the same system; then ditches drain the water laterally.

The site has been monitored by the HydroSciences Laboratory for more than 10 years. The equipment comprises 17 piezometers in the tailings, automatic systems for continuous water discharge acquisition and a microcosm for aerobic water treatment. This intensive instrumentation has enabled documentation of the main hydro-bio-geo-chemical characteristics of the site.

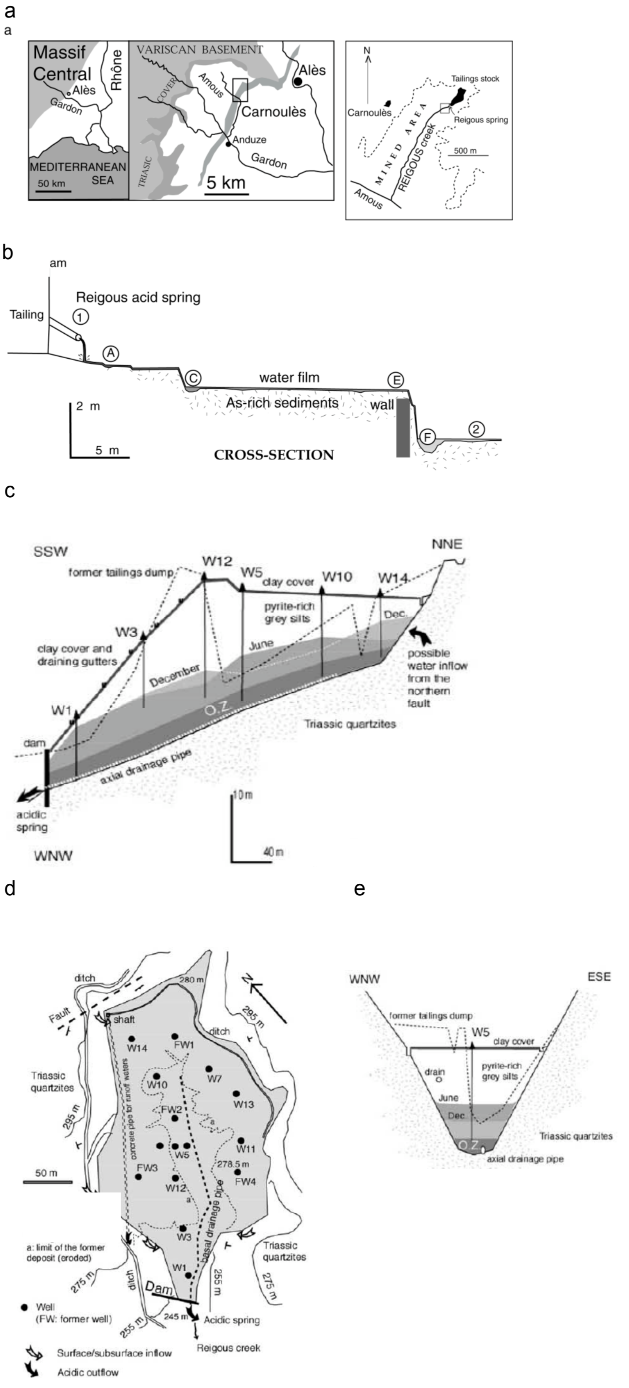
3.2 The tailings stock: a reverse oxidation zone

The general hydrochemistry and aquifer hydrodynamics have been broadly characterised by Koffi et al., (2003), and Casiot et al., (2003a). The clay cover and the low permeability of the waste material (10^{-7}m/s) considerably limit infiltration of rainwater into the tailings. During extreme rainy events, sinkholes formed in the tailing but even after refilling, AMD generation continues in absence of an oxidation zone at the surface. Variations in the water table, calculations of the water balance and flow modelling indicate subsurface water inputs and water flow along the bedrock within a more permeable sandy horizon. The primary region of oxidation is thus located at the base of the tailings, where the oxygen rich rainwater can penetrate directly.

The AMD is mainly generated in the northern part of the tailings. These acidic waters (2<pH<5) are characterized by elevated concentrations of Fe (1.60–3.35g/L), As (130–4.34g/L) and sulphates (5.80–14.3 g/L). During recharge periods when the oxygen concentrations in the aquifer are close to saturation values, extreme As (up to 12g/L) and Fe (up to 20g/l) concentrations have been observed in the borehole W5 (Fig.1). This As and Fe build-up is explained not only by pyrite oxidation but also by dissolution in acidic conditions of the secondary As-rich oxides-minerals, which precipitate during dry periods characterized by oxygen-deficient conditions. The As and Fe concentrations in the spring of the Reigous Creek are consequently always lower due to mixing with less-contaminated water originating from other zones of the tailings.

The pyrite oxidation reaction is generally mediated by acidophilic iron-oxidizing microorganisms (Silverman and Ehrlich 1964) which play a major role in maintaining availability of Fe(III), which is an efficient oxidant of pyrite at low pH, where the abiotic oxidation rates by dissolved oxygen are slow (Edwards et al. 1999). Bruneel et al. (2005) inventoried the bacteria present in the Carnoules tailings. Cultivable bacterial strains of *Thiomonas* and *Acidithiobacillus ferrooxidans* were shown to be present. Molecular methods, Terminal-Restriction Fragment Length Polymorphism (T-RFLP), and a search of the 16S rRNA gene library indicated low diversity. The structure of the community varies in relation to the water chemistry. At low concentrations (1mg/L) of dissolved oxygen and in moderately acidic conditions (pH=5.7), the dominant organisms are related to the uncultured clone BA31 affiliated with *Desulfosarcina variabilis,* a sulphate-reducing bacteria (SRB), *Acidithiobacillus ferrooxidans* and the uncultured clone BVB20, closely related to *Thiobacillus*. At high concentrations (12 mg/L) of dissolved oxygen and with low pH values (pH<2), microbial diversity is lower and 65% of the population is related to the uncultured bacterium clone AS6 affiliated with *Desulfosarcina variabilis*.

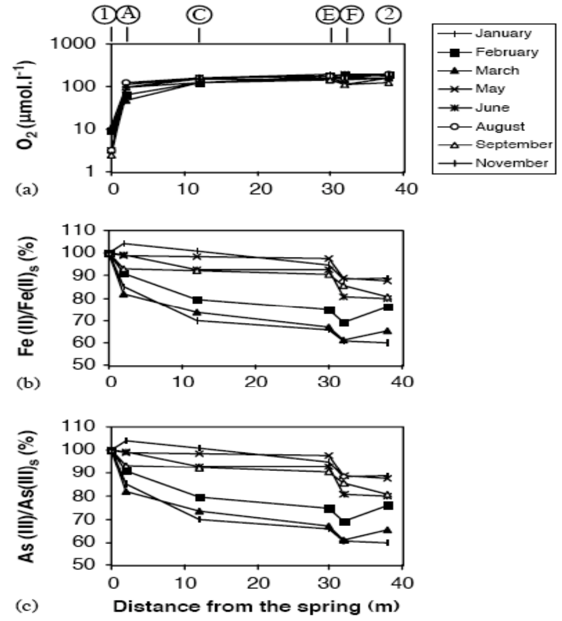
Fig. 1: Maps showing the location of the Carnoules site (a), a sketch map of the first 30 meters of the Reigous Creek (COW) showing the locations of the sampling stations.(b), cross-sections (c,e) and map (d) of the Carnoules tailing deposit. (OZ:oxidising zone) Variations in water level are given for December and June 2002.



3.3 The natural attenuation of As concentrations in the first 30 meters of the Reigous Creek

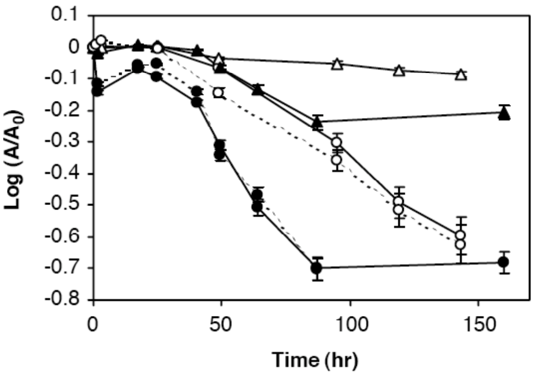
The source of Reigous Creek is acid (2<pH<3) and rich in dissolved iron, arsenic and sulphate ([Fe] = 0.5-1 g/L; [As] = 50-350 mg/L; $[SO_4^{2-}]$=2.0-7.7g/L) predominantly in the reduced forms: As(III) and Fe(II). Water discharge ranges between 0.8 and 1.7 L/s. The rapid oxygenation of water facilitates oxidation of Fe(II) and precipitation of Fe-As yellow to ochre precipitates. During the first 30 m of downflow, the process removes 2 to 60% of the As initially present in the water (Fig. 2, Casiot et al., 2003b).

Fig. 2. Variations in O_2 (a), Fe(II) (b) and dissolved As(III) (c) along the Reigous creek. Fe and As concentrations are expressed as a percentage of their concentration in the spring water (suffix s). Total dissolved As varies as As(III). 1, A, C, E, F, 2: Sample locations (cf. Fig. 1b).



The mineralogy of the precipitates is reported in Morin et al (2003). In winter, the precipitation of Fe(III)-As(III) predominates, in the form of nano-crystals of tooeleite, a very rare mineral. In summer, the precipitate is amorphous and contains mainly Fe(III) and As(V). The reasons for this seasonal difference are not completely understood, but cannot be linked to water temperature, which remains about the same (14-16°C) in the vicinity of the source. Laboratory experiments showed that the oxidation processes that take place in Reigous Creek are mediated by bacteria (Casiot et al, 2003b, Fig.3). In this context, seasonal variations in community structures may well play a role in determining the nature of the precipitate as also suggested by laboratory experiments (Morin et al., 2003; Casiot et al., 2003b, Bruneel et al., 2003, Duquesne et al., 2003).

Figure 3: Kinetics of Fe (triangles) and As removal (circles); free bacteria cells (open symbols). a bacterial precipitate is present (fixed bacteria) (closed symbols); UV light (solid line); experiments in the dark (dotted line). A is the concentration of Fe(II) or total dissolved As in the aqueous phase and A0 is the concentration in the Carnoules spring water before incubation



3.4. Spatial and temporal variations in pH, and in concentrations of metals and metalloids along the Reigous Creek

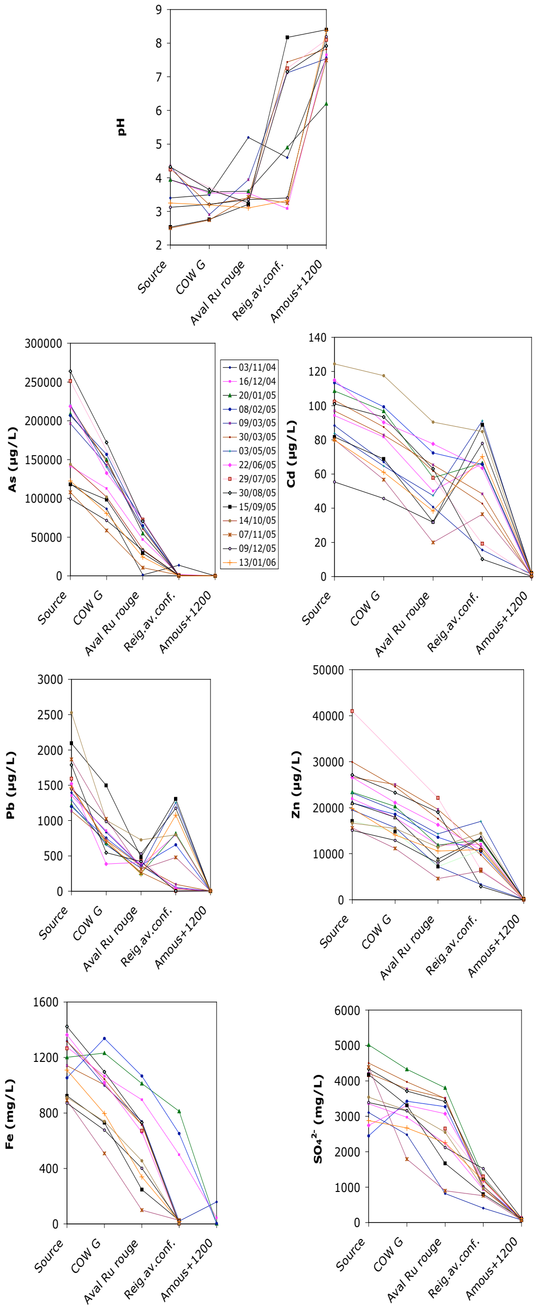
Concentrations of dissolved metals and metalloids concentrations of sulphate and pH were monitored for more than one year along the river continuum between the source of the Reigous and the station 1200 m in the Amous River. The results are presented in Fig.4.

The water of the lower Reigous Creek was nearly neutral during the low water flow period, whereas during the high water flow period, which generally occurs in autumn, it was acidic (3.1<pH<3.4). With the exception of Cd, Pb and, to a lesser extent, concentrations of dissolved Zn generally decreased between the source of the Reigous and the confluence with the Amous River. This decrease is related to (i) dilution with non-polluted seepage and (ii) coprecipitation of metals and As with Fe oxides that precipitate all along the Reigous Creek and at the Amous-Reigous confluence (Casiot et al., 2005).

About 30 m away from its source, the Reigous Creek receives contributions from small tributaries. Those coming from the left bank do not drain either the mineralised area or the former mining installations. However, the water coming from the right bank drains abandoned mine galleries and quarries where pyrite is still present. The increase in Cd, Pb, and Zn, which occurs at station Reigous av.conf., thus probably reflects the inputs from the former mine quarries.

At the confluence with the Amous River (Fig.1), the Reigous discharge ranges between 0.6 and 20L/s. The Amous discharge ranges between 50 and 150L/s. Upstream from the confluence, the Amous River is not affected by AMD and the concentrations of dissolved metals, arsenic and sulphate, which are generally several orders of magnitude lower than in the Reigous Creek, do not provide evidence of contamination but simply reflect the natural regional background. Downstream from the confluence, the dissolved concentrations in the Amous River increase drastically and the dissolved concentrations of Cd sometimes exceed the French regulatory limit for the conservation of satisfactory biodiversity ([Cd]=1.3 µg/L). Casiot et al. (2005) showed that the increase in pH that occurs where the two rivers meet leads to the precipitation of large amounts of Fe in the form of ferrihydrite which scavenges As(III). However this natural attenuation process is not efficient at high water temperatures. In addition, reductive processes may also seasonally contribute to the reduction of Fe-oxides and to the release of As into solution.

Fig.4: pH, dissolved metal, As and sulphate concentrations in the Reigous creek and in the Amous River. The stations on the X-axis are ranked according to their distance from the Reigous Spring: COWG: 40m, Aval Ru rouge: 300m, Reigous av. conf.: 1120m; Amous 1200: 2300m.



Hence, the Amous River can be still considered as seriously affected by mine drainage up to where it meets the Gardon river at Anduze.

Table 1 shows the annual metal fluxes of the Reigous Creek calculated on the basis of monthly sampling.

These fluxes are generally low compared to those transported by the Rhone River to the Mediterranean Sea (Guieu et al., 1993). Nevertheless, Ollivier (2005) showed that the contribution to the total Rhone fluxes increases drastically during flood events that affect the Gardon. To cite one example, the flood event of September 2002 represented respectively 26% and more than 30% of the particulate load of Sb and Pb transported by the Rhône River at the city of Arles.

Table 1: Metal fluxes in the Reigous Creek.

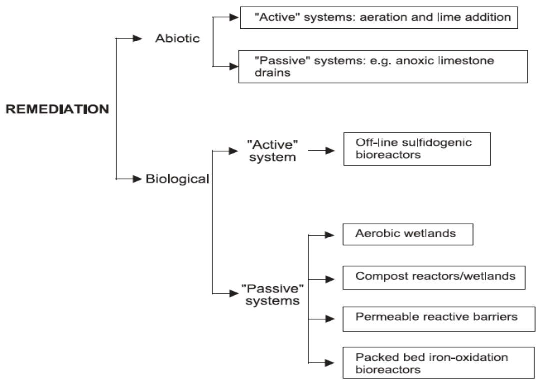
	Reigous flux (kg/an)
SO_4^{2-}	80761
Fe	2807
Zn	785
Mn	630
Al	440
As	207
Pb	42
Ni	20
Cu	9.8

4 EXPLORING WAYS FOR CHEMICAL REMEDIATION. RESULTS OF PRELIMINARY STUDIES

Johnson and Hallberg (2005) recently presented a review of AMD remediation strategies in which they distinguished abiotic or biotic treatments and subsequent active or passive treatments (Fig.5).

Active treatments require continuous intervention, for example the supply of chemical products. Passive treatments exploit processes that occur in natural systems. Their maintenance costs are generally lower than for active treatments. Biological processes and bioremediation are generally based on the capacity of microorganisms to catalyse chemical reactions, which immobilise metals and/or neutralise the water acidity.

Figure 5: Different AMD remediation strategies (Johnson and Hallberg, 2005).



The aerobic systems that precipitate Fe(III) and associated metals (ochres) generate acidity and so are generally reserved for treatment of alkaline waters. They are also particularly effective (even in acid waters) for eliminating arsenic, which is very present in the AMD. The most popular passive systems are based on reductive processes. These systems generate alkalinity and are therefore effective for treating acid waters. They also eliminate sulphates, which are transformed into hydrogen sulphide while the insoluble metal sulphides (FeS, PbS) precipitate. Such systems are very frequently used to treat subsurface waters in the form of reactive barriers including a layer of limestone or packed bed bioreactors where bacteria are immobilised onto a solid matrix. Natural or constructed wetlands or peat bogs are also commonly used to treat leaching mine water.

A combination of these two systems was tested in the Carnoules site between 1999 and 2002 in the framework of the European project PIRAMID (Passive in Situ Remediation of Mine Drainage). The aerobic remediation pond was installed under a greenhouse cover (180 m^2) made of metal arches covered with a polyethylene film. Because it required flat ground, the experimental station was set up about 120 m downstream from the acidic spring. Water was supplied from the spring with a black PVC pipe (1 inch in diameter) that flowed into a PVC tank (250 l) from which 1 to 3 different ponds could be supplied. The ponds were all identical in size (4x2 m), but differed in structure, some being flat with ridges and other having cascades. The water inflow was low (1 to 3 L/min). Due to water acidity (pH 3), all taps and pipes were made of PVC. Concrete structures that could be dissolved by acidic waters were not used.

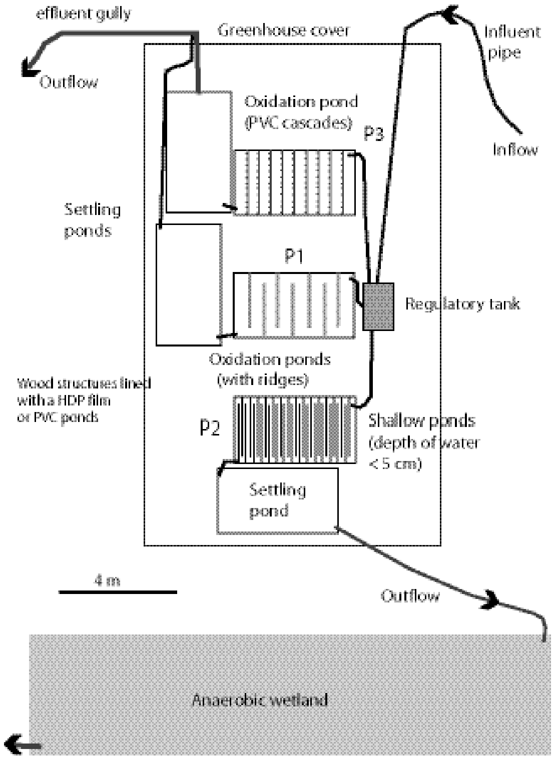
The construction of the anaerobic wetland (50 m^2) began in May 2001. First a HD polyethylene film was placed at the bottom and then covered with a 50–cm-thick layer of peat, but this was unsuccessful because of the low permeability of the peat (10^{-7} m/s) so that the water flowed over the surface of the peat instead of through it. The peat filling was thus replaced by compost (45 % Organic Matter, 1.5 % N) through which the water circulated slowly (1.5 Lmin). Spontaneous growth of Phragmites occurred in the western part of the wetland. Unfortunately the pond was destroyed by the September 2002 Mediterranean flood.

The results obtained for the removal of As in aerobic ponds are given in Table 2. The values for P2 and P3 are only indicative as there were marked variations and monitoring only continued for a few months. Nevertheless the cascade system (P3) is clearly more efficient than the system with ridges (P1, P2), and, on one occasion, it reached 50% of treatment efficiency. Two types of functional problems were observed: technical and bacterial.

Settling ponds can be added at the outflows to recover the precipitated colloidal matter.

The results obtained for the removal of As in aerobic ponds are given in Table 2. The values for P2 and P3 are only indicative as there were marked variations and monitoring only continued for a few months. Nevertheless the cascade system (P3) is clearly more efficient than the system with ridges (P1, P2), and, on one

Figure 6: Sketch map of the passive in-situ remediation (PIR) system for the removal of As-rich ochre in Carnoulel AMD.



occasion, it reached 50% of treatment efficiency. Two types of functional problems were observed: technical and bacterial.

Table 2: As removal from solution in the Reigous Creek (COW) and in the experimental ponds (P1, P2, P3).

Pond (P1) was a wooden structure using stakes and boards made of chestnut. The inside surface was covered with a HD polyethylene film. The path the water took was controlled by wooden ridges spaced 50 cm apart. Water depth was less than 8 cm. Pond 2 (P2) was of similar design but was made of PVC and included narrow PVC ridges (spaced 10 cm apart). Pond 3 (P3) was based on a cascade system including 10 small PVC basins (200x50x3 cm) overlapping along a stair-like structure. The overall slope was less than 10 %.

name	Size (m)	Surface (m^2)	water depth (cm)	water flow (L/min)	Residence time (hr)	As removal (%)	As removal g/day/m^2
COW	35x2	70	2 - 50	40	1	30	40
P1	4x2	8	3-8	1 - 3	2	11	8
P2	4x2	8	2-5	1 - 3	3	15	10
P3	4x2	8	2-5	1-3	0.5	20	5

Overall, the removal of arsenic was more efficient in the Reigous Creek than in PIR where several problems were encountered. The influent pipes quickly filled with bacterial accretions and sandy material from the tailings. A rise in water resulting from blocking of the outflow pipes sometimes occurred (P1, P2), allowing anoxic conditions and an unexpected release of soluble As from the bottom sediments. Finally, the system sometimes became anaerobic with the development of thick bacterial films on the surface of the water that prevented oxygen diffusion.

5 CONCLUSION

The 10-year study at the Carnoules site considerably improved our understanding of the biogeochemical processes that control the formation of AMD and the natural attenuation of arsenic in the system. This knowledge is a prerequisite for any remediation project.

Field observations showed that percolation of water from the surface of the tailing stock does not play a role in the generation of AMD which arises from the contact between oxygen-rich groundwater and pyrite. A model taking into account these diffuse inputs was developed enabling simulation of water fluxes at the outlet of the tailing stock which is the actual spring of the Reigous Creek.

The spring water contained up to 300mg/L of As in the form of As(III), 30% of which was lost in less than 30 meters through coprecipitation with Fe. The resulting ochres contained 20% of As in the form of nanocristals of tooeleite (As(III)-Fe(III)) or amorphous ferric-arsenate (Fe(III-)-As(V)).

These intense removal processes do not concern metals (Pb, Zn, Cd, Tl) that are present in the Reigous Spring. Moreover, in the lower part of the Reigous Creek, our studies clearly highlighted other sources of Pb, Cd and, to a lesser extent, Zn, these probably being the mine quarries and the mine galleries. 'All these factors will have to be taken into consideration in any future remediation plan. The confluence with the Amous river results in a further dilution and removal of metals and As from solution through coprecipitation with Fe-oxides. However, pollution persists since As is eventually released into solution when changes occur in the physicochemical conditions of the water. And the fine ochre precipitates that sediment in the Amous River represent a threat to aquatic life.

These natural attenuation processes may encourage those planning to develop passive in situ-remediation systems. The first step would be to set up an aerobic pond to remove As and Fe. This type of treatment immobilizes small amounts of sulphate and is thus intended to minimize the quantity of toxic mud that will have to be disposed of in a class 1 landfill. Anaerobic wetlands can be arranged in series. These are expected to remove insoluble metals and possibly As sulfides. The main problem at Carnoules is lack of space in a very narrow valley where Mediterranean storms are particularly devastating.

Further work is necessary to optimize the functioning of the treatment process to remove 2 to 7 T/yr of As over a period of about 500 years. Another challenge would be to block the generation of AMD inside the tailings themselves.

REFERENCES

ACHTERBERG, E., BRAUNGARDT, C., MORLEY, N.H., ELBAZ-POULICHET, F., LEBLANC, M., 1999. Impact of Los Frailes mine spill on riverine, estuarine and coastal waters in southern Spain. Water Research, 33, 3387-3394.

BRUNEEL, O., PERSONNE, J.C., CASIOT, C. , LEBLANC, M. , ELBAZ-POULICHET, F., LE FLECHE, A. and GRIMONT, P.A.D, 2003. Mediation of arsenic oxidation by *Thiomonas* sp. in acid mine drainage (Carnoulès, France). Journal of Applied Microbiology, 95, 492-499.

BRUNEEL, O., KOFFI , K., CASIOT , C., DURAN, R., FOURCANS, A., ELBAZ-POULICHET, F., LEBLANC, M., PERSONNE, J.C., 2005. Microbial diversity in pyrite-rich tailings impoundment (Carnoulès, France) Geomicrobiology Journal, 22,1-9.

BRUNEEL O., DURAN R., CASIOT C., ELBAZ-POULICHET F., PERSONNE J.C., 2006. Diversity of microorganisms involved in Fe-As-rich acid mine drainage waters of Carnoulès (France). Applied and Environmental Microbiology, 72, 551-556.`

CASIOT, C., LEBLANC, M., BRUNEEL, O., PERSONNÉ, J.C., KOFFI, K., ELBAZ-POULICHET, F., 2003a. Formation of As-rich waters within a tailings impoundment (Carnoulès, France) :. Aquatic Geochemistry,. 9, 273-290.

CASIOT' C., MORIN, G., BRUNEEL' O., PERSONNÉ, J.C., LEBLANC, M., DUSQUESNE, C., BONNEFOY, V. and ELBAZ-POULICHET' F., 2003b. Bacterial immobilization and oxidation of arsenic in acid mine drainage (Carnoulès creek, France). Arsenic behaviour in the aqueous phase. Water Research, 37, 2929-2936.

CASIOT C, LEBRUN S, MORIN G, BRUNEEL O, PERSONNÉ JC, ELBAZ-POULICHET F, 2005. Sorption and redox processes controlling arsenic fate and transport in a stream impacted by acid mine drainage. Science of the Total Environment, 347, 122-130.

DUQUESNE, K. , CASIOT, C., MORIN, G , PERSONNE, C., ELBAZ-POULICHET, F. , LEBLANC, M., BRUNEEL, O., BONNEFOY, V., 2003. Immobilization of arsenite and ferric iron by Acidithiobacillus ferroxidans in acid mine drainage, Applied and Environmental Microbiology, 69, 10, 6165-6173.

EDWARDS KJ, GOEBEL BM, RODGERS TM, SCHRENK MO, GIHRING TM, CARDONA, MM, HU B, MCGUIRE MM, HAMERS RJ, PACE NR, BANFIELD JF. 1999. Geomicrobiology of pyrite (FeS2) dissolution: case study at Iron Mountain, California. Geomicrobiol. J. 16:155–179.

FAUCHERRE, J., 1964. Rapport sur l'analyse des eaux de l'Amous. Université de Paris, Faculté des Sciences de Reims. 6pp.

GUIEU, C., ZHANG, J., THOMAS, A.J., MARTIN, J.M., BRUN-COTTAN, J.C., 1993. Significance of atmospheric fallout on the upper layer water chemistry of the North-Western Mediterranean. J. of Atm. Chem., 17, 45-60.

JOHNSON, D. , HALLBERG, K., 2005. Acid mine drainage remediation options : a review, Sci. Tot. Env., 338-314.

KOFFI, K. ; LEBLANC, M. ; JOURDE, H. ; CASIOT, C. ; PISTRE, S. ; GOUZE, P. and ELBAZ-POULICHET, F., 2003. Reverse oxidation zoning at a mine tailings stock generating arsenic-rich acid waters (Carnoulès, France), Journal of the International Mine Water Journal of the International Mine Water Association, 22, 1, 7-14.

MORIN, G., JUILLOT, F., CASIOT, C., BRUNEEL, O., PERSONNÉ, J.C., ELBAZ-POULICHET, F., LEBLANC, M., ILDEFONSE, P, and CALAS, G., 2003, Bacterial immobilization and oxidation of arsenic in acid mine drainage (Carnoulès creek, France). XANES and XRD evidence of As(V)- or As(III)-Fe(III) gels and tooeleite. Env. Sci. Technol. 37, 1705-1712.

OLLIVIER, P., 2005. Interface continnt-océan. Géochimie du Rhône (flux et bilan d'érosion) et transfert d'eaux souterraines en Camargue (Apport des isotopes du radium). Ph-D thesis University Aix-Marseille III. 244pp.

SILVERMAN MP, EHRLICH HL. 1964. Microbial formation and degradation of minerals. In: Umbreit WW, editor. Advances in Applied Microbiology, New York: Academic Press. p 153–206.

YOUNGER, P., COULTON, R., FROGATT, E., 2005. The contribution of science to risk-based decision-making: lessons from the development of full-scale treatment measures for acidic mine waters at Wheal Jane, UK, Sci Total Environ 2005;338, 137-154.